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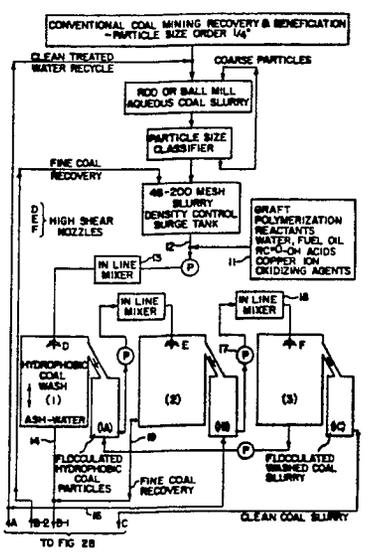
(54) A process for the beneficiation of coal and beneficiated coal product.

(57) An improved beneficiated coal products is disclosed comprising coal particles which have been rendered hydrophobic and oleophilic by forming a polymer coating thereon. According to the process an aqueous slurry containing the coal particles is admixed with a fuel oil and a polymerisation mixture preferably containing one or more long chain carboxylic acids which are polymerised in situ on the coal particles. The hydrophobic coal particles are then separated from the aqueous medium by froth flotation preferably in several steps by atomising the flocculated coal particles onto the surface of a mass of wash water. Hydrophilic ash particles separate into the wash water whilst the flocculated hydrophobic, oleophilic coal particles are recovered. Following recovery the flocculated particles are de-watered mechanically. Additional but optional treatments include neutralisation and admixing with oil to form coal-in-oil mixtures, and subjecting the particles to a second graft polymerisation procedure.



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A process for the beneficiation of coal and beneficiated coal product

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 pulverized 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 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 0.10 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. 3,376,168 (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), 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 pulverizing 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.

As a summary of background for the present invention, it is 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 a beneficiated coal product comprised of a particulate coal having a surface and being characterised by having low ash and sulfur content. The particulate coal is coated with a polymer of an organic unsaturated monomer, the coating of such polymer being sufficient to render the particulate coal both hydrophobic and oleophilic.

In a more specific aspect of the invention, the particulate coal is coated with an insoluble hydrocarbon fuel and the organic unsaturated monomer comprises a water insoluble fatty acid of the structure RCOOH wherein R is an unsaturated moiety containing at least 8 carbon atoms. In a further aspect of the invention, the beneficiated coal product further comprises a minor amount of a water insoluble hydrocarbon fuel oil; the particulate coal is from 48 to 200 mesh in size and the hydrocarbon fuel is a number 2 fuel oil.

In another aspect of the invention a beneficiated coal oil mixture is provided comprises of a beneficiated particulate coal and a hydrocarbon oil as the continuous phase with the particulate coal being suspended in the hydrocarbon. The coal-oil mixture is treated with a salt forming compound and the resultant mixture is stable, gel like and thixotropic.

In a more specific aspect the coal-oil mixture of the invention comprises about 50 wt. percent coal based on the total weight of the mixture.

In another aspect of the invention, a process is provided for beneficiating coal which comprises introducing particulate coal into a water stream and chemically treating the particulate coal to render the coal hydrophobic and oleophilic. The coal is thereafter separated from unwanted ash and sulfur normally present in the coal by an oil and water separation technique wherein at least a portion of the unwanted ash and sulfur enter the water phase and the particulate coal is removed in a froth phase.

In more specific aspects of the process, the particulate coal is treated in the water stream with (a) a free radical polymerization catalyst; (b) a free radical catalyst initiator; (c) a fuel oil; and (d) an organic unsaturated monomer. The free radical polymerization catalyst employed include organic or inorganic peroxides such as hydrogen peroxide, benzoyl peroxide, oxygen and air. The free radical catalyst initiators comprise active metal ions such as the ions of copper, iron, zinc, arsenic, antimony, tin and

cadmium. The organic unsaturated monomers include oleic acid, naphthalenic acid, vegetable seed oil fatty acid, unsaturated fatty acid, methyl and ethyl methacrylate, methyl and ethyl acrylate, acrylonitrile, vinylacetate, styrene, cracker gasoline, dicyclopentadiene, coker gasoline, polymer gasoline, soybean oil, castor oil, Venezuelan crude and bunker fuel, tall oil and corn oil.

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 a solid or 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, 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 for beneficiating coal can be employed during particle size reduction of the coal. Among the substances that can be treated are: mine run, refuse piles, coal processing fines and the like. Generally, the coal is suspended in or wetted by water sufficient to permit fluid flow for the beneficiation treatment.

