A process for the beneficiation of coal and beneficiated coal product.
Description

This invention relates to the art of beneficiating coal to reduce the amount of ash and sulfur in the coal and to improve the transportation characteristics of coal-oil mixtures. More particularly, this invention relates to an improved process for beneficiating coal and the products produced thereby.

Considerable efforts have been expended toward providing procedures for beneficiating coal. Beneficiation involves generally the reduction of ash and sulfur content in coal. Among the processes being explored is a technique wherein coal is ground to a relatively fine powder and washed with water to physically separate the unwanted ash which dissolves in the water. Unfortunately, this process can result in a beneficiated coal product having an unduly high water content, which substantially reduces the energy value of the coal. Additionally, coal present in a water stream can give rise to transportation difficulties due to undue settling, etc. Consequently, substantial efforts are being directed to processes and products for suspending coal in a carrier such as fuel oil. United States Letters Patent No. 4,101,293 describes the use of emulsifiers for such a purpose. Other techniques provide particulate coal suspended in oil, but such techniques can require the removal of undue amounts of cleaning water by e.g., thermal treatment.

As a separate development, it has been suggested that pulverised coal can be subjected to cleaning using a fuel oil and water mixture, the coal being extracted in an oil phase, but the separate coal of this method can still settle from the oil phase.

No process has been suggested for beneficiating coal to produce a coal product which is non-settling and does not require intermediate thermal extraction of unwanted water.

In a wholly different art there has been developed a process termed 'chemical grafting'. According to this process, an organic material is grafted onto a substrate using site initiators which create locations for chemically bonding the material substrate. In United States Letters Patent No. 4,033,852 (Horowitz) chemical grafting is disclosed as a means for making a percentage of coal soluble in a solvent. This soluble coal in a solvent does not incorporate suspended coal particles.

Chemical grafting, as disclosed in the above Horowitz patent, is made to occur in the presence of minor amounts of additive chemicals, generally a polymerizable unsaturated vinyl monomer is included used in amounts constituting from 0.5 to 10% by weight of the coal to be treated. Also included is a free radical catalyst system employed in amounts ranging from 0.001 to 0.1 wt. percent of the monomer. The free radical catalyst initiator disclosed in the patent consists of an organic peroxide catalyst added to the reaction in an amount between 0.05 to 2.5 wt percent of the monomer. A quantity of free radical initiator metal ions, usually noble metals, are present in the free radical catalyst system, disclosed in that patent. Monomers said to be used for chemical grafting to the coal included vinyl oleate, vinyl laurate stearate and other known monomers, unsaturated natural or synthetic organic compounds.

The metal ion catalyst initiator disclosed in the Horowitz patent is silver presented in the form of silver salts such as silver nitrate, silver perchlorate and silver acetate. United States Letters Patent No. 3,376,188 (Horowitz) discloses that other metal ions, such as platinum, gold nickel or copper can be used when chemically grafting the polymerizable monomers onto the backbone of preformed polymers, illustratively, cellophane and dinitrated nitrocellulose. This patent does not relate to beneficiating coal.

As further background, for many years it has been known that finely divided coal particles could be agitated under specific control conditions with carefully selected liquid hydrocarbon fuels to cause preferential wetting of the coal surface with the water insoluble fuel fraction in an aqueous admixture. The process is generally known as 'Spherical Agglomeration'. Summary reports in spherical agglomeration process development apparently show that the specific gravity of the hydrocarbon liquid, its origin and chemical and physical quality and the nature of the agitation are all interrelated. Operational variables appear to be critical and present substantial impediments to uniform operation. The coal particles used in this process are previously crushed to a fine powder, i.e. less than about 200 mesh (Tyler: i.e. less than 74 micrometres) and are often thermally dried. Also, the resulting product exhibits short shelf life and is difficult to use in a burner.

As further background, equipment and methods are generally known for reducing mined coal to various particle sizes by, e.g., crushing, grinding and pulverising in either a dry or wetted state. A portfolio of such processes are presented in the periodical Coal Age, January 1978, pages 66 through 83.

A further proposal for the beneficiation of coal is made in FR— 2 393 053 and the corresponding United States Patent No. 4217 109. In accordance with that proposal coal is converted into a liquid fuel by pulverizing the coal and dispersing the coal powder in water with the aid of a polyelectrolyte and polyphosphate dispersants which undergo selective adsorption by the coal and impurity particles and thereby bring about differential charging of the coal and impurity particles. The differentially charged particles can then be separated, for example, by virtue of their different settling rates in aqueous media, or different migration rates in an applied electric field, or even by virtue of the magnetic properties of coal particles containing magnetic impurities such as pyritic sulfur. Particular amongst the polyelectrolytes used as selective dispersants in that proposal are preformed polycarboxylic acids and
preformed acidic polymers such as polyacrylic acid. The beneficiated coal product of that process is therefore essentially hydrophobic and dispersible in water, in contrast to the beneficiated coal product of the present invention which is essentially hydrophobic and oleophilic.

As a summary of background for the present invention, it is therefore apparent that efforts have been made to render coal more acceptable and economic as a source of energy. Systems have been suggested for beneficiating coal by, e.g., crushing the coal into small sized particles and washing these particles for removal of ash and residue. Systems have been developed for mixing coal particles with fuel oil for use in burners, thereby taking advantage of the low cost and availability of coal. Each of these systems has disadvantages which have prevented its widespread use.

In its broadest aspect, the present invention is directed to the production of beneficiated coal product comprised of a particulate coal having a hydrophobic, oleophilic surface and being characterized by having low ash and sulfur content. Besides being suitable for direct use as a low-ash, low-sulfur fuel, the beneficiated coal product of this invention is also readily dispersible in heavy fuel oils to provide a readily transportable, stable liquid fuel product.

In a broad aspect, the present invention resides in a process for the beneficiation of raw coal by the removal of sulfur and ash-forming impurities therefrom, characterized by the steps of:

(a) crushing the raw coal,
(b) contacting the crushed raw coal particles in suspension in an aqueous suspension medium containing water and from 1—10% by weight, based on the weight of the crushed raw coal particles, of a liquid, water-insoluble hydrocarbon fuel, with a polymerizable mixture comprising: i) one or more organic monomers capable of undergoing polymerization in the presence of a free radical catalyst and initiator, ii) a free radical catalyst and iii) a free radical initiator, thereby preferentially to render the coal particles both hydrophobic and oleophilic by the graft polymerization of said monomer or monomers in said medium in the presence of said coal particles whilst leaving the sulfur and ash-forming impurities essentially hydrophobic;
(c) selectively separating the hydrophobic, oleophilic coal particles from the aqueous suspension medium, thereby to leave in said medium said essentially hydrophilic and ash-forming impurities;
(d) washing the separated hydrophobic, oleophilic coal particles to remove further hydrophilic impurities therefrom; and
(e) mechanically separating the washed hydrophobic, oleophilic coal particles from the washing medium, thereby to recover a particulate beneficiated coal/oil product comprising discrete hydrophobic, oleophilic coal particles and sorbed liquid hydrocarbon, said oil/coal product containing less than about 20% water on a weight basis, and of course the direct product of that process.

In another aspect of the invention, there is provided a beneficiated coal-oil mixture comprising beneficiated coal particles produced as above dispersed in a hydrocarbon oil as the continuous phase. If desired this coal-oil mixture can be treated with a salt forming compound reactive with acidic groups on the surface of the disperse particles to provide a resultant mixture which is stable, gel like and thixotropic.

Such coal-oil mixtures may contain about 50 wt percent coal based on the total weight of the mixture.

As the free radical polymerization catalyst employed in the process of the present invention both organic or inorganic peroxides such as hydrogen peroxide, benzoyl peroxide, oxygen and air can be used. Suitable free radical catalyst initiators comprise active metal ions such as ions of copper, iron, zinc, arsenic, antimony, tin and cadmium. The organic unsaturated monomers which may be used in this invention are preferably liquid at room temperature and include oleic acid, vegetable seed oil fatty acid, unsaturated fatty acid, methyl and ethyl methacrylate, methyl and ethyl acrylate, acrylonitrile, vinylacetylene, styrene, dicyclopentadiene, soybean oil, castor oil, tall oil and corn oil. Preferably, the monomers in this invention are water-insoluble organic acids having the general structure RCOOH wherein R is an ethylenically unsaturated group of at least 8 carbon atoms in size.

