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(84) Designated Contracting States: AT BE DE FR GB IT NL SE (7) Applicant: THE STANDARD OIL COMPANY Midland Building Cleveland, Ohio 44115(US)

(72) Inventor: McGarry, Philipp E. 518 Columbia Avenue Palmerton Penns. 18071(US)

(72) Inventor: Herman, David E .
Box 50B, Star Route
Jim Thorpe Penns. 18229(US)

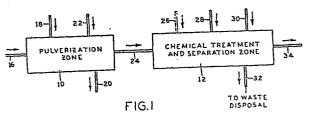
(74) Representative: Brauns, Hans-Adolf, Dr. rer. nat. et al, Hoffmann, Eitle & Partner, Patentanwälte Arabellastrasse 4 D-8000 Munich 81(DE)

[54] Process for beneficiating coal employing low amounts of additives.

(5) A process for beneficiating coal is disclosed which comprises:

a) contacting pulverized coal with water, a polymerization reaction medium comprising a polymerizable monomer and polymerization catalyst therefor under polymerization reaction conditions, and a fluid organic medium facilitating contact of the surface of the coal particles with the polymerization reaction medium, to provide surface-treated coal particles, the total combined quantity of polymerizable monomer and fluid organic medium not exceeding about 2.0% by weight of the coal; and.

separating surface-treated coal particles from the water.
 The coal beneficiated products resulting therefrom are also disclosed.



PROCESS FOR BENEFICIATING COAL EMPLOYING LOW AMOUNTS OF ADDITIVES

Known world resources of coal and other solid carbonaceous fuel materials are far greater than the known resources of petroleum and natural gas combined. Despite this enormous abundance of coal and related solid carbonaceous materials, reliance on these resources, particularly coal, as primary sources of energy, has been for the most part discouraged. The availability of cheaper, cleaner burning, more easily retrievable and transportable fuels, such as petroleum and natural gas, has in the past, cast coal to a largely supporting role in the energy field.

Current world events, however, have forced a new awareness of global energy requirements and of the availability of those resources which will adequately meet these needs. The realization that reserves of petroleum and natural gas are being rapidly depleted in conjunction with skyrocketing petroleum and natural gas prices and the unrest in the regions of the world which contain the largest quantities of these resources, have sparked a new interest in the utilization of solid carbonaceous materials, particularly coal, as primary energy sources.

As a result, enormous efforts are being extended to make coal and related solid carbonaceous materials
equivalent or better sources of energy than petroleum or natural gas. In the case of coal, for example, much of this effort is directed to overcoming the environmental problems associated with its production, transportation and combustion. For example, health and safety hazards associated with coal mining have been significantly reduced with the onset of new legislation governing coal mining. Furthermore, numerous techniques have been explored and developed to make coal cleaner burning, more suitable for burning and more readily transportable.

- Gasification and liquefaction of coal are two such known techniques. Detailed descriptions of various coal gasification and liquefaction processes may be found, for example, in the Encyclopedia of Chemical Technology,
- 5 Kirk-Othmer, Third Edition (1980) Volume 11, pages 410-422 and 449-473. Typically these techniques, however, require high energy input, as well as the utilization of high temperature and high pressure equipment, thereby reducing their widespread feasibility and value.
- Processes to make coal more readily liquefiable have also been developed. One such process is disclosed in U.S. Patent No. 4,033,852 (Horowitz, et al). This process involves chemically modifying the surface of the coal, the effect of which renders a portion of the coal more readily liquefiable than the natural forms of coal.

In addition to gasification and liquefaction other methods for converting coal to more convenient forms for burning and transporting are also known. For example, the preparation of coal-oil and coal-aqueous mixtures are described in the literature. Such liquid coal mixtures offer considerable advantages. In addition to being more readily transportable than dry solid coal, they are more easily storable, and less subject to the risks of explosion by spontaneous ignition. Moreover, providing coal in a fluid form makes it feasible for burning in conventional

mixtures and their preparation are disclosed in U.S. Patent 30 No. 3,762,887, U.S. Patent No. 3,617,095 and U.S. Patent No. 4,217,109 and British Patent No. 1,523,193.

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apparatus used for burning fuel oil. Such a capability can greatly facilitate the transition from fuel oil to

coal as a primary energy source. Typical coal

Regardless, however, of the form in which the coal is ultimately employed, the coal must be cleaned because it contains substantial amounts of sulfur and nitrogen compounds and mineral matter, including significant quantities of metal impurities. During combustion, these materials enter the environment as sulfur dioxides, nitrogen oxides and compounds of metal impurities. If coal is to be accepted as a primary energy source, it must be cleaned to prevent pollution of the environment, either by cleaning the combustion products or the coal prior to burning.