In another aspect of the invention, the hydrocarbon fuel fraction serves along with the water as a carrier for a chemical grafting polymerization reaction wherein the unsaturated monomer reacts on the surface of the coal to cause the original water wetted coal surfaces to become chemically altered by covalent bonding of polymerizable monomers to the surfaces of the coal being processed. The coal surfaces become preferentially wetted by water insoluble hydrocarbon fuels such as aliphatic or aromatic fuel, heavy fuel oils, kerosenes, and the like.

The organic unsaturated monomers broadly useful for the purposes of this invention include polymerizable organic monomers having at least one unsaturated group which includes such monomers that are liquid at room temperatures. Illustratively the list includes oleic acid, naphthalenic acid, vegetable seed oil fatty acid, unsaturated fatty acid, methyl and ethyl methacrylate, methyl and ethyl acrylate, acrylonitrile, vinylacetate, styrene, cracker gasoline, dicyclopentadiene, coker gasoline, polymer gasoline, soybean oil, castor oil, Venezuelan crude and bunker fuel, tall oil, corn oil and other monomers as are shown in the prior art.

Preferably, the organic unsaturated monomers adapted for use in the invention are water insoluble organic acids having the general structure RCOOH wherein R is more than about 8 carbon atoms in size and is preferably unsaturated. Excellant results have been obtained using the material tall oil a derivative of the wood pulp industry and corn oil which comprises glycerides of a number of fatty acids and unsaturated vegetable seed oil fatty acids. The carboxyl moiety

of these materials is not essential but is particularly advantageous as will be seen hereafter.

The above-identified additives can be added at the initial process stages, e.g., during pulverization of the raw coal to a particulate size of from 48 to 200 mesh, 0.1 to 79 microns or finer. It is preferred to add the free radical polymerization catalyst at the end of or after the final pulverization of the coal. It can be present, however, and added at any time in the coal attrition cycle (i.e., during reduction to 48 to 200 mesh) along with the remainder of the chemical grafting additives described above.

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 and recycle of the water.

Lime can be used, if desired, to aid ash removal from the water phase. It has been established as preferable and advantageous, however, 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. In practice, the free radical polymerization catalyst is more efficiently utilized if withheld until all the other additive components (metal ion and polymerizable monomer) have been allowed to obtain a maximum degree of dispersion in the final, finely pulverized water wetted coal slurry.

As the chemical grafting reaction is completed by the peroxide treatment, the now hydrophobic and oleophilic beneficiated coal particles flocculate and float to the surface of the liquid mass. The ash, still remaining hydrophilic, tends to settle and is removed in the water phase.

The recovered flocculated hydrophobic coal is re-dispersed 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 water wash 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 onto 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.

Following the plural water-washing-high shear redispersion of the coal flocculates and the further removal of ash thereby released to the water phase, in our preferred practice the coal is again subjected to a second graft polymerization step using the chemical grafting reagent mixture including the unsaturated RCOOH acids (tall oil fatty acids), hydrogen peroxide, water soluble copper salt, fuel oil and water as used priorly in the process. However, the second graft polymerization step, while preferred, is not absolutely essential. The treated coal, beneficiated to provide a dry coal product containing a small water content, a small amount of fuel oil and an improved BTU content can thereafter be recovered for 'dry' fuel use.

A non-settling, fluid, pumpable, storable liquid coal-oil mixture (C.O.M.) may be prepared starting at this point. One need

not essentially perform the second graft polymerization step. However, it is a preferred mode of practice of the invention. One may elect to merely incorporate a further small but effective amount of a free fatty acid (RCOOH acid) where the R group may or may not be unsaturated as in the preferred practice referred to immediately above.

The recovered washed hydrophobic coal, freed of a major amount of the ash originally present, is further dehydrated to very low water levels solely by mechanical means, illustrated by centrifuging, pressure or vacuum filtration, etc., thus avoiding the essential use of thermal energy to remove residual water requiring costly heating of the entire coal mass. As the treated coal is now hydrophobic and oleophilic or oil wetted, water is more readily removed.

At this point the treated coal is electively ready to prepare a fluid coal-oil-mixture (C.O.M.). Additional quantities of fuel oils, as demanded, are blended with the treated 'dry' coal at any desired ratio. Preferred ratio is about 1:1 by weight.

Two avenues of further treatment remain open. If RCOOH is used in the chemical grafting step to render the surface of the coal particles oleophilic and hydrophobic, the grafted acid group, as well as the added fatty acid group, can be further reacted through their active, acidic hydrogen atom with an alkali or alkaline earth metal or a variety of selected metal ions. Through selection of metal ions, the 'drop point' of the final liquefied clean-oil-mixture (C.O.M.) thixotropic liquid fuel products can be controlled.