The process of this invention provides a beneficiated hydrophobic and oleophilic coal product of relatively low water content which can be further dehydrated to a remarkable degree without use of thermal energy. The ash content of the coal is reduced to very low levels and mineral sulfur compounds present are removed. The final coal product has enhanced BTU content, and can be burned as such or, as already indicated, combined with fuel oil to produce a mixture of coal and fuel oil as a burnable fuel. Alkali metal and alkaline earth metal ions can thereafter be employed to convert the coal-oil mixture to a thixotropic gel-like fuel having excellent dispersion stability. The thixotropic flowable fuels are useful as sources of thermal energy. The dry coal product can, if desired, alternatively be redispersed in aqueous systems for pumping of the fluid aqueous coal slurry thus formed through pipelines and the like.

The process of the invention may be applied to the beneficiation of raw coal from a variety of sources, e.g., mine run, refuse piles, coal processing fines and the like.

The liquid hydrocarbon fuel oil present in minor amounts in the aqueous suspension medium during the graft polymerisation step is preferably a No. 2 fuel oil.

The above-identified components of the polymerizable mixture, i.e. the monomer, the catalyst and the initiator, can be added at the initial process stages, e.g. during pulverization of the raw coal, and in the presence of the aqueous/
hydrocarbon suspension medium. However, for more efficient catalyst utilization, it is preferred to add the free radical polymerization catalyst at the end of or after the final pulverization of the coal and dispersion of the other additives therewith. On the other hand it has been established as more preferable and advantageous to withhold addition of all of the chemical grafting components until after reduction of the particle size of the coal in its final milling operation.

The chemical grafting reaction occurs in an aqueous medium in the presence of the above-described reactants. The peroxide catalyst (organic peroxide, oxygen, air, hydrogen peroxide) is added to the described water insoluble unsaturated organic acid and the metal initiator of the free radical forming catalyst.

The organic unsaturated monomer becomes coated onto the coal particles. Without intending to be limited by any theory or mechanism, titration and extraction tests have indicated that the organic unsaturated monomer is believed chemically attached or grafted onto the coal surface. Further polymerization of the monomer is believed to result in the coal being coated with the polymer of the unsaturated monomer. By virtue of proper selection of monomer, the coal is rendered hydrophobic and oleophilic and can be immediately cleaned and recovered. The hydrophobic finely divided particles flocculate and float on the surface of the water. Upon water wetting and settling, the larger percentage of ash present in the original coal remains hydrophilic in surface character, it settles and tends to remain dispersed in the water and can be pumped off below the flocculated coal for further separation and disposal of ash and recovery of the water. Lime can be used, if desired, to aid ash removal from the water phase.

Following recovery, the flocculated hydrophobic coal is washed, preferably by redispersal as a slurry in fresh wash water with good agitation. Initially, it was found successful to provide needed dispersion of the hydrophobic coal particles in the wash water steps by use of recirculating high shear centrifugal pumps. It has been discovered, however, that advantageously if the coal-oil-water flocculates are more effectively broken up by higher shear means, water held in the interstices of the flocculated coal particles (which hold an additional quantity of ash) is brought into more effective wash water contact and more of the total ash content is removed from the recovered hydrophobic coal particle conglomerate.

Increased efficiency of ash removal during the wash step has been obtained by resorting to equipment producing high liquid velocities and high shear rates. This has been accomplished more efficiently by ejecting the coal-oil-water flocculates into fresh wash water under atomizing pressure through a spray nozzle, thus forming minute droplets, momentarily in the air, but directed with force into and on the surface of fresh wash water mass. Some air is thereby incorporated into the system. This improvement is being disclosed as the best mode in the ash removal step of the preferred embodiment of this application. Preferably a plurality of successive high shear washing/flotation steps are performed before final mechanical drying of the coal-oil flocculates.

The drying of the recovered wash hydrophobic coal, free of a major amount of the ash originally present, is finally dehydrated to very low water levels solely by mechanical means, e.g. by centrifuging, pressure or vacuum filtration, etc., thus avoiding the use of thermal energy to remove residual water and the consequential requirement for costly heating of the entire coal mass. As the treated coal at this stage is hydrophobic and oleophilic water is quite readily removed by mechanical means.

At this point a first product of the invention is obtained, i.e. a particulate, beneficiated coal product having essentially hydrophobic and oleophilic surface characteristics. This first product may be used as such as a "dry" fuel or subjected to further treatments hereinafter identified.

In a first treatment the dry first product can be used to prepare a fluid coal-oil-mixture (C.O.M.) by blending a further quantity of fuel oil with the treated "dry" coal at any desired ratio. A preferred ratio is about 1:1 by weight.

Two other avenues of further treatment also remain open. For example, if an acidic monomer RCOOH is used in the chemical grafting step to render the surface of the coal particles oleophilic and hydrophobic, the grafted acid groups can be further reacted through their active, acidic hydrogen atoms with an alkali or alkaline earth metal or a variety of selected metal ions, to convert the acidic groups on the surface of the coal particles into salt form. If used in conjunction with the first treatment mentioned above, the "drop point" of the final liquified coal-oil-mixture (C.O.M.) can be controlled. The coal extended liquid fuel oil products obtained in this way have unique properties. Among them is the quality of thixotropy which gives structure of gel-like viscosity increase to the fuel oil extended coal. When the liquid is at a state of rest, or when it is below its "drop point", the gel structure is unbroken. However, upon stirring or agitation as by a circulating pump or agitation or heating above the "drop point", the structure in the product is broken down, and the liquid flows normally but is non-Newtonian in nature. The "drop point" temperature is influenced in particular by the selection of the metal ion.

In yet a further treatment, the first product of the invention, i.e. the mechanically dried, hydrophobic, oleophilic beneficiated coal particles, can be dispersed in water to provide an aqueous coal dispersion suitable for pumping through pipelines for long distances, particularly those beneficiated coal products derived from carboxylic acid containing monomers and in which the acidic hydrogen atoms have subsequently
been replaced by alkali metal atoms, especially sodium.

In addition to, or instead, any of the foregoing further treatments, a further desirable, but optional, further treatment of the first product of the invention comprises subjecting the mechanically dried beneficiated coal particles to a second graft polymerization treatment carried out in precisely the same way as before, and using the same materials, that is to say by contacting the recovered particles in suspension in an aqueous medium containing a minor amount of water-insoluble liquid hydrocarbon fuel with a further quantity of the polymerization mixture comprising an organic monomer capable of undergoing free radical polymerization in the presence of a free radical catalyst and initiator, a free radical catalyst and a free radical catalyst initiator. As the monomer, the catalyst and the initiator, the same materials as hereinbefore listed may be used, and as before, —COOH groups appearing in the final polymer can optionally be neutralized with alkali, alkaline earth or other metal containing neutralizing agents.

The invention is further described with reference to the accompanying drawings, in which:

Figures 1A and 1B taken together represent a first process in accordance with this invention; and

Figures 2A and 2B taken together represent a second and more preferred process in accordance with the invention.

Referring more specifically to Figures 1A and 1B, raw coal from the mine is reduced by conventional mine operations to relatively uniform top size particles as indicated, recovered fines from mine ponds or tailings can be equally used. If the larger 1" ± size (2.5 cm) is used as a starting point, a hydro roll crusher reduces the coal to about 1/4" (6 mm) particle size coarse aqueous slurry.

To this aqueous coal slurry, after it has been further reduced below 1/4" (6 mm) in particle size, is added a composite chemical grafting reagent mixture, which may, or may not, contain the free radical polymerization catalyst. It has been found that hydrogen peroxide, H₂O₂, is satisfactory for this purpose. The other components to be added are: the polymerizable water insoluble monomer, preferably an R-COOH acid where R is an ethylenically unsaturated group of at least 8 carbon atoms; a reactive metal ion site catalyst initiator salt; a minor amount of selected fuel oil, e.g. a No. 2 fuel oil.