Accordingly, physical as well as chemical coal cleaning (beneficiation) processes have been extensively explored. In general, physical coal cleaning processes involve pulverizing the coal to release the impurities, wherein the fineness of the coal generally governs the degree to which the impurities are released. However, because the costs of preparing the coal rise exponentially with the amount of fines to be treated, there is an economic optimum in size reduction. Moreover, grinding to even the finest sizes is not effective in removing all impurities.

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Based on the physical properties that effect the separation of the coal from the impurities, physical coal cleaning methods are generally divided into four categories: gravity, flotation, magnetic and electrical methods.

In contrast to physical coal cleaning, chemical coal cleaning techniques are in a very early stage of development. Known chemical coal cleaning techniques include, for example, oxidative desulfurization of coal (sulfur is converted to a water-soluble form by air oxidation), ferric salt leaching (oxidation of pyritic sulfur with ferric sulfate), and hydrogen peroxide sulfuric acid leaching. Other methods are also disclosed in the abovenoted reference to the Encyclopedia of Chemical Technology, Volume 6, pages 314-322.

- In the chemical coal cleaning processes disclosed and claimed in U.S. Patent Nos. 4,332,593 and 4,304,573, and in United States Government Report No. 2694 (Department of Energy) entitled "Fuel Extension by
- 5 Dispersion of Clean Coal in Fuel Oil", all of which disclosures are incorporated by reference herein, raw coal is first cleaned of rock and/or other extraneous materials as may be required and then pulverized, preferably in the presence of water, to a relatively fine average particle
- 10 size. An aqueous slurry of the finely pulverized coal is contacted with a polymerization reaction medium comprising a polymerizable monomer and polymerization catalyst therefor, and a fluid organic medium such as a distillate fuel for dispersing the coal and the polymerization reaction medium.
- 15 As a result of polymerization taking place, the surface of the coal particles is rendered highly hydrophobic and oleophilic. While it is not completely understood and while not wishing to be bound by theory, it is believed that this surface treatment involves the formation of a
- polymer or coating on the surface of the coal particles by molecular grafting of polymeric side chains on the coal molecules. The surface-treated coal particles are readily separated from unwanted ash and sulfur-containing components which are present in the aqueous component of the slurry.
- 25 Moreover, the hydrophobic coal can be readily further dehydrated to very low water levels without employing costly thermal energy. The clean, very low moisture content coal resulting from this process can then be employed as is, i.e., as a dry solid product, or further processed
- 30 to advantageous coal-oil or coal-aqueous mixtures. In an improvement on this process disclosed and claimed in U.S.

- 1 patent application Serial No. 230,061 filed January 29, 1981, the aforedescribed processes of beneficiating coal are further improved by the use of a frothing agent which, in the presence of water and a gas such as air, promotes the for-
- 5 mation of small bubbles which collect the hydrophobic, oleophilic coal particles at the surface of the slurry from which they may be removed by such techniques as skimming. At the same time impurities pass into the water from which they are later withdrawn as tailings. In this manner,
- 10 greater separation of chemically cleaned coal from the impurities-laden aqueous phase of the slurry can be readily achieved.

It has now been discovered that the chemical coal cleaning processes described above such as the processes

- 15 of aforesaid United States Patent Nos. 4,332,593 and 4,304,573 can be further improved by reducing the total combined amount of polymerizable monomer and fluid organic medium employed. Working at relatively low levels of combined monomer and fluid organic medium, it has been ob-
- 20 served that the amount of impurities present in the coal, collectively referred to as ash and sulfur, can be significantly further reduced. Moreover, since the amount of moisture retained by the treated coal is also appreciably reduced, less thermal energy need be expended in drying 25 the coal.

Broadly stated, the present invention provides a process for beneficiating coal which comprises:

a) contacting pulverized coal with water, a polymerization reaction medium comprising a polymerizable monomer and polymerization catalyst therefor under polymerization reaction conditions, and a fluid organic medium facilitating contact of the surface

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- of the coal particles with the polymerization reaction medium, to provide surfacetreated coal particles, the total combined quantity of polymerizable monomer and fluid organic medium not exceeding about 2.0% by weight of the coal; and,
- b) separating surface-treated coal particles from the water,

The term "coal" shall be understood herein to include all solid carbon formations including coal in all of its varieties, shale oil, tar sands, coke, graphite, mine tailings, coal fines from mine ponds or tailings and the like, containing appreciable quantities of one or more impurities whose removal in whole or in part is desired.

The sole figure is a flow diagram of a coal beneficiating process according to an embodiment of the invention herein.