If one wishes to slurry the recovered coal in water to produce a stable dispersion and suspension, as might be required for pumping through pipelines for extended distances, the acidic hydrogen can be replaced with an alkali metal ion, illustratively sodium.

However, it is more likely that a fluid suspended fine particle solid coal product extended with a fuel oil hydrocarbon will find the greatest commercial demand. In this case the metal is selected for the desirable 'drop point' of the liquefied coal-oil fuel product. Alkaline earth metal ions are quite useful for this purpose.

It has been discovered that conversion of the acidic hydrogen ion, traceable to the hydrogen of the RCOOH additions (and in the chemical grafting in some instances) to a metal ion; illustratively sodium, potassium, calcium, (the alkali and alkaline earth metals) surrounding the surfaces of the beneficiated coal particles allows ready dispersion of the coal in fuel oils of most all grades to produce a gel or structure which retards settling almost indefinitely. The 'drop point' (the temperature at which the gel structure allows free flow of the liquid coal-oil-fuel) appears to be controllable by the metal ion selection. Other metal ions may also be useful alone or in admixture to control the 'drop point'.

Coal extended liquid fuel oil products of this invention 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 has also been influenced by the selection of the metal ion.

Thus, the versatility of the pulverized coal is increased, the energy content is increased, undesirable ash is removed and the potential for a widely expanded market for coal as a fluid fuel provide means for further conservation of petroleum.

It is anticipated that the fluidized version where fuel oils of various grades are the carriers will become of major importance as a liquefied coal-oil product as herein described.

This invention chemically alters the surface of the coal particles so that they both repel water and invite union with the fluidizing liquid fuel in which the coal particles are dispersed. This chemical surface reaction is carried out principally in water.

Reduction of ash content (the principal source of mineral sulfur in coal) is extremely important in obtaining an acceptable coal. The ash content of coal is present in extremely fine states of subdivision in the coal. The surface treatment of the coal provides a strongly oil-loving quality. Advantageously, the freely divided ash remains water-loving or hydrophilic thus facilitating selective separation of coal and ash.

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" $\pm$ size (2.5 cm) is used as a starting point a hydro roll crusher reduces the coal to about a 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, H_2O_2, is satisfactory for this purpose. The other components to be added are: the polymerizable water insoluble monomer, preferably an RCOOH acid where R is more than about 8 carbon atoms and is unsaturated; a reactive metal ion site catalyst initiator salt; a minor amount of a selected 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 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 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 in 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 counter-current water-wash steps.

The chemically grafted pulverized coal (with most of the ash originally present in the raw coal 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 beneficiation, the water content of the grafted washed product can be in the order of 6-12% by weight.

The recovered 'dry' beneficiation 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 RCOOH acid is added. The added acid can be the same as the unsaturated acid used in the chemical grafting step. However, the acid need not be unsaturated. Saturated RCOOH acids such as stearic acid and the series of both crude and refined naphthenic acids recovered from refining of crude oils, etc. can be used. Water soluble alkali hydroxide metal is now added to the coal-oil mixture. This neutralizes the free fatty acid hydrogens on 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 beneficiation 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, but it is preferred not to use a large percentage over 48 mesh.

The aqueous slurry leaving the rod mill is put through a classifier and all particles more than about 48 mesh 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 first of three water-wash steps where the chemical grafting reactants are added.

An aqueous chemical grafting reagent mixture when complete and useful for the initial graft initiating 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 provide metal ion initiator sites. Cost 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 (H_2O_2) added directly or produced, in situ, with air or oxygen, but which is here preferentially hydrogen peroxide constitutes about 1-5/8 lbs (.74 kg) of H_2O_2 in solution of 30% H_2O_2-70% 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 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 now 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 break up 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 hydrophilic 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 step which enhances the efficiency of the operation.

In passing the hydrophobic polymer-oil surfaced 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 floc 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 floc.

The coal floc itself is of lesser 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 floc. The coal floc 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 surfaces, 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 floc 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 overflows 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, grafted, clean coal slurry is thereupon 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 surfaces and the water physically occluded 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 that 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 conveyor, 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 desire to create a second reactive, grafting procedure). In this latter election, 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 storably 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

2000g, 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 in a hydro crusher 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, 100g of fuel oil, 2-1/2g sodium pyrophosphate and 1g of copper nitrate were incorporated into the above mill batch in the initial mill loading. Before the mill was discharged 1-1/2g of H_2O_2 in solution (30% H_2O_2 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 at as low as 20°C but it is preferred to use at least 30°C water temperature. The water preferably contains a phosphate conditioning agent.