The coarse coal slurry, now in the presence of the above chemical grafting reagent mixture, is further reduced in size to about 48 to 200 mesh (Tyler: 74 to 295 μm) or better. Preferably, the peroxide catalyst is added at this point, i.e., in the fine milling stage.

The coal becomes extremely hydrophobic as the chemical grafting occurs. When milling ceases the now hydrophobic coal flocculates and separates from the aqueous phase and thus from the remainder of the mill charge. Considerable ash separates out in the water phase at this point. The floating flocculated hydrophobic coal is recovered (a screen may be advantageously used for separation and recovery of the flocculated coal) and is passed through a plurality of wash steps wherein good agitation with high speed mixers and high shear of the hydrophobic coal-water wash dispersion as indicated above causes release of additional ash to the water phase, which ash is removed in the water phase. The water-wetted ash suspension is recovered into further settling tanks and is sent to waste. The process water is recycled and re-used. Additional ash and sulfur can be removed from the grafted coal-oil conglomerate by a series of countercurrent water-wash steps.

The chemically grafted pulverized coal (with most of the ash originally present in the raw removed) is dewatered to a very low water level by centrifuging. In the process before chemical grafting the water content of the coal is in the order of 22 to 28%. After graft polymerization of the coal and total benefication, the water content of the grafted washed product can be in the order of 8—20% more usually 6—12% by weight.

The recovered "dry" benefication treated coal mass can be used directly as a "dry coal" product as a fuel without further addition of fuel oil. Preferably, however, as indicated above, a sufficient quantity of fuel oil is admixed with the beneficiated coal to produce a coal-oil mixture.

Thus, the mechanically dewatered coal ("dry" beneficiated treated coal is transferred to a coal-oil dispersion premixer; additional R-COOH acid is added along with additional initiator, catalyst and fuel oil. The added acid can be the same as the unsaturated acid used in the chemical grafting step. However, in a modification the acid used at this stage need not be unsaturated and saturated R-COOH acids such as stearic acid and the series of both crude and refined napthenic acids recovered from refining of crude oils, etc. can be used. Additionally water soluble alkali hydroxide metal can be added to the coal-oil mixture to neutralize free fatty acid hydrogen atoms and about the hydrophobic coal particles.

The formation of the coal-oil mixture can be carried on continuously or batchwise, in e.g., paint grinding equipment where heavy small grinding media are used to shear the dispersion into a non-settling fuel product of thixotropic nature by further metal ion source addition, such as calcium hydroxide to form an alkaline earth metal salt or soap. Other metal soaps are also useful as indicated herein.

Referring more specifically to Figures 2A and 2B of the drawings, Figures 2A and 2B in conjunction with the following will expand and illustrate the best mode.

By conventional coal mining recovery and benefication processes with run of the mine coal or on the reworking of mine tailings or solids from coal recovery ponds, this process begins with conventionally obtained particulate coal reduced to about 1/4" (6 mm) in size, more or less. Of all
coal ground or crushed commercially, it is believed that 50—60% becomes too fine for commercial use. The “waste” fine coal sources are excellent sources of raw coal for the present invention.

The coal is introduced into a ball or rod mill, or other pulverizing and size reduction equipment. The water is preferably treated with sodium pyrophosphate and/or other organic and inorganic water treatment materials. These materials operate as dispersants.

So far as is known, there is no objection if a large percentage of the product of the wet milling is smaller than 200 mesh (Tyler: 74 μm), but it is preferred not to use a large percentage over 48 mesh (Tyler: 295 μm).

The aqueous slurry leaving the rod mill is put through a classifier and all particles more than about 48 mesh (Tyler: 295 μm) are returned for further size reduction.

The material leaving the classifier is passed to a surge tank where the density of the coal slurry is adjusted. Fine coal recovered from later processing can be introduced here. The graft polymerization reaction generally occurs prior to the addition of the chemical grafting reactants.

An aqueous chemical grafting reagent mixture complete and useful for the initial grafting purposes herein contains about 1/2 lbs (0.2 kg) tall oil fatty acids, 100 lbs (45 kg) liquid water insoluble hydrocarbon (usually a selected grade of fuel oil), 1 lb (.45 kg) of, illustratively, copper nitrate. (Other metal ions are also known to be useful to prepare ion initiator sites. Sulfur in general rules out their practical use.) A last essential element, the free radical processing peroxide catalyst which may be any of the known organic peroxides or inorganic peroxides (H₂O₂), added directly or produced in situ, with air or oxygen, but which is here preferentially hydrogen peroxide constitutes about 1-5/6 lbs (.74 kg) of H₂O₂ in solution of 30% H₂O₂—70% water strength. The amount of chemical grafting catalyst/polymerization mixture is exemplary of that required for treating about 2000 lbs (908 kg) of the described, high pulverized coal product (by dry weight) in aqueous slurry.

In practice it has been found advantageous but not essential, to withhold the peroxide or free radical polymerization catalyst addition until just after the slurry is pumped from the surge tank.

Chemical grafting takes place very rapidly as the finely ground and aqueous coal slurry leaves the surge tank, and is intimately admixed with the chemical grafting or polymerization mixture described above. This mixture of reactants 11 is pumped into the coal slurry discharge line 12, and is passed through an in-line mixer 13 under some pressure. Reaction takes place rapidly. The coal surfaces previously treated become more strongly oleophilic and hydrophobic than heretofore and are no longer wetted by the aqueous phase.

The stream of treated hydrophobic coal, wetted with polymer and fuel oil under pressure along with the accompanying water phase, is fed through a high shear nozzle D where the velocity of the stream and the shearing forces break up the coal flocculant-wash-water slurry into fine droplets which pass through an air interface within the wash tank (1) and impinge downwardly upon and forcefully jetted into the mass of the continuous water phase collected in the first wash tank (1).

The high shearing forces created in nozzle D and as the dispersed particles forcefully enter the surface of the water phase breakup the coal-oil-water flocs thereby water-wetting and releasing ash from the interstices between the coal flocs and break up the coal flocs so that exposed ash surfaces so introduced to the water phase, are separated from the coal particles and migrate into the mass water phase. The finely divided coal particles whose surfaces are surrounded by polymer and fuel oil also now contain air sorbed in the atomized particles delivered from and through the shear effects of the nozzle. The combined effects on the treated coal, including the chemical grafting and fuel oil plus sorbed air, cause the flocculated coal to decrease in apparent density and to float on the surface of the water, separating the flocculated coal upwardly from the major water mass in wash tank (1) and then to overflow into the side collector (1A).

The still hydrophobic ash remains in the bulk water phase, tends to settle downward in wash tank (1) by gravity, and is withdrawn in an ash-water stream 14 from the base of the vessel. Some small amount of fine coal which may not be separated completely is transferred with the water phase (withdrawn ash-water component) to a fine coal recovery station 15 (see Figure 2B).

It is of interest to review the various physical phenomena that occur in each wash stage which enhances the efficiency of the operation.

In passing the hydrophobic polymer-oil surfactant coal-in-water slurry through the nozzle D, unwanted mineral ash containing a larger percentage of objectionable mineral sulfur and inert non-combustibles is intimately interfaced with water. This ash is preferentially water-wetted and tends to enter the water phase and stay wetted thereby. Passage of the finely divided aqueous slurry of coal flocc through the nozzle and through air space and surface impingement, all under high shearing stress, causes air to be sorbed by the system and be occluded in the coal flocc.

The coal flocc itself is of lower density than coal itself due to the chemically polymerized organic layer on its surface which is less dense than water, the fuel oil present which is sorbed on the oleophilic-hydrophobic coal particle and sorbed air present in the flocc. The coal flocc thereby assumes a density less than water and as it repels water by its increased hydrophobic quality quickly floats to the surface of the water present. The ash, on the other hand, remains hydrophilic and is, in effect, repelled by the treated coal surface, preferentially into the water phase. The density of the ash is greater than water and tends to settle
out downwardly through the water mass. While we do not wish to be bound by theory, the foregoing factors are believed explanatory of the excellent and remarkably complete separation of the high sulfur containing hydrophilic ash from the graft polymerized hydrophobic coal and improved coal recovery. Reducing sulfur content overcomes most of the consistent objections to coal as a fuel.