In accordance with the present invention, coal
in pulverized form is combined with water, polymerization
reaction medium and a fluid organic medium which facilitates
contact of the surface of the coal particles with the reaction medium. The average particle size of the coal can vary
widely with finer particle sizes rendering the impurities

25 present in the coal more accessible to removal. The advantage of conducting the process upon very fine particle
size coal can, however, be offset by the cost of the additional energy required to achieve such particle size. In
general, a particle size of from about 48 to about 200 mesh
(Tyler Standard screen size) or greater will provide acceptable results with a reasonable expenditure of energy. So
far as is known, there is no objection if a larger percentage
of the coal is smaller than 200 mesh but it is preferred

1 if no large percentage is much above the 48 mesh size. After leaving the size reduction operation, the coal can be screened to remove particles exceeding 48 mesh which are then returned for further size reduction. Reduction 5 of the raw coal can be carried out in the absence of added liquid but for convenience is preferably carried out in the presence of water. If size reduction in the presence of water is contemplated, it may be advantageous to add a small quantity of a water treating agent to enhance 10 the wettability of the coal and facilitate pulverization. Such water treating agents include dispersants, surfactants, wetting agents and the like. Preferred water conditioning additives are sodium carbonate, sodium pyrophosphate and the like. It may also be further advan-15 tageous to employ water which has previously been treated in an ion exchange technique.

The quantity of water in admixture with the coal can vary over wide limits provided a sufficient amount is ultimately present to result in an apparent aqueous phase and an apparent flocculent phase containing surface-treated coal particles as more fully described hereinafter. It is generally preferred to employ only as much water as is necessary to provide the aforesaid phases in order to minimize the overall amount of water which must be processed. In contrast to prior art beneficiation processes which typically are carried out upon coal slurries containing from about 90% to about 95% water by weight, the present process works very well with slurries containing from about 65% to about 95% water by weight.

Any polymerizable monomer can be employed in the polymerization reaction medium herein. While it is more convenient to utilize monomers which are liquid at ambient temperature and pressure, gaseous monomers which contain olefinic unsaturation permitting polymerization with the

same or different molecules can also be used. Thus, monomers intended to be employed herein may be characterized by the formula XHC = CHX' wherein X and X' each may be hydrogen or any of a wide variety of organic radicals or inorganic substituents. Illustratively, such monomers include ethylene, propylene, butylene, tetrapropylene, isoprene, 1,3-butadiene, pentadiene, dicyclopentadiene, octadiene, olefinic petroleum fractions, styrene, vinyltoluene, vinylchloride, vinylbromide, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, N-methylolacrylamide, acrolein, maleic acid, maleic anhydride, fumaric acid, abietic acid, and the like.

A preferred class of monomers for the purposes of the present invention are unsaturated carboxylic acids, esters, or salts thereof, particularly those included within the formula O wherein R is an olefinically RC - OR'

unsaturated organic radical, preferably containing from about 2 to about 30 carbon atoms, and R' is hydrogen, a salt-forming cation such as an alkali metal, alkaline earth metal or ammonium cation, or a saturated or ethylenically unsaturated hydrocarbyl radical, preferably containing from 1 to about 30 carbon atoms, either unsubstituted or substituted with one or more halogen atoms, carboxylic acid groups, 25 hydroxyl groups and/or hydroxyl groups in which the hydroxyl hydrogens may be replaced with saturated and/or unsaturated acyl groups, the latter preferably containing from about 8 to about 30 carbon atoms. Specific monomers conforming to the foregoing structural formula include unsaturated fatty acids such as oleic acid, linoleic acid, linolenic acid, rincinoleic acid, mono-, di- and tri-glycerides of one or more unsaturated fatty acids, and other esters of unsaturated fatty acids, acrylic acid, methacrylic acid, methylacrylate, ethylacrylate, ethylhexylacrylate,

1 tertiary-butylacrylate, oleylacrylate, methylmethacrylate,
 oleylmethacrylate, stearylacrylate, stearylmethacrylate,
 laurylmethacrylate, vinylstearate, vinylmyristate, vinyl laurate, soybean oil, cottonseed oil, palm oil, dehydrated
5 castor oils, tall oil, corn oil, and the like. For the
 purpose of this invention tall oil and corn oil have been
 found to provide particularly advantageous results. Corn
 oil is especially preferred.

While the cause and effect relationship between
10 polymerization (or possibly dimerization or oligomerization
as the case may be) of monomer and the development of
hydrophobic, hydrophilic characteristics on the surface
of the coal particles is not known with certainty, there
does appear to be a connection between the two. In practice,
an amount of monomer will be employed which will provide
these hydrophobic, hydrophilic characteristics to an
appreciable extent. It is a particular feature of the
present invention to minimize the combined use of monomer
and fluid organic medium consistent with the need to
20 obtain coal having a suitable degree of hydrophobic,
hydrophilic surface properties. In general, the monomer
can be used at a level of from about .005% to about .10%, and
preferably, 0.1% to about .05%, by weight of dry coal.

reaction medium can be selected from among any such materials commonly used to effect polymerization of ethylenically unsaturated monomers. Typically, for the purposes of this invention, a catalytic amount of those catalysts of the so-called free radical type are preferred.