The recovered, mechanically dried cleaned treated coal aggregate was admixed with oil and an additional 60 gm 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) dicyclopentadiene, f) dodecyl methacrylate, g) octadiene 1, 7, h) 2, 2, 4 trimethyl pentene -1, i) glycidyl methacrylate and j) soyabean 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 exhibited thixotropic quality depending upon the metal ion selected to displace 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 H_2O_2. 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 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 200 mesh (more or less) in a conditioned water (sodium tetraphyrophosphate) 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 H_2O_2. 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 or in excess of about 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, vinylacetate, 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, dicyclopentadiene, 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 unsaturated water insoluble monomeric organic acid having the general structure RCOOH where R is unsaturated and has at least about 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 rosin acids. All of the unsaturated fatty acids available from vegetable seed oils, illustratively soyabean 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 illustrated 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 phenomona 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 3,376,168 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 backboned 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 drops off. If the temperature is below this range, not only does ash removal become 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 RCOOH additions, 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 efficiency of coal recovery has been noted where H_2O_2 is used.

In the graft monomer polymerization addition step, use of fuel oil of the order of 5% in the catalyst carrier appears to function to provide better coal recovery 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 instances. 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 surfactants of the anionic, non-ionic and cationic classes may be valueable additions in some instances. 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 66% (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 operative. Undoubtedly modifications both in ratio of reactants as well as their ratio to the weight of coal being processed can be operationally varied within a wide range. The limiting factors will, of course, be modified by the economics of established commercial plant experience.

In the coal slurry prepared for coal size reduction, the percentages of coal and water will be variable, again depending on pulverizing 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 floccu-late, 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 composition.

The fact that it is usual in coal mining operations that coal milled to 28 mesh 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 invention, 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. Temperatures 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 6% water and the dry clean coal Product I is generally not more thanabout 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 beneficiated coal product comprising particles of coal having a low ash and sulfur content, characterised in that said particles are rendered hydrophobic and oleophilic by a surface coating comprising a polymer of one or more organic monomers.

2. A coal product according to claim 1 further comprising from 0.1 to 10% by weight of a water-insoluble, liquid hydrocarbon fuel oil.

3. A coal product according to claim 1 or 2, characterised by a water content of from 6 to 20% by weight.

4. A coal product according to claim 1, 2 or 3, characterised in that the polymer is derived from a monomer charge containing one or more unsaturated carboxylic acids of the formula RCOOH, where R is an ethylenically unsaturated group of at least 8 carbon atoms.

5. A coal product according to any one of claims 1-3, characterised in that the unsaturated organic monomer is selected from oleic acid, naphthalenic acid, vegetable seed oil fatty acid, unsaturated fatty acid, methyl and ethyl methacrylate, methyl and ethyl acrylate, acrylonitrile, vinyl acetate, styrene, cracker gasoline, dicyclopentadiene, coker gasoline, polymer gasoline, soybean oil, castor oil, Venezuelan crude, bunker fuel and tall oil.

6. A beneficiated coal-oil mixture comprising a coal product as claimed in any one of claims 1-5 dispersed in a liquid hydrocarbon.

7. A coal-oil mixture according to claim 6, wherein the polymer coating on the coal particles comprises units derived from an unsaturated monomer containing a free carboxylic acid group, and wherein, in said coal-oil mixture, said groups are in salt form.

8. A coal beneficiation process characterised by treating the coal in particulate form in an aqueous medium to render the particles hydrophobic and oleophilic, and separating the hydrophobic, oleophilic particles from the aqueous medium.

9. A process according to claim 8, characterised in that said particles are rendered hydrophobic and oleophilic by forming a polymeric coating on said particles by *in situ* polymerisation of monomer charge comprising one or more unsaturated organic monomers.

10. A process according to claim 9, wherein said polymerisation is effected in an aqueous medium which contains also a water-insoluble hydrocarbon fuel and the particles are recovered as a coal/oil mixture.

11. A process according to claim 10, characterised in that said particles are rendered hydrophobic and oleophilic by contacting

the particles in said aqueous medium with a polymerisation mixture comprising

i) a free radical polymerisation catalyst,

ii) a free radical catalyst initiator,

iii) a fuel oil, and

iv) an unsaturated organic monomer.

12. A process according to claims 9, 10 or 11, wherein the monomer charge used to form said polymeric coating on the coal particles comprises one or more unsaturated acids of the formula RCOOH, where R is an ethylenically unsaturated group of at least 8 carbon atoms.