By the foregoing technique not only is the ash removed from the treated coal product improved in percentage, but the entrapped air and the more hydrophobic and oleophilic coal surfaces provide a marked increase in efficiency of total beneficiated treated coal recovered.

The wash process of the first wash is repeated in essence through a counter-current wash system, the coal progressing to a cleaner state through sequential overflow and recovery in wash tanks (1), (2), and (3), while clean wash water becomes progressively loaded with water soluble and water wetted solid impurities extracted in the wash water as the cleaned water is recycled from water recycle line A into the second washed floc recovery tank (1B) through recycle water line 16. Fresh or recycled treated wash water into tank (1B) is dispersed into the floc and the resultant slurry removed by pump 17 from its base with the second washed overflow floc from tank (1B) through an in-line mixer 18 into wash tank (3) through shear nozzle means F.

The separated ash water wash water from wash tank (3) is removed from the base of wash tank (3) and is pumped counter-currently into the first washed floc tank (1A) where it is, in turn, pumped with the overflow floc collected in tank (1A) through an in-line mixer and nozzle E into wash tank (2). The ash-water wash water containing any coal particles which did not float and overflow into (1B) are removed by line 19 from the bottom section of wash tank (2) and are forced into a fine coal recovery line B-1 through which recovered coal is collected in a series of tanks at coal recovery 15 where fine coal otherwise lost is recovered. The intimately admixed ash-water suspension containing some small amounts of particulate coal is separated in the wash water recovery system by passing it through settling and classifier apparatus and finally through a centrifuge where high ash-low water solids are recovered and expelled for removal from the process. Suspended solids-free wash water is further treated at 20 to control the condition of the recovered water before recycle. The clean treated process water is recycled to produce the original aqueous coal slurry and such other water make-up as the overall process may require when material flow is in balance.

The washed coal flocculate enters the final wash step from (1B). From the in-line mixer 18 the floc-water slurry under pressure passes through shear nozzle F. The water-coal particle admixture is again atomized and collected in wash tank (3). Velocity and high shear through the nozzles D, E, and F allow wash water contact with any ash previously retained in the interstices of the coal floc, thereby assisting ash removal in each wash step. The massive water phase created in the wash tanks (1), (2) and (3) floats the flocculated coal-oil-air mass to the top of the series of wash tanks (1), (2) and (3) and overflowing the coal floc sequentially into collector tanks (1A), (1B) and (1C). Fine floc overflow from tank (3) into tank (1C) carries the washed floc in an aqueous stream to a mechanical de-watering means through line C.

The beneficiated, cleaned, coal slurry is thereafter de-watered remarkably completely without requiring thermal energy. Illustrated here is a centrifuge, one advantageous mechanical means for the purpose. Note also, the 'dry' recovered coal product at this point in the process requires no thermal evaporation of water due to the reduced attraction for water between the large coal-oil-air phase and the smaller oil-calcium phase reduced therebetween in the flocculated 'dry' coal recovered from the mechanical drying step. The dry hydrophobic cleaned coal can be used advantageously at this point as a higher energy content-sulfur reduced fuel which may be referred to as Product I. This fuel can be utilized in direct firing.

However, the principal practical purpose of this invention is to provide a liquid fuel which is easily pumped as a liquid, but which is of such rheological quality as to form a thixotropic liquid. A thixotropic liquid is one which has 'structure' or tends to become viscous and gel-like upon standing quiescent but which loses viscosity and the 'structure' or gel decreases markedly and rapidly upon subjecting the thixotropic liquid to shearing stresses, as by agitation through mixing and pumping processes or by heating above the 'drop point'.

In the preferred practice of this invention the dry, beneficiated, coal Product I coming from the conveyer, following mechanical water removal, is mixed with a quantity of fuel oil (illustratively 1:1 by weight), preferably heated to reduce viscosity in cases where the fuel oil is of a heavy viscosity grade, in pre-mix tanks to again provide a pumpable fluid mixture.

A preferred, but alternative practice, is to subject the fuel-oil-coal mixture in the pre-mix tanks to an additional graft polymerization step, following the general reaction procedure as in the first graft polymerization. In this case the RCOOH acids are employed, as illustrated by tall oil fatty acids, oleic acid, etc. However, in an alternative modification of the process, it is permissible and operative to employ an RCOOH acid which is saturated (if there is no reactive, grafting procedure). In this latter electro, peroxide and metal ion initiator need not be incorporated with the added saturated or unsaturated fatty acid addition. Naphthenic acids are illustrative.

The non-fluid admixture of polymer surface grafted coal, fuel oil and RCOOH acid is substantially neutralized with a water soluble alkali metal and the fluidized particulate containing fuel oil-coal is pumped through an in-line mixer. Alkaline earth metal ions, from, for example, a
calcium hydroxide solution are incorporated in the stream in an amount to react, at least in part, by double decomposition reactions to form the alkaline earth metal soaps or salts of the acid moiety previously neutralized with the alkali metal. Other metal ions may also be selected at this point to modify the ‘drop point’ of the final Product II, liquefied coal-oil mixture (C.O.M.).

The fluid coal-oil mass is then subjected to further high shear processing in a high shear milling device, such as is used in dispersing pigments in oils to produce paint products.

A liquid clean coal-oil-fuel mixture, having no tendency to settle out, is stably recovered to provide a flowable high energy source for a wide variety of end uses.

The following Examples are further illustrative of the invention.

Example I

2000 g. Illinois #6 coal having 5.35% ash content reduced to about 1/4" (6 mm) size lumps was reduced in particle size to between about 48 to 200 mesh (Tyler 74—295 μm) in a hydrocrusher roll grinding unit in an aqueous liquid slurry where the liquid phase is about 5% of total as fuel oil and about 65% water. The coal solids are about 30% of the total fluid slurry.

A chemical graft polymerization mixture consisting of 500 mg tall oil, 100 g of fuel oil, 2-1/2 g sodium pyrophosphate and 1 g of copper nitrate were incorporated into the above mill batch in the initial mill loading. Before the mill was discharged 1-1/2 g of H₂O₂ in solution (30% H₂O₂ in water) was incorporated and graft polymerization of polymer on the coal surface was completed. The aqueous slurry was removed shortly thereafter from the mill, transferred to a settling vessel and the hydrophobic grafted coal was recovered by removing it from the surface of the water phase on which it floated. The water phase contained the hydrophobic ash which was discarded. Water used was between 30° and 40°C for all processing steps.

After several re-dispersions and recoveries in and from fresh softened wash water the agglomerated grafted coal was recovered. After filtering on a Buchner funnel the water content was about 15%. Coal normally processed without the grafting step will retain from 20—50% water when ground to the same mesh size. Washing can be effective as at low as 20°C but it is preferred to use at least 30°C water temperature. The water preferably contains a phosphating conditioning agent.

The recovered, mechanically dried cleaned treated coal aggregate was admixed with oil and an additional 60 g/m of tall oil. After thorough intermixing, caustic soda equivalent to the acid value of the mix was reacted with the free carboxyl groups of the tall oil.

After standing for several months no settling of the coal-liquid fuel mixture was observed.

Example II

A series of runs were made similar to the detail of Example I, but substituting gram equivalent amounts of a series of polymerizable monomers for the tall oil (acids) as follows: a) styrene monomer, b) methyl methacrylate, c) methacrylic acid, d) oleic acid, e) dicyclomethanide, f) dodecyl methacrylate, g) octadene 1,7, h) 2,2,4 trimethylpentene-1, i) glycyl methacrylate and j) soya bean oil fatty acids. Chemical grafting of the surface of the pulverized, treated coal was similarly altered to the strongly hydrophobic nature and processed similarly to Example I. In each case the same amount of tall oil (acids) was admixed in the recovered coal aggregate after de-watering. Acidity was neutralized with caustic and similar liquid fuel suspensions were prepared. All exhibit thixotropic quality depending on the metal ion selected to display the sodium ion of the alkali metal hydroxide originally added. No settling was observed over several weeks study independent of the polymerizable monomer selected.