Their amounts include from about 10-1000 ppm of catalyst, preferably 10-200 ppm (parts per million) based on the amount of dry coal. Thus, illustratively, catalysts contemplated herein include benzoyl peroxide, methylethyl ketone peroxide, tertbutylhydroperoxide, hydrogen peroxide,

35 ammonium persulfate, di-tert-butylperoxide, tert-butyl-

perbenzoate, peracetic acid, and including such nonperoxy free radical initiators as the diazo compounds,
such as l-l-bis-azo-isobutyro nitrile and the like.
Hydrogen peroxide is especially preferred for use herein.

Moreover, free radical polymerization systems commonly employ free radical initiators which function to initiate the formation of free radicals. purposes herein, any of the initiators disclosed in the 10 prior art can be used. Specifically, some of these initiators include, for example, sodium perchlorate and perborate, sodium persulfate, potassium persulfate, ammonium persulfate, silver nitrate, water soluble salts of noble metals such as platinum and gold, water soluble salts of 15 iron, zinc, arsenic, antimony, tin and cadmium. larly preferred initiators herein are the water soluble copper salts, i.e., cuprous and cupric salts, such as copper acetate, copper sulfate and copper nitrate. Most advantageous results have been obtained herein with cupric ni-20 trate, Cu(NO₃)₂. Further initiators contemplated herein are also disclosed in U.S. Patent Application Serial No. 230,063 filed January 29, 1981. These initiators include metal salts of naphthenates, tallates, octanoates, etc., said metals including copper, cobalt, chromium, mercury, manga-25 nese, nickel, tin, lead, zinc, iron, rare earth metals and mixed rare earths. Amounts of initiator contemplated for use herein are generally in the range from about 10-1000 ppm (parts per million) of the metal portion and preferably 10-200 ppm, based on the amount of dry coal.

It is, of course, understood that the catalyst shall be present in any catalytically effective amount.

Optimum quantities employed will depend upon such factors as the nature and concentration of the monomer, the pressure and temperature under which polymerization occurs, the

1 reaction rate desired, and so forth, and can be determined for a particular beneficiation process employing simple procedures as is evident to those skilled in the art. Ambient pressure will ordinarily be used for reasons of 5 process economy and simplicity and for the same reasons, ambient temperatures or slightly higher will also be favored although it is, of course, recognized that polymerization will readily occur within a broad temperature range, e.g. from about 0°C to about 200°C. For example, at ambient 10 pressure and within the preferred temperature range of from about 20° to about 50°C, employing corn oil (a mixture of triglycerides typically averaging an unsaturated fatty acid content, based on the free acids, of about 86%) as the polymerizable monomer, hydrogen peroxide can be used 15 as catalyst at a level of from about 0.01% to about 0.1% by weight of dry coal with good results.

The process of this invention further requires the use of a fluid organic medium to facilitate contact of the surface of the coal particles with the polymeriza-20 tion reaction medium. Fluid organic media included within the scope of this invention, are for example, fuel oil, such as No. 2 or No. 6 fuel oils, other hydrocarbons including benzene, toluene, xylene, hydrocarbon fractions such as naphtha and medium boiling petroleum fractions (boiling 25 point 100°-180°C), dimethylformamide, tetrahydrofuran, tetrahydrofurfuryl alcohol, dimethylsulfoxide, methanol, ethanol, isopropyl alcohol, acetone, methylethylketone, ethylacetate, and the like, and mixtures thereof. purpose of this invention, fuel oil is a preferred fluid 30 organic medium. The maximum amount of fluid organic medium which can be used herein represents a critical aspect of the present invention and, in combination with polymerizable monomer, must not exceed 2.0% by weight of the coal being processed. By itself, it is preferred to use from about

1 0.10% to about 1.0%, and more preferred, from about 0.20% to about 0.50% fluid organic medium by weight of coal.

It is further within the scope of the present invention to employ a frothing agent herein in order to effect greater recovery of surface-treated coal from process water as described and claimed in aforesaid U.S. patent application Serial No. 230,061 filed January 29, 1981.

The frothing agents which are optionally intended for use herein can be selected from among any of the known and conventional materials used to effect frothing in coal which are suitable for use herein include aliphatic alcohols such as methylisobutyl carbinol (MIBC) which is a preferred frothing agent herein, the cresylic acids, eucalptus oils, camphor oils and pine oils, all of which are slightly soluble in water. Water soluble frothers which can be used herein include alkyl ethers and phenyl ethers of propylene and polypropylene glycols.

will depend in large measure upon the volume of slurry
undergoing treatment and the coal content thereof and is
related to other process parameters as will be readily
understood by those skilled in the art. Amounts of frothing
agent ranging from about 0.005% to about 0.5% or higher, and
preferably from about 0.01% to about 0.1%, by weight of dry
coal being treated generally provide good results. The point
of addition is not critical; however, to avoid the possibility
that frothing might interfere with the surface treating
phase of the coal cleaning process, it is preferred to
add the frothing agent to the slurry only after significant
polymerization has taken place, i.e., from about 1 minute
to about 2 hours following contact of the coal with the
polymerization reaction medium.