13. A process according to claim 9, 10 or 12, wherein the monomer charge used to form said polymeric coating on the particles comprises one or more of the following: oleic acid, naphthalenic acid, vegetable seed oil fatty acid, unsaturated fatty acid, methyl and ethyl methacrylate, methyl and ethyl acrylate, acrylonitrile, vinyl acetate, styrene, cracker gasoline, dicyclopentadiene, coker gasoline, polymer gasoline, soybean oil, castor oil, Venezuelan crude, bunker fuel and tall oil.

14. A process according to any one of claims 9-13, wherein the hydrophobic, oleophilic coal particles are separated from the aqueous medium by froth flotation.

15. A process according to claim 14, characterised in that separation step comprises ejecting an oil-water mixture containing the hydrophobic, oleophilic coal particles through a high shear nozzle onto the surface of a body of wash water so as to impinge thereon, thereby causing the 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.

16. A process according to claim 14 or 15, characterised in that the separation of the hydrophobic, oleophilic coal particles from the aqueous suspension medium is carried out in two or more flotation steps.

17. A process according to claim 14, 15 or 16, characterised in that following separation of the hydrophobic oleophilic coal particles by flotation, the recovered flocculated coal particles are further de-watered by mechanical means.

18. A process according to any one of claims 9-17, characterised in that the recovered hydrophobic oleophilic coal particles are subsequently dispersed in a liquid hydrocarbon to form a coal-in-oil mixture.

19. A process according to claim 18, characterised in that free carboxylic acid groups in the polymer coating on the coal particles are neutralised by replacement of the acidic hydrogen atoms by alkali metal or alkaline earth metal atoms.

20. A process according to any one of claims 9-19, characterised in that the recovered hydrophobic oleophilic coal particles are subjected to a further graft polymerisation treatment in which a further monomer charge is polymerised in situ in contact with the hydrophobic, oleophilic coal particles.

21. A process according to claim 20, in which the further monomer charge comprises one or more monomers of the formula RCOOH, where R is an ethylenically unsaturated group containing at least 8 carbon atoms.

22. A process according to claim 18 or 19, characterised in that the hydrophobic, oleophilic coal particles are dispersed in said hydrocarbon in admixture with one or more saturated or unsaturated carboxylic acids of the formula RCOOH where R is a saturated or unsaturated group of at least 8 carbon atoms.