Example III

As in Example I, except 2 grams of butyl peroxide were used in the graft polymerization step in place of H₂O₂. The water was treated with 2 grams of Triton X-100 (Registered Trade Mark) and 25 g of sodium pyrophosphate present in the originally slurry water. The ash in the water phase was filtered out after treating with lime. The ash content was reduced from about 4.28% to about 1.9% after five separate washings where the water was also treated with the same conditioning agents. The tall oil (acids) used in the graft polymerization plus the tall oil added after processing were neutralized, first with caustic soda, and later treated with an equivalent amount of a water soluble alkaline earth metal (calcium hydroxide). The recovered mechanically dried clean coal-oil product was further reduced with fuel oil to a flowable viscosity. The viscosity quality, or rheology, of the system indicated it was of thixotropic gel-like nature, indicating no settling was to be expected upon standing.

In the initial work, it was considered probably advantageous to incorporate the chemical grafting components comprising the RCOOH unsaturated monomer acids (tall oil), the metal ion initiator catalyst, which initiates the free radical formation from the peroxide, and the peroxide free radical polymerization catalyst before the coal had been reduced to the ~48 mesh size (Tyler, less than 295 μm) by fine grinding techniques.

A study of the addition times indicated more favourable ash removal and coal recovery by first reducing the coal to less than about 48 micron size in conditioned water aqueous slurry. Thereafter, one incorporates the metal initiator for the free radical peroxide catalyst, fuel oil, and the water insoluble polymerizable monomer. The free radical catalyst is withheld until just after completion of the grinding steps and before recovery for the washing steps. Up to this time the actual graft of polymerization of the monomer is delayed.
The following illustrates the best mode and practice presently known.

The coal is reduced to about 200 mesh (Tyler: 74 μm) in a conditioned water (sodium tetraphosphate) slurry. 2000 grams of coal are in the mill. To the mill contents are added 1/2 gram tall oil acids, 100 grams fuel oil and 1 gram of metal initiator (Cu as copper nitrate). The batch is held at 30°C. Just as the milling is to be discontinued, there is added 1.64 grams of H₂O₂. The mill contents are pumped by a high shear centrifugal pump into a receiving vessel equipped with a high speed agitator. The coal-water slurry is maintained in dispersed state in the receiving vessel for about ten minutes and is then pumped at high pressures through a fine spray nozzle where high shearing stresses atomize the slurry into fine droplets. The air atomized droplets are directed onto and into the surface of a conditioned wash water containing vessel where the ash separates into the water and the now aerated coal particles rise and float on the surface and are recovered and vacuum filtered or centrifuged. Initial ash content was 4.45 and the ash content of the treated clean coal product was 1.50%. It was also found that 1905 g clean coal was recovered in excess of 95% coal recovery.

Monomers previously used in chemical grafting and polymerization procedures in the main require pressure as they are gaseous. However, for the purposes of this invention where total economics of the process are extremely critical only monomers that are liquid at room temperature are used. Additionally, some of the prior art monomers are capable of producing a hydrophobic surface on the high surface areas of the pulverized coal, but are not as oleophilic in character as others. For the purposes of this invention and in the chemical grafting and polymerization step methyl and ethyl methacrylate, methyl and ethyl acrylate, acrylonitrile, vinyl acetate, and styrene are useful as illustrative.

In the chemical grafting step, one may successfully use an unsaturated monomer which is a liquid at room temperatures and not having the polar carboxyl radical. Examples of monomers found effective in chemical grafting of coal include: styrene, cracker gasoline, dicyclopenta diene, coker gasoline, polymer gasoline all of which are available from various refinery processes.

It is our preferred practice, however, and from our research, it is preferred to use an unsaturate water insoluble monomeric organic acid having the general structure RCOOH where R is unsaturated and has at least 8 carbon atoms in the hydrocarbon moiety. Economically attractive and extremely efficient is tall oil, a well known by-product in paper manufacture which is available in various grades of purity. One grade is generally in excess of 95% oleic acid, most of the remainder being resin acids. All of the unsaturated fatty acids available from vegetable seed oils, illustratively soybean oil, fatty acids are useful. Dehydrated castor oil fatty acids are relatively expensive, but are useful.

After the chemical grafting step has been completed and usually after all water-washing, additional RCOOH is advantageous. All of the above class of unsaturated long chain organic acids can be used. In the secondary use, if a second graft polymerization is not elected, it is also feasible to expand the class of useful organic RCOOH acids to include those where R is saturated and this class is especially opened to include both highly refined naphthenic acid as well as a variety of fairly unique sources of naphthenic acid, illustratively Venezuelan crudes and certain bunker fuels known to contain many naphthenic acid fractions. Rosin acids are also useful.

Naphthenic acid may also be reactive through a resonance phenomena and be substantially equivalent in reactivity to the unsaturated RCOOH acids in the grafting step. While initial trials indicate some reactivity despite the fact that naphthenic acids are saturated, these latter acids have not yet been established as fully useful for the chemical grafting step, '...

The reactive metal ion site catalyst initiator salts of the prior art disclosed by U.S. Patents 4,033,852, and 3,375,168 to Horowitz mention as useful, namely: silver nitrate, silver perchlorate, silver acetate and other noble metal ions include platinum and gold. Nickel and copper have also been mentioned as useful in initiating, free radical development from the peroxide catalyst to thus stimulate grafting of reactive polymerizable monomers to the backbone of preformed polymers. These metal initiator ions are used in the form of their water soluble salts.

We prefer to use the copper ion as the best mode presently known in our process. However, very preliminary evidence indicates that a rather larger number of other known catalytically active metals may be operative for the ends of the present invention. Of possible value are Fe, Zn, As, Sb, Sn and Cd, though not limiting by their mention. Thus, the term metal ion catalyst initiator tentatively includes all the catalytically active metal salts which can be used to provide polymerizably active metal ion sites on the pulverized coal surfaces.

Process water used is preferably between 30° and 40°C. If the temperature exceeds this generally optimum range it has been observed while there is no coal loss, ash removal becomes less complete, but coal recovery drops off in the process. Washing can be carried out at lower temperatures but at about 30° overall improvement has been noted. Coal recovery of about 95% has been obtained with water content by vacuum filtration reduced to about 12% by weight. Water conditioning has been found useful.

 Soxhlet extraction of our chemically grafted coal indicates very little free oil is removed (excluding the fuel oil process additions). The acid value of the Product I coal was found substantially equivalent to the RCOOH acid used both in the
grafting step or steps and the later ROOH addi-
tions, whether saturated or unsaturated in the R

group.

In early work the chemical grafting step was
activated by use of organic peroxides normally
used in the art of free radical polymerization
reactions. However, it was found that hydrogen
peroxide was a provident substitute therefor,
introducing economy of operation. Higher ef-
ciciency of coal recovery has been noted where
\( \text{H}_2\text{O}_2 \) is used.

In the graft polymerization addition step, use of
fuel oil of the order of 5% in the catalyst carrier
appears to function to provide better coal re-
covery and is about optimum. More or less than
5% is not operationally critical.

Conditioning of the water will vary with the
water source as is well known. Zeolite water
treatment may be advantageous in some inst-
ces. Other methods of water conditioning is a
specialized art, and may provide advantages over
and beyond mere treatment with the known
phosphate additives, illustratively tetra sodium
pyrophosphate. Minor additives of organic sur-
factants of the anionic, non-ionic and cationic
classes may be valuable additions in some inst-
ces. Again, economics of their use weighed
against advantages in ash removal and coal
recovery may be quite specific to the coal being
treated and the source of process water.

As the process water can be recovered recycled
from ash settling reservoirs, a large part of the
initial water costs can be reduced.

Coal recovery may be improved by a two stage
addition of the chemical grafting additives. In
other words, two complete and separate graft
polymerization reaction mixture additions and
reactions may be carried out on the fine particle
coal during the processing, if desired. Early work
has indicated advantage. Ash reduction of the
order of 68% (1.5% residual ash in coal products)
has been recovered in some of the trial runs.