- 1 The process herein contemplates conventional flotation recovery techniques, intermittent or continuous skimming of the surface-treated coal from the surface of the slurry being an entirely suitable technique. The 5 recovered coal flocculate can, if desired, be subjected to one or more further cycles of chemical surface treatment and/or washing to effect still greater separation of impurities and/or recovery of treated pulverized coal.
- A particularly effective technique for separating 10 the treated coal particles from unwanted ash and sulfur in the water phase is an aeration spray technique wherein a coal froth phase is formed by spraying or injecting the treated coal-water slurry into the surface of cleaning water as is described and claimed in U.S. Patent Nos.
- 15 4,347,126 and 4,347,127 incorporated herein by reference.

 Briefly, according to the method and apparatus there

 described the coal slurry is injected through at least

 one spray nozzle at pressures for example at from about 15
 20 psi to a spaced-apart distance above the water surface

 20 into the water surface producing aeration and a frothing
 - o into the water surface producing aeration and a frothing or foaming of the coal particles, causing these particles to float to the water surface for skimming off.

Referring to the drawing, raw coal entering through line 16 is cleaned of unwanted rock, heavy ash and the like 25 and is crushed in the presence of water, added through line 18, in pulverization zone 10 to provide an aqueous coal slurry. The rock and ash leave pulverization zone 10 through line 20. In pulverization zone 10 the particulate coal in the slurry is ground to particle sizes of about 48 to 300 mesh, 30 preferably about 80% of the particles being of about a 200 mesh size. A water conditioning agent such as described hereinbefore may also be added through line 22 to assist

in the separation of impurities.

The aqueous coal slurry is fed to a chemical and separation zone 12 through line 24 where it is admixed with fuel oil and polymerizable monomer such as corn oil introduced through line 26. The fuel oil can 5 act as a diluent for the monomer. Polymerization catalyst such as hydrogen peroxide and free radical initiator such as cupric nitrate are also added to zone 12 via line 28 and admixed therein. Preferably, the reactants, coalaqueous slurry and carrier oil are sprayed into at least one froth flotation vessel (not shown) in zone 12 wherein a coal froth phase and an aqueous impurity containing phase ensue. Optionally, frothing agent is also added to the slurry in zone 12 through line 30 to induce frothing.

The aqueous impurity containing phase containing 15 ash and sulfur is removed through line 32 and may be sent to, e.g., waste disposal treatment.

The coal froth phase, containing cleaned coal particles, is removed such as by skimming or otherwise and recovered through line 34. The recovered coal which 20 may be dried can be used as is, such as for example in the formation of coal-oil or coal-aqueous mixtures or may be used as a particulate coal for burning.

The following examples in which all percentages are by weight are further illustrative of the process

25 herein for beneficiating coal.

EXAMPLES 1 - 7

A series of coal beneficiating runs were carried out upon Pittsburgh Seam coal at varying levels of polymerizable monomer (i.e., corn oil) and fluid organic medium (i.e., No. 2 fuel oil) to demonstrate the improved levels of ash reduction and moisture reduction obtained at relatively low levels of combined monomer and fluid organic medium.

ground coal having a maximum particle size of about 570 microns containing 200 grams coal and 500 grams water were subjected to further size reduction employing grinding times of 5, 10, 15, 30 and 60 minutes, respectively. The individual slurries were thereafter combined with varying quantities of No. 2 fuel oil and corn oil as indicated in Table I below as well as 1.0 ml. of a 5% aqueous solution of hydrogen peroxide catalyst and 5 ml. of a 50 mg./ml. solution of sodium pyrophosphate and 2 ml. of a 50 mg./ml. aqueous solution of cupric nitrate. The results of each coal beneficiation run are set forth in Table I as follows:

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TABLE I

1 EFFECT OF THE AMOUNT OF MONOMER AND FLUID ORGANIC MEDIUM ON BENEFICIATION OF PITTSBURGH SEAM COAL

| | Example | Coal Grinding Time (Min.) | Product Ash % | | % Coal Recovery | Filter Cake Moisture % |
|----|---------|-----------------------------|---------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 5 | | 5% No. 2 | Fuel Oil: | 0.50 lb/to | Corn Oil | <u>.</u> |
| J | 1 | 5 10 15 30 60 | 3.79 3.64 3.73 3.99 3.70 | 37.2 42.1 41.9 33.8 43.0 | 98.9 95.8 99.8 95.7 99.6 | 24.9 26.2 22.0 28.0 33.4 |
| | | 2 1/2% No. | 2 Fuel (| Dil; 0.50 lb, | ton Corn | Oil |
| 10 | 2 | 5 10 15 30 60 | 3.84 3.77 3.67 3.60 3.51 | 39.2 40.5 43.8 44.7 43.8 | 89.6 92.8 92.0 85.6 93.6 | 21.0 25.8 21.7 26.8 29.6 |
| | | 1% No. 2 H | Tuel Oil; | 0.50 lb/ton | Corn Oil | |
| 15 | 3 | . 5 10 15 30 60 | 3.75 3.66 3.45 3.35 3.15 | 41.4 42.4 46.3 46.7 48.5 | 92.5 85.4 84.3 86.1 80.7 | 19.4 22.3 28.7 34.4 34.7 |
| | | 0.5% No. 2 | Fuel Oil | l; 0.50 lb/to | on Corn Oi | .1 |
| 20 | 4 | 5 10 15 30 60 | 3.60- 3.43 3.16 3.05 2.64 | 44.2 43.2 50.2 51.9 58.4 | 79.8 81.1 71.8 72.6 56.5 | 20.9 28.7 27.0 30.2 39.3 |
| | • | 0.5% No. 2 | Fuel Oil; | 0.30 lb/tor | Corn Oil | |
| 25 | 5 | 5 10 15 30 60 | 3.29 3.27 3.24 2.67 2.49 | 48.4 48.3 48.6 58.0 60.7 | 78.0 74.7 76.8 41.0 45.3 | 18.0 23.7 23.2 28.7 35.4 |
| | | 0.5% No. 2 | Fuel Oil; | 0.10 lb/tor | Corn Oil | |
| 30 | 6 | 5 10 15 30 60 | 3.21 2.97 2.97 2.62 2.16 | 48.1 52.5 52.9 58.2 64.7 | 69.8 60.2 51.7 49.3 13.2 | 24.7 19.0 22.4 28.7 34.8 |

TABLE I

EFFECT OF THE AMOUNT OF MONOMER AND FLUID ORGANIC MEDIUM ON BENEFICIATION OF PITTSBURGH SEAM COAL

| | Example | Coal Grinding Time (Min.) | | % Ash Elimination | % Coal Recovery | Filter Cake Moisture % |
|---|---------|---------------------------------|-----------|----------------------|--------------------|------------------------------|
| 5 | | 0.5% No. | 2 Fuel Oi | 1; 0.10 lb/t | on Corn O | <u>il</u> |
| | 7 | 5, | 3.10 | 50.6 | 50.9 | 24.4 |
| | | 10 | 2.73 | 56.2 | 46.0 | 24.4 |
| | | 15 | 2.49 | 60.0 | 29.4 | 28'.7 |
| | | 30 | 1.77 | 71.5 | 1.0 | 53.1 |
| | | 60 | 1.96 | 68 .7 | 3.0 | 42.7 |

As these data show, the amount of ash retained 1 in the coal (for a given grinding time) begins to decline noticeably with the reduction in combined quantities of fuel oil and corn oil to 2.0% by weight of the dry coal 5 and below. At the same time, the degree of ash elimination from the recovered beneficiated coal increases significantly at the lower fuel oil/corn oil levels. While the actual percentages of beneficiated coal recovery falls off sharply as very low levels of fuel oil and corn oil are used, 10 this result is readily offset by recycling the non-surface treated coal to the surface treatment step herein until substantially complete recovery of the coal is effected. The filter cake moisture levels are actual moisture levels of product. Filtrations were standardized to show the com-15 parative data. The actual amounts of retained moisture in the recovered coal were far smaller and in the case of Examples 3 to 7 which are illustrative of the process ofthis invention, were substantially less than the amounts . of retained moisture in the beneficiated coals resulting 20 from the processes of Examples 1 and 2.

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EXAMPLES 8 - 11

The general beneficiating procedure employed with Examples 1 to 7 was employed herein except that the coal was Freeport Seam and all of the runs were carried out in accordance with the process of this invention. The results are set forth in Table II as follows:

TABLE II

EFFECT OF THE REAGENT AMOUNT OF MONOMER AND FLUID
ORGANIC MEDIUM ON BENEFICIATION OF LOWER FREEPORT SEAM
COAL

| | | | COAD | | | |
|----|---------|--------------------------------|--------------------------------------|--------------------------------------|---------------------------------------|--------------------------------------|
| 10 | Example | Coal Grinding Time, min. | Product Ash % | % Ash Elimination | % Coal Recovery | Filter Cake Moisture % |
| | | 1% No. 2 | Fuel Oil; | 0.50 lb/ton | Corn Oil | |
| 15 | 8 | 5 10 15 30 60 | 3.54 3.25 3.54 2.78 2.83 | 3.5 66.4 64.4 71.6 71.0 | 77.7 63.3 83.5 51.2 58.1 | 21.8 26.0 28.7 36.0 38.6 |
| | | 0.5% No. | 2 Fuel Oil | ; 0.50 lb/to | on Corn Oil | <u>_</u> |
| 20 | 9 | 5 10 15 30 60 | 3.23 3.55 2.69 2.57 2.48 | 66.6 63.1 72.2 73.3 74.3 | 66.9 71.15 45.9 38.7 41.2 | 28.2 26.3 34.1 38.7 40.1 |
| | | 0.5% No. | 2 Fuel Oil | ; 0.30 lb/to | on Corn Oil | L |
| 25 | 10 | 5 - 10 15 30 60 | 2.86 3.79 2.74 3.09 2.28 | 70.0 59.4 71.2 67.1 76.8 | 53.9 56.6 44.0 64.5 33.1 | 20.5 28.8 31.3 43.0 43.0 |
| | | 0.5% No. | 2 Fuel Oil | ; 0.10 lb/to | on Corn Oil | <u>.</u> |
| 30 | 11 | 5 10 15 30 60 | 3.12 2.83 2.69 2.66 2.42 | 68.1 67.4 71.3 71.7 73.8 | 51.6 54.9 44.0 43.0 38.3 | 28.9 29.2 33.0 41.9 43.2 |

These data further demonstrate the advantageous effect of reducing the combined level of monomer and fluid organic medium in the coal beneficiating process of this invention.

EXAMPLES 12 - 15

The beneficiating procedure of Examples 8 to 11 was substantially repeated but with Pocohontas Seam coal. The results which further demonstrate the improvements provided by the instant invention are set forth in Table III as follows:

TABLE III

EFFECT OF THE AMOUNT OF MONOMER AND FLUID REACTION MEDIUM ON BENEFICIATION OF POCOHONTAS SEAM COAL

| | MEDIUM O | N DUNDI ICIII | TON OF TO | COHOMIND DIVIN | COAL | |
|----|----------|--------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 10 | Example | Coal Grinding Time, min. | Product Ash % | & Ash Elimination | % Coal Recovery | Filter Cake Moisture % |
| | | 5% No. 2 | Fuel Oil; | 0.50 lb/ton | Corn Oil | ÷ |
| 15 | 12 | 5 10 15 30 60 | 2.08 1.77 1.83 1.77 1.71 | 46.8 55.2 52.5 55.8 57.5 | 86.7 76.9 71.6 83.8 91.6 | 21.1 31.5 29.1 31.7 26.2 |
| | | | | 1; 0.50 lb/to | | |
| 20 | | 5 10 15 30 60 | 1.95 1.75 2.08 2.02 1.74 | 52.6 52.4 47.3 51.3 61.1 | 83.5 73.6 69.8 77.6 51.1 | 24.2 28.8 23.6 30.9 40.0 |
| | | 0.5% No. | 2 Fuel Oi | 1; 0.30 lb/to | n Corn Oil | <u>L</u> |
| 25 | 14 | 5 10 15 30 60 | 1.86 1.75 1.67 1.77 1.67 | 57.5 56.9 57.0 58.1 61.3 | 82.0 65.6 40.5 54.8 51.7 | 21.5 32.5 36.5 31.0 40.6 |
| | | 0.5% No. | 2 Fuel Oi | 1; 0.10 lb/to | n Corn Oil | <u>L</u> . |
| 30 | 15 | 5 10 15 30 60 | 1.78 1.87 1.78 1.63 | 52.7 56.3 57.7 62.1 60.8 | 77.5 62.7 64.7 54.6 43.5 | 19.3 23.7 29.6 32.1 35.2 |

While it is not completely understood at this time and without intending to be limited by any theory, it is believed that the above-described advantageous results are achieved by employing selectively low amounts of polymerizable monomer and fluid organic medium not exceeding about 2.0% by weight of the dry coal, by a unique combination wherein sufficient additives are present to achieve the desired chemical treatment, but which are of sufficiently low level so as to avoid undue agglomeration of the coal particles which might hinder or impair coal recovery by avoiding agglomerated coal from being lost in the wash stream.

Obviously, other modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that changes may be made in the particular embodiments of this invention which are within the full intended scope of the invention as defined by the appended claims.