23. A process according to claim 22, wherein said acid is a naphthenic acid.

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FIG. IA

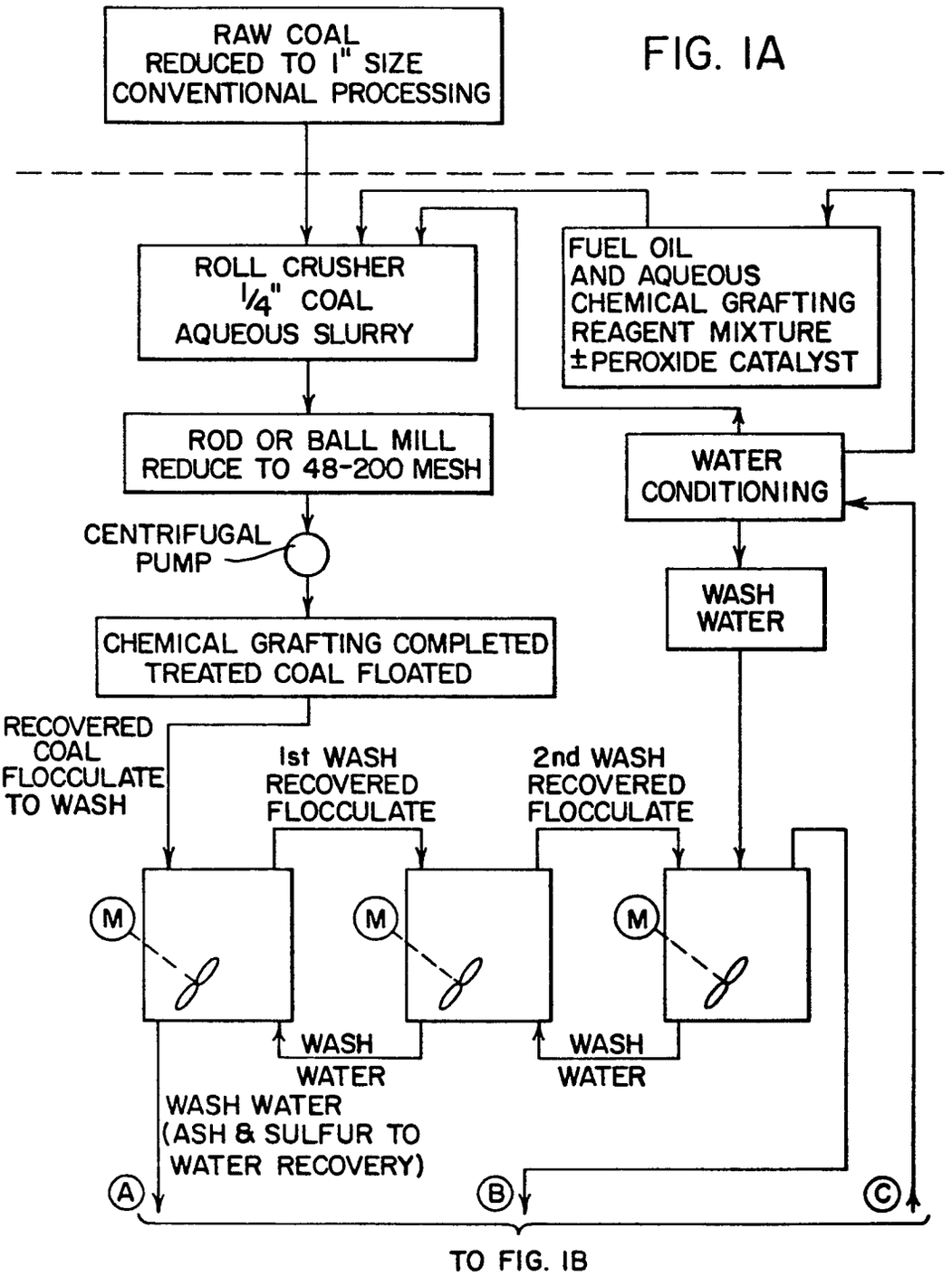
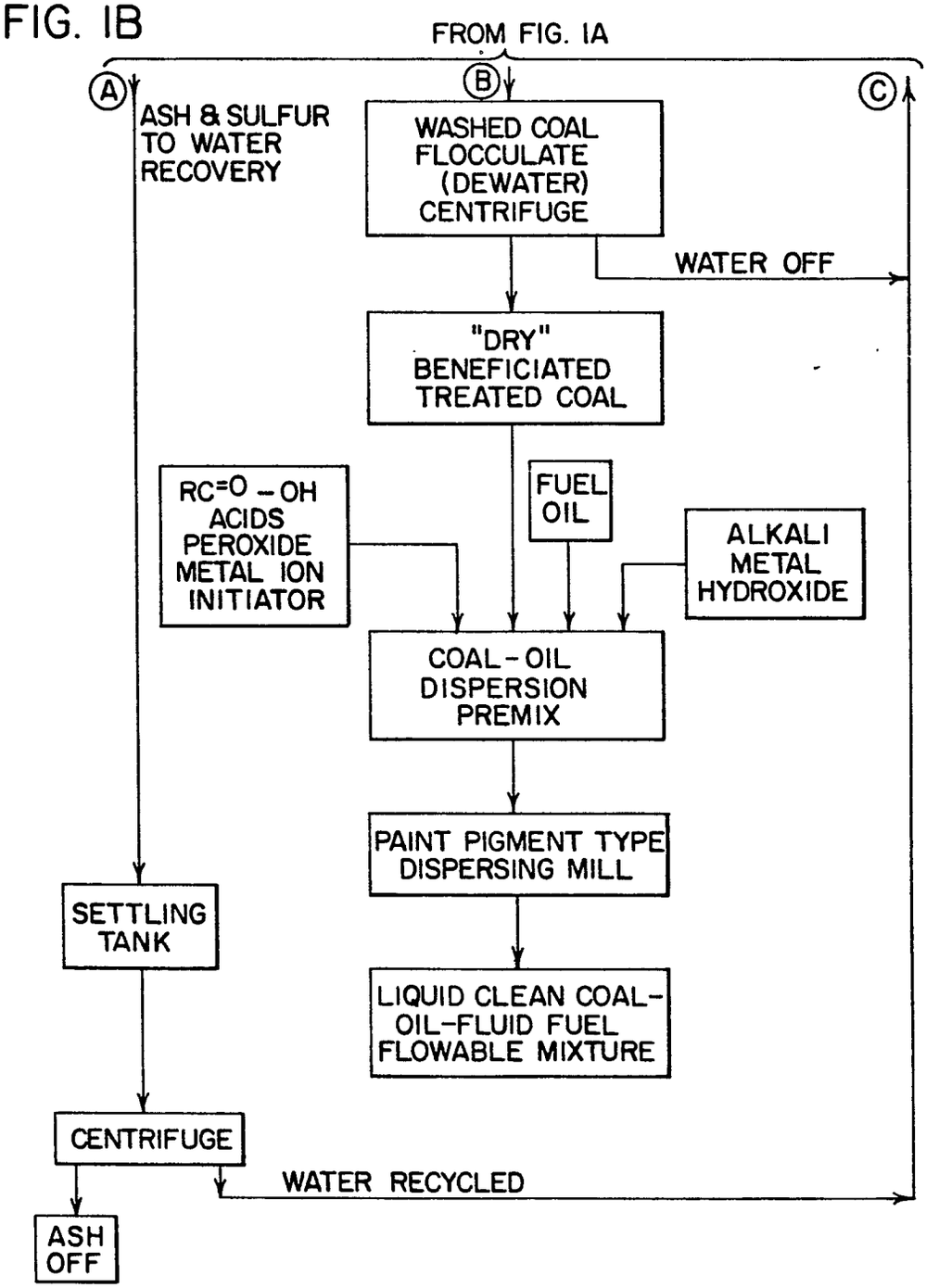