The total amount of chemical grafting additives
shown in the Examples is satisfactory and oper-
ative. Undoubtedly modifications both in ratio
of reagents as well as their ratio to the weight of
carbon being processed can be operationally varied
within a wide range. The limiting factors will, of
course, be modified by the economics of estab-
lished commercial plant experience.

In the slurry prepared for coal size reduc-
tion, the percentages of coal and water will be
variable, again depending on pulvurising
methods used as well as sources of coal and
water. These ratios can be readily determined for
a given set of conditions by one skilled in the coal-
grinding arts.

An unexpected advantage has been found in the
relatively small water content of the recovered
oil treated-grafted coal flocculate, and the relative
ease of removal of water by purely mechanical
means, e.g., centrifuge, pressure filtration, etc.,
which are adapted to continuous processing. No
thermal energy is required for water removal and
drying. Again, the advantages of the disclosed

process are reflected in the relatively small capital
expenditure (estimated 2/3 of the prior art coal
beneficiation plants) for plant and plant operation
expenses.

Fuel oil used for production of fluidized coal is
possible with all grades of fuel oil, even including
#6 fuel oil, which is of extremely variable com-
position.

The fact that it is usual in coal mining opera-
tions that coal milled to 28 mesh (Tyler: 589 \( \mu \text{m} \))
leaves behind about 40% of the original coal in a
finer mesh size, and not presently of saleable use,
provides an opportunity for practical use of these
mine tailings. Coal freeze-up in below-freezing
weather will not occur with the dried solid coal
Product I or II as disclosed, both because there
will not be water pick-up in storage as well as the
'dry state' of the shipment of the product. In the
fluidized, thixotropic form (Product II) of the in-
vention, the product can be transferred by
pumping.

Coal loss during the washing steps has been of
the order of 10%. Experience thus far indicates
refinements of the present process will improve
(reduce) losses of raw material.

In use of some fuel oils in producing the
liquefied Product II, it is advantageous to heat the
components together in the pre-mixer. Tempera-
tures in the general range of 65—107°C have been
found useful.

Very little water has been lost in the processing
and water lost in the final products is generally
replaced by the water inherently in the coal from
the prior art processing or inherently present.
Product II contains not more than about 8% water
and the dry clean coal Product I is generally not
more than about 12% water.

Inasmuch as the water is recycled, the only
waste product from the process is the centrifuged
ash. No thermal energy is used in drying, hence
the process is environmentally sound.

Claims

1. A process for the beneficiation of raw coal by
the removal of sulfur and ash-forming impurities
therefrom, comprising the steps of
(a) crushing the raw coal,
(b) contacting the crushed raw coal particles in
suspension in an aqueous suspension medium
containing water and from 1—10% by weight,

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based on the weight of the crushed raw coal
particles, of a liquid, water-insoluble hydrocarbon
fuel, with a polymerizable mixture comprising: i)
one or more organic monomers capable of under-
going polymerization in the presence of a free
radical catalyst and initiator, ii) a free radical
catalyst and iii) a free radical initiator, thereby
preferentially to render the coal particles both
hydrophobic and oleophilic by the graft poly-
merization of said monomer or monomers in said
medium in the presence of said coal particles
whilst leaving the sulfur and ash-forming impuri-

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ties essentially hydrophilic;
(c) selectively separating the hydrophobic,
oleophilic coal particles from the aqueous suspension medium, thereby to leave in said medium said essentially hydrophilic sulfur and ash-forming impurities;

(d) water washing the separated hydrophobic, oleophilic coal particles to remove further hydrophilic impurities therefrom; and

(e) mechanically separating the washed hydrophobic, oleophilic coal particles from the washing medium, thereby to recover a particulate beneficiated coal/oil product comprising said hydrophobic, oleophilic coal particles and sorbed liquid hydrocarbon, said coal/oil product containing less than about 2% water on a weight basis.

2. A process according to claim 1, wherein components i) and ii) of the polymerizable mixture and the aqueous and hydrocarbon component of the suspension medium are added to the raw coal particles during crushing, and components ii) of the polymerization mixture is added subsequently.

3. A process according to claim 1 or 2, wherein the free radical catalyst is hydrogen peroxide.

4. A process according to claim 1, 2, or 3, wherein the monomer component of said polymerizable mixture comprises one or more water-insoluble unsaturated acids of the formula RCOOH, where R is an ethylenically unsaturated group of at least 8 carbon atoms.

5. A process according to claim 1, 2, or 3, wherein the monomer component of said polymerizable mixture comprises one or more of the following: oleic acid, vegetable seed oil fatty acid, methyl or ethyl methacrylate, methyl or ethyl acrylate, acrylonitrile, vinyl acetate, styrene, dicyclopentadiene, soybean oil, castor oil, corn oil or tall oil.

6. A process according to any one of claims 1—5, wherein, in step c) the hydrophobic, oleophilic coal particles are separated from the aqueous medium by froth flotation.

7. A process according to any one of claims 1—6, wherein in step d), the separated hydrophobic, oleophilic coal particles are contacted with said wash water under conditions of high agitation, thereby to form a froth containing said particles, the froth containing said particles then being recovered and passed to step e) for the mechanical removal of the water therefrom.

8. A process according to claim 7, characterised in that washing step d) comprises ejecting an aqueous fluid through a high shear nozzle onto the surface of a body of wash water so as to impinge forcibly thereon, thereby causing remaining hydrophilic ash particles to separate out into the aqueous phase and the hydrophobic, oleophilic coal particles flocculate as an oil/coal phase on the surface of the wash water, and recovering the flocculated coal particles from the surface of the wash water.

9. A process according to claim 7 or 8, characterised in that in step d) the hydrophobic, oleophilic coal particles are subjected to a plurality of successive wash-flotation steps.

10. A process according to any one of claims 1—9, wherein the beneficiated, hydrophobic, oleophilic coal particles recovered as the product in step e) are further treated in suspension in an aqueous medium containing a minor amount of a water-insoluble, liquid hydrocarbon fuel with a polymerizable mixture comprising an organic monomer capable of undergoing free radical polymerization in the presence of a free radical initiator and catalyst, thereby to form a further graft polymerized hydrophobic, oleophilic organic coating on the beneficiated coal particles, and recovering the further treated particles from the aqueous suspension medium.

11. A process according to claim 10, wherein the organic monomer used in said further treatment is a monomer as defined in claim 4 or 5.

12. A process according to any one of claims 1—11, wherein the monomer used in step b), and/or in the additional treatment as defined in claim 10 or 11, is a monomer containing a free carboxylic acid (—COOH) group or groups, and after recovery of the beneficiated coal particles in step e), or after recovery of the further treated particles according to claim 10 or 11, and the carboxylic acid groups in the graft polymerized coating after polymerization are neutralized by reaction with an alkali or alkaline earth metal or other metal-containing neutralizing agent.

13. A process according to any one of claims 1—12, wherein the said water-insoluble liquid hydrocarbon present in the aqueous suspension during contact of the coal particles with said polymerizable mixture is No. 2 fuel oil.

14. A process according to any one of claims 1—9, wherein the beneficiated coal particles recovered as the product in step e) are further treated in suspension in an aqueous medium with a saturated fatty acid and optionally neutralized with an alkali or alkaline earth metal, or other metal containing neutralizing agent.

15. A process according to claim 14 wherein the saturated acid is napthenic acid.

16. A transportable coal-oil mixture comprising particles of a beneficiated, hydrophobic, oleophilic coal product obtained by a process claimed in any one of claims 1—15, dispersed in a liquid hydrocarbon carrier.

17. A coal-oil mixture according to claim 16 which contains beneficiated coal particles obtained by the method of claim 12, i.e. by neutralization of carboxylic acid groups present on the surface of the coal particles and resulting from the use of a carboxylic acid containing monomer, characterised in that the neutralization is effected after dispersion of the beneficiated coal particles in the hydrocarbon carrier.