CLAIMS:

- 1. A process for beneficiating coal which comprises:
- polymerization reaction medium comprising a polymerizable monomer and polymerization catalyst therefor under polymerization reaction conditions, and a fluid organic medium facilitating contact of the surface of the coal particles with the polymerization reaction medium, to provide surface-treated coal particles, the total combined quantity of polymerizable monomer and fluid organic medium not exceeding about 2.0% by weight of the dry coal; and
 - b) separating surface-treated coal particles from the water.
- 2. The process of Claim 1 wherein the coal has an average particle size of from about 48 to about 200 mesh.
 - 3. The process of Claim 1 wherein the polymerizable monomer is represented by the general formula XHC = CHX' wherein X and X' each may be hydrogen, an organic radical or an inorganic substituent.
 - 4. The process of Claim 3 wherein the polymerizable monomer is represented by the general formula

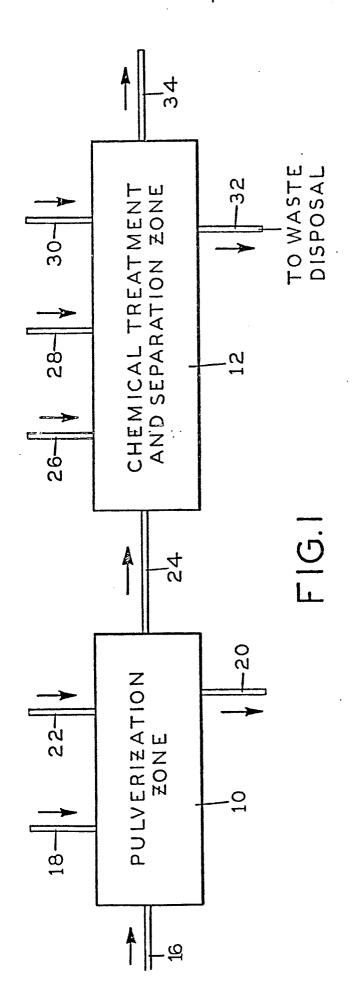
O RC - OR'

wherein R is an olefinically unsaturated radical or a saturated or ethylenically unsaturated hydrocarbyl radical, unsubstituted or substituted with one or more halogen atoms, carboxylic acid groups, hydroxyl groups and/or hydroxyl groups in which the hydroxyl hydrogen may be replaced with saturated and/or unsaturated acyl groups.

- 5. The process of Claim 4 wherein R contains from 2 to about 30 carbon atoms.
 - 6. The process of Claim 1 wherein the polymerizable monomer is a mono-, di- or tri-glyceride of one or more unsaturated fatty acids.
 - 7. The process of Claim 6 wherein the polymerizable monomer is corn oil.
 - 8. The process of Claim 7 wherein from about .005% to about .10% polymerizable monomer by weight of dry coal is used.
 - 9. The process of Claim 8 wherein from about 0.01% to about 0.05% polymerizable monomer by weight of dry coal is used.
- 10. The process of Claim 1 wherein the polymerization catalyst is an inorganic or organic peroxide.
 - 11. The process of Claim 10 wherein the polymerization catalyst is hydrogen peroxide.
- 12. The process of Claim 11 wherein the hydrogen peroxide is present at a level of from about 0.01% to about 0.1% by weight of monomer.
 - 13. The process of Claim 1 wherein a frothing agent is employed.
- 14. The process of Claim 13 wherein the frothing agent is selected from the group consisting of methylisobutyl carbinol, cresylic acid, eucalyptus oil, camphor oil, pine oil, alkyl ether or phenyl ether of propylene, and polypropylene glycols.
- 15. The process of Claim 13 wherein the frothing agent is employed at a level of from about 0.005% to about 0.5% by weight of the mixture of coal, water, polymerization reaction medium and fluid organic medium.

- 1 agent is employed at a level of from about 0.01% to about 0.1% by weight of the mixture of coal, water, polymerization reaction medium and fluid organic medium.
- 5 17. The process of Claim 1 wherein the fluid organic medium is a fuel oil.
 - 18. The process of Claim 1 wherein the fluid organic medium is used at a level of from about 0.10% to about 1.0% by weight of coal.
- 19. The process of Claim 18 wherein the fluid organic medium is used at a level of from about 0.20% to about 0.50% by weight of coal.
 - 20. The process of Claim 1 wherein the polymerization reaction medium further comprises a free radical initiator.
 - 21. The process of Claim 20 wherein the free radical initiator is a water soluble copper salt.
 - 22. The beneficiated coal produced by the process of Claim 1.
- 23. The process of Claim 1 wherein said polymerizable monomer is corn oil, said polymerization catalyst comprises hydrogen peroxide and cupric nitrate and said fluid organic medium is fuel oil.

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EUROPEAN SEARCH REPORT

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| Category | | th indication, where appropriate, vant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Ci.4) | | |
| х | EP-A-0 057 577 * Page 17, line 23 * | (GULF & WESTERN) 8 - page 20, line | 1-23 | B 03 D 1/02 C 10 L 9/10 | | |
| х | * Page 6, line : | (GULF & WESTERN) 16 - page 12, line nes 1-16; page 30, | 1-12, 17-23 | - | | |
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| Y : pai doo A : tec O : not | CATEGORY OF CITED DOCU rticularly relevant if taken alone rticularly relevant if combined w cument of the same category shnological background n-written disclosure ermediate document | E: earlier after the community of the another D: documn L: documn C: member | T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document | | | |