FIG. IB


FROM FIG. IA
A
B
C
ASH & SULFUR TO WATER RECOVERY
WASHED COAL FLOCCULATE (DEWATER) CENTRIFUGE
WATER OFF
"DRY" BENEFICIATED TREATED COAL
RC=O – OH ACIDS PEROXIDE METAL ION INITIATOR
FUEL OIL
ALKALI METAL HYDROXIDE
COAL – OIL DISPERSION PREMIX
PAINT PIGMENT TYPE DISPERSING MILL
SETTLING TANK
LIQUID CLEAN COAL-OIL-FLUID FUEL FLOWABLE MIXTURE
CENTRIFUGE
WATER RECYCLED
ASH OFF

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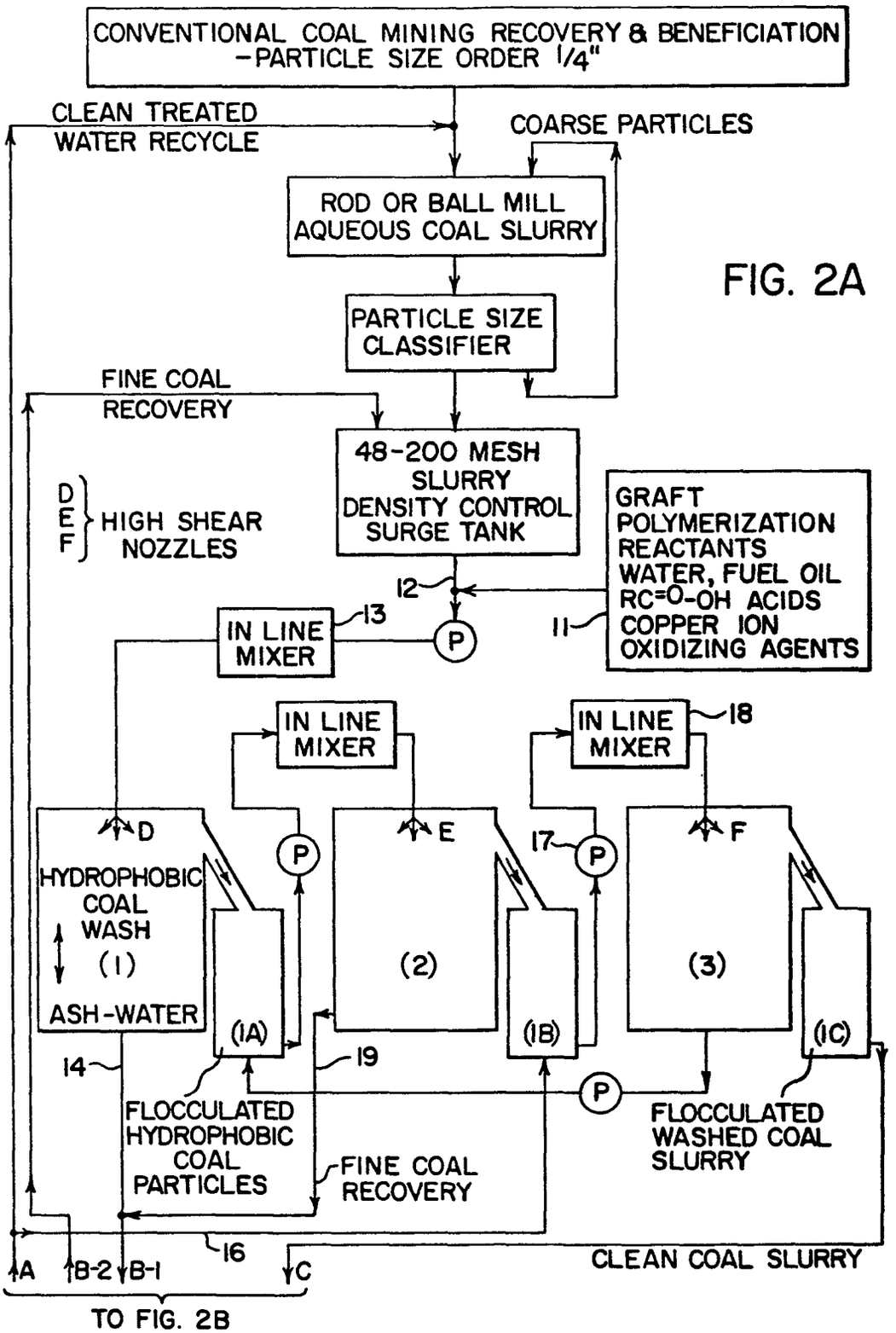