18. A transportable coal-water mixture comprising particles of a beneficiated hydrophobic, oleophilic coal product obtained by a process claimed in any one of claims 1—13, dispersed in an aqueous liquid carrier.

19. A coal-water mixture according to claim 18, characterised in that the beneficiated particles have been obtained using a carboxylic acid containing monomer, the carboxylic acid groups on
the surface of the beneficiated particles subsequently having been neutralized with an alkali metal.

Revendications

1. Procédé pour l’enrichissement de charbon brut par élimination du soufre et des impuretés génératrices de cendres qu’il contient, caractérisé par les opérations de
   (a) broyage du charbon brut,
   (b) mise en contact des particules de charbon brut broyé en suspension dans un milie de suspension aqueux contenant de l’eau et 1 à 10 % en poids, rapporté au poids de particules de charbon brut broyé, d’un hydrocarbure combustible liquide, insoluble dans l’eau, avec un mélange ultérieurement composé de
   i) un ou plusieurs monomères organiques susceptibles de subir une polymérisation en la présence d’un catalyseur et d’un promoteur de radicaux libres,
   ii) un catalyseur de radicaux libres et iii) un promoteur de radicaux libres, de façon à rendre préférentiellement les particules de charbon à la fois hydrophobes et oléophiles par la greffe-polymérisation dudit ou desdits monomères dans le milieu en présence desdites particules de charbon brut tout en laissant le soufre et les impuretés génératrices de cendres à l’état essentiellement hydrophile;
   (c) séparation sélective des particules de charbon hydrophobes et oléophiles d’avec le milieu de suspension aqueux, en vue de laisser dans le milieu le soufre et lesdites impuretés génératrices de cendres essentiellement hydrophiles;
   (d) lavage à l’eau des particules de charbon hydrophobes et oléophiles séparées pour en éliminer plus complètement les impuretés hydrophiles; et
   (e) séparation mécanique des particules de charbon hydrophobes et oléophiles lavées d’avec l’agent de lavage, afin de récupérer un produit charbon enrichi/huile comportant lesdites particules de charbon hydrophobes et oléophiles et de l’hydrocarbure liquide absorbé, ledit produit huile/charbon contenant moins d’environ 20 % en poids d’eau.

2. Procédé selon la revendication 1, caractérisé en ce qu’on ajoute les constituants i) et ii) du mélange polymérisable et le composant aqueux et hydrocarbure du milieu de suspension aux particules de charbon brut pendant le broyage, et l’on ajoute ultérieurement le constituant iii) du mélange de polymérisation.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que le catalyseur de radicaux libres est l’eau oxygénée.

4. Procédé selon la revendication 1, 2 ou 3, caractérisé en ce que le constituant monomère dudit mélange polymérisable est constitué par un ou plusieurs acides insaturés insolubles dans l’eau de formule ROOCOr, où R est un groupe éthylénique insaturé comptant au moins 8 atomes de carbone.

5. Procédé selon la revendication 1, 2 ou 3, caractérisé en ce que le constituant monomère dudit mélange polymérisable comporte l’un ou plusieurs des corps suivants: acide oléique, acide gras d’huile de graines végétales, méthacrylate de méthyle ou d’éthyle, acrylate de méthyle ou d’éthyle, acrylonitrile, acétate de vinyle, styrène, dicyclopentadiène, huile de soja, huile de ricin, huile de blé ou talhôl.

6. Procédé selon l’une quelconque des revendications 1 à 5, caractérisé en ce que dans l’opération d) on sépare les particules de charbon hydrophobes et oléophiles d’avec le milieu aqueux par flotation.

7. Procédé selon l’une quelconque des revendications 1 à 6, caractérisé en ce que dans l’opération d), on met les particules de charbon hydrophobes et oléophiles séparées en contact avec l’alcool de lavage des conditions de forte agitation, pour former par là la mousse contenant lesdites particules, la mousse contenant ces particules étant ensuite récupérée en envoyée subir l’opération e) pour l’élimination mécanique de l’eau qu’elle contient.

8. Procédé selon la revendication 7, caractérisé en ce que l’opération de lavage d) comprend l’éjection d’un fluide aqueux à travers une buse à haut cisaillement sur la surface d’une masse d’eau de lavage de façon qu’il frappe à force cellérienne, amenant par là les particules de cendres hydrophiles restantes à se séparer en phase aqueuse et les particules de charbon hydrophobes et oléophiles à flotter sous forme de phase huile/ charbon sur la surface de l’eau de lavage et la récupération des particules de charbon flottantes à partir de la surface de l’eau de lavage.

9. Procédé selon la revendication 7 ou 8, caractérisé en ce que dans l’opération d) on soumet les particules de charbon hydrophobe et oléophiles à une pluralité d’opérations de lavage-flotation successives.

10. Procédé selon l’une quelconque des revendications 1 à 9, caractérisé en ce qu’on soumet les particules de charbon hydrophobe et oléophile enrichi récupérées en tant que produit dans l’opération e) en suspension dans un milieu aqueux contenant une quantité mineure d’hydrocarbure combustible liquide insoluble dans l’eau avec un mélange polymérisable comprenant un monomère organique susceptible de subir une polymérisation de radicaux libres et la présence d’un promoteur et d’un catalyseur de radicaux libres à un traitement supplémentaire, pour former ainsi une nouvelle couche organique hydrophobe et oléophile greffée et polymérisée dans le produit de charbon enrichi, et l’on récupère les particules ayant subi le traitement supplémentaire à partir du milieu de suspension aqueux.

11. Procédé selon la revendication 10, caractérisé en ce que le monomère organique utilisé dans ledit traitement supplémentaire est un monomère tel que défini dans la revendication 4 ou 5.

12. Procédé selon l’une quelconque des revendications 1 à 11, caractérisé en ce que le monomère utilisé dans l’opération b) et, ou dans le
tratamiento suplementario según la revendación 10 o 11, es un monómero conteniendo un o plural de grupos acido carboxílico libre (→COOH), y después recuperación de las particulas de charbon enrique en el operación e), o después recuperación de las particulas siempre su traslado suplementario según la revendación 10 o 11, se neutraliza las grupos acidos carboxílicos en la couche grefée-polymérisée après polymérisation en reaccion con un metal alcalin o alcalino-terreux o un autre agent neutralisant content en un metal.

13. Procédé selon l’une quelconque des revendications 1 à 12, caractérisé en ce que ledit hydrocarbure liquide insoluble dans l’eau présent dans la suspension aqueuse pendant mise en contact des particules de charbon avec le dit mélange polymérisable est du mazout n° 2.

14. Procédé selon l’une quelconque des revendications 1 à 9, caractérisé en ce qu’on soumet les particules de charbon enrichi récupérées en tant que produit dans l’opération e) à un traitement supplémentaire dans un milieu aqueux avec un acide gras saturé et on les neutralise éventuellement avec un metal alcalin ou alcalino-terreux, ou autre agent de neutralisation contenant un metal.

15. Procédé selon la revendication 14, caractérisé en ce que l’acide saturé est de l’acide naphténique.

16. Mélange charbon-huile transportable constitué par des particules d’un produit de charbon hydrophobe et oéophile enrichi obtenu par un procédé selon l’une quelconque des revendication 1 à 15 dispersé dans un hydrocarbure liquide porteur.

17. Mélange charbon-huile selon la revendications 16 contenant des particules de charbon enrichi obtenues par le procédé selon la revendication 12, c’est-à-dire par neutralisation de groupes acide carboxylique présents sur la surface des particules de charbon et résultant de l’utilisation d’un monomère contenant un acide carboxylique, caractérisé en ce qu’on opère la neutralisation après dispersion des particules de charbon enrichi dans l’hydrocarbure porteur.

18. Mélange charbon-eau transportable constitué par des particules d’un charbon hydrophobe et oéophile enrichi obtenues par un procédé selon l’une quelconque des revendications 1 à 13 dispersées dans un liquide aqueux porteur.

19. Mélange charbon-eau selon la revendication 18, caractérisé en ce que les particules enrichies ont été obtenues en utilisant un monomère contenant un acide carboxylique, les groupes carboxyliques présents sur la surface des particules enrichies ayant été ultérieurement neutralisées par un metal alcalin.