FIG. 2A

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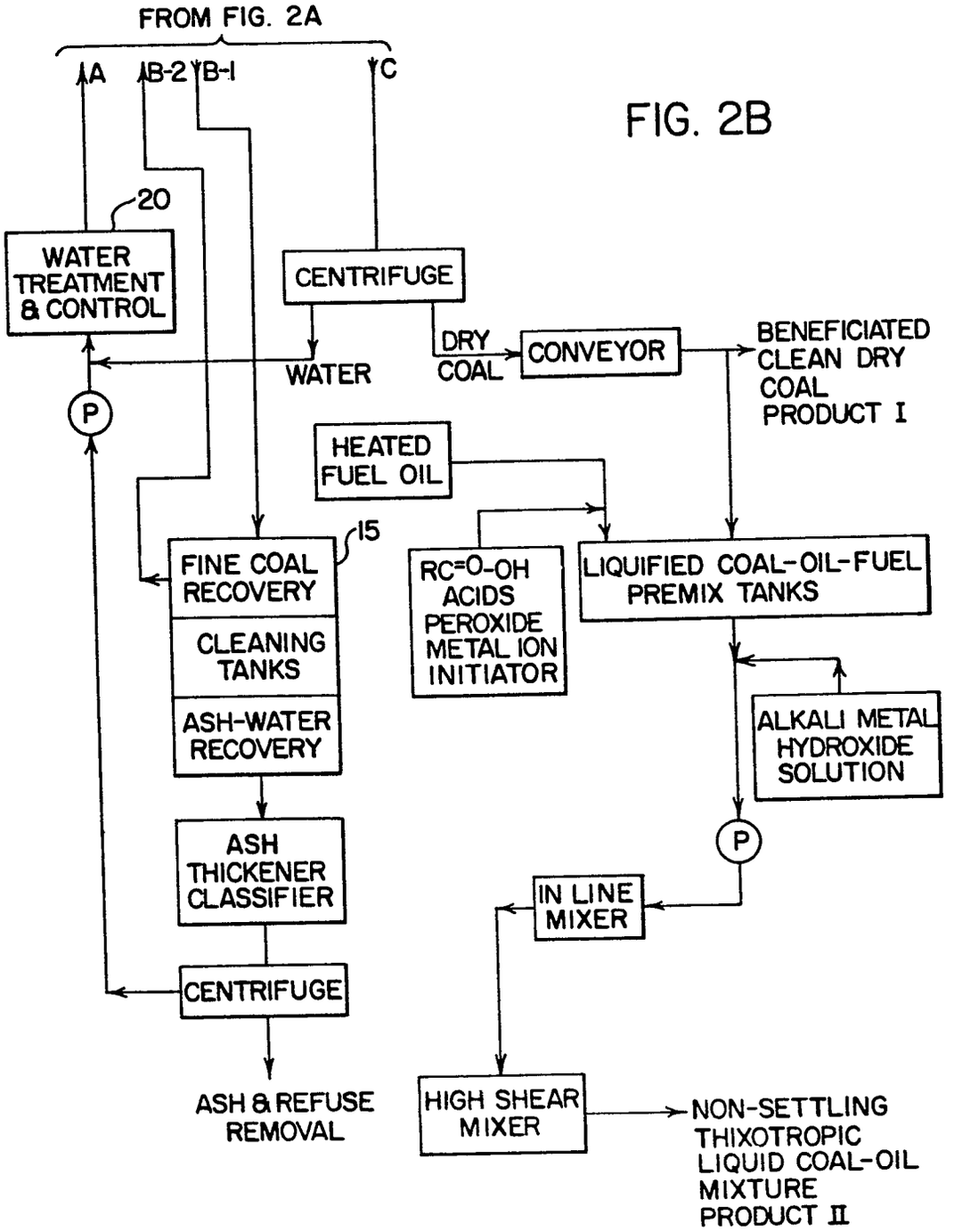

FIG. 2B