**Patentansprüche**

1. Verfahren zur Aufbereitung von Rohkohle durch das Entfernen von Schwefel und aschebildenden Verunreinigungen, umfassend die Schritte
   a) Zerkleinerung der Rohkohle,
   b) Berührung der zerkleinerten Rohkohle-
   partikel in Suspension in einem wässrigen Suspensionsmedium, welches Wasser und 1–10 Gew.% eines flüssigen, wasserunlöslichen Kohlenwasserstoff-Brennstoffes, berechnet vom Gewicht der zerkleinerten Rohkohlepartikel, enthält, mit einer polymerisierbaren Mischung mit: i) einem oder mehreren organischen Monomeren, die die Fähigkeit haben, in Gegenwart eines freien radikalen Katalysators und Initiators zu polymerisieren, ii) einem freien radikalen Katalysator und iii) einem freien radikalen Initiator, wodurch die Kohlepartikel durch die Pfropfpolymerisation des genannten Monomers oder der Monomere in dem genannten Medium in Gegenwart der genannten Kohlepartikel vorzugsweise sowohl hydrophob als auch oleophil gemacht werden; während der Schwefel und die aschebildenden Verunreinigungen im wesentlichen hydrophil gelassen werden;

   c) Selektive Trennung der hydrophoben, oleophilen Kohlepartikel vom wässrigen Suspensionsmedium, wodurch in dem genannten Medium der genannte im wesentlichen hydrophile Schwefel und die aschebildenden Verunreinigungen zurückbleiben;

   d) Waschen der getrennten hydrophoben, oleophilen Kohlepartikel mit Wasser zur weiteren Entfernung von hydrophilen Verunreinigungen; und

   e) Mechanische Trennung der gewaschenen hydrophoben, oleophilen Kohlepartikel vom gewaschenen Medium, wodurch ein korpuskulares aufbereitetes Kohle/Ol-Produkt gewonnen wird, das die genannten hydrophoben, oleophilen Kohlepartikel und sorbierten flüssigen Kohlenwasserstoff enthält, wobei das genannte Kohle/Ol-Produkt weniger als ungefähre 20% Wasser auf Gewichtsbasis enthält.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Bestandtei i) und ii) der polymersierbaren Mischung und der wässrige Kohlenwasserstoff-Bestandteil des Suspensionsmediums der Kohle während der Zerkleinerung beigemischt werden, und der Bestandteil ii) der Polymerisationsmischung anschließend beigemischt wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der freie radikale Katalysator Wasserstoffperoxid ist.

4. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß der Monomerbestandteil der genannten polymerisierbaren Mischung eine oder mehrere wasserunlösliche ungesättigte Säuren der Formel RC(OH) enthält, wobei R eine äthylenartig-ungesättigte Gruppe von mindestens 8 Kohlenstoffatomen ist.

5. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß der Monomerbestandteil der genannten polymerisierbaren Mischung mindestens eines oder mehrere der folgenden enthält: Ölsäure, Fettsäuren von Pflanzensamenöl, Methacrylsäuremethylester oder Methacrylsäureäthylerster, Acrylsäuremethylester oder Acrylsäureäthylerster, Acrylnitril, Vinylacetat, Styrol, Dicyclopentadien, Sojabohnenöl, Rizinussöl, Maisöl oder Taliöl.
6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß im Schritt c) die hydrophoben, oleophilen Kohlepartikel vom wäs- serigen Medium durch Schaumflotation getrennt werden.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß im Schritt d) die getrennten hydrophoben, oleophilen Kohlepartikel mit dem genannten Waschwasser unter heftiger Bewegung in Berührung gebracht werden, wo- durch ein Schaum gebildet wird, der diese Partikel enthält, wobei der diese Partikel enthaltende Schaum dann gesammelt und zur mechanischen Entfernung des Wassers zu Schritt e) weiterge- führt wird.

8. Verfahren nach Anspruch 7, dadurch gekenn- zeichnet, daß beim Waschschritt d) ein wässriges Fluid durch eine stark scherende Düse auf die Oberfläche einer Waschwasserfläche so ausge- stoßen wird, daß es zwangsläufig darauf abprallt, wodurch restliche hydrophile Ascheteilchen in die wässrige Phase abgetrennt und die hydrophoben, oleophilen Kohlepartikel als Öl/Kohle-Phase auf der Oberfläche des Spülwassers ausgeflockt wer- den, und die ausgeflockten Kohlepartikel von der Oberfläche des Waschwassers gewonnen werden.


10. Verfahren nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß die aufber- reiteten, hydrophoben oleophilen Kohlepartikel, die als das Produkt im Schritt e) gewon- nen wurden, in Suspension in einem wässrigen Medium, welches eine geringe Menge eines wasserunlöslichen, flüssigen Kohlenwasserstoff- Brennstoffes enthält, mit einer polymerisierbaren Mischung weiter behandelt werden, die ein organi- nisches Monomer enthält, das in Gegenwart eines Frei-Radikal-Initiators oder -katalysators einer Frei-Radikal-Polymerisation unterworfen werden kann, wodurch ein weiterer mikropor- polymerisierter hydrophober, oleophiler organischer Überzug auf den aufbereiteten Kohlepartikeln gebildet wird, und die weiterbehandelten Partikel aus dem wässrigen Suspensionsmedium gewonnen werden.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das in der genannten Weiter- behandlung verwendete organische Monomer ein im Anspruch 4 oder 5 definierter Monomer ist.

12. Verfahren nach einem der Ansprüche 1 bis 11, dadurch gekennzeichnet, daß das in Schritt b) und/oder in der in Anspruch 10 oder 11 definier-

ten zusätzlichen Behandlung verwendete Mono- mer ein Monomer ist, das eine freie Karbonsäure (—COOH)-Gruppe oder Gruppen enthält, und daß nach der Gewinnung der aufbereiteten Kohle- partikel in Schritt e), oder nach der Gewinnung der weiterbehandelten Partikel gemäß Anspruch 10 oder 11, und die Karbonsäuregruppen im pfpolymerisierenden Überzug nach der Poly- merisation durch Reaktion mit einem Alkali oder Erdalkalimetall oder einem anderen metallich- hältigen Neutralisationsmittel neutralisiert wird.

13. Verfahren nach einem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß der genannte flüssige Kohlenwasserstoff, der in der wässrigen Suspension während der Berührung der Kohle- partikel mit der genannten polymerisierbaren Mi- schung ein Heizöl Nr. 2 ist.

14. Verfahren nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß die als das Pro- dukt in Schritt a) aufbereiteten Kohlepartikel in Suspension in einem wässrigen Medium mit einer gesättigten Fettsäure weiterbehandelt und mit einem Alkali oder Erdalkalimetall, oder einem anderen metallerhaltigen Neutralisationsmittel wahlweise neutralisiert werden.

15. Verfahren nach Anspruch 14, dadurch gekennzeichnet, daß die gesättigte Säure Naphten- säure ist.


CONVENTIONAL COAL MINING RECOVERY & BENEFICIATION
- PARTICLE SIZE ORDER 1/4"

CLEAN TREATED WATER RECYLE → COARSE PARTICLES

ROD OR BALL MILL AQUEOUS COAL SLURRY → PARTICLE SIZE CLASSIFIER

48-200 MESH SLURRY DENSITY CONTROL SURGE TANK

GRAFT POLYMERIZATION REACTANTS WATER, FUEL OIL RC=O-OH ACIDS COPPER ION OXIDIZING AGENTS

HIGH SHEAR NOZZLES

IN LINE MIXER

D → HYDROPHOBIC COAL WASH (1)

ASH-WATER (1A)

FLOCCULATED HYDROPHOBIC COAL PARTICLES

FINE COAL RECOVERY

TO FIG. 2B

CLEAN COAL SLURRY

A 18-2 18-1 18 C

B F 17

FLOCCULATED WASHED COAL SLURRY

19

18

TO FIG. 2B

FIG. 2A