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54 **Beneficiated coal, coal mixtures and processes for the production thereof and an arrangement for producing a beneficiated coal product.**

57 This invention relates to the beneficiation of coal and more particularly to an improved process for the beneficiation of coal and separation of impurities therefrom and the formation of stable beneficiated coal mixtures, such as coal oil mixtures. Further more an arrangement for producing beneficiated coal product is described.

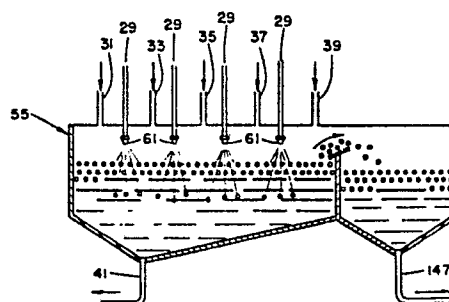


FIG. 4

BENEFICIATED COAL, COAL MIXTURES AND PROCESSES
FOR THE PRODUCTION THEREOF AND AN ARRANGEMENT FOR
PRODUCING A BENEFICATED COAL PRODUCT

This invention relates to the beneficiation of coal and more particularly to an improved process for the beneficiation of coal and separation of impurities therefrom and the formation of stable beneficiated coal mixtures, 5 such as coal oil mixtures.

Known resources of coal and other solid carbonaceous fuel materials in the world are far greater than the known resources of petroleum and natural gas combined. Despite this enormous abundance of coal and related solid 10 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, 15 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 20 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, has sparked a new interest in the utilization of solid carbonaceous materials, particularly 25 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

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1 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
5 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
10 such known techniques. Detailed descriptions of various
coal gasification and liquefaction processes may be found,
for example, in the Encyclopedia of Chemical Technology,
Kirk-Othmer, Third Edition (1980) Volume 11, pages 410-422
and 449-473. Typically, these techniques, however, require
15 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
20 in U.S. Patent No. 4,033,852 (Horowitz, et al.). This
process involves chemically modifying a portion of the
surface of the coal in a solvent media, the effect of which
renders the coal more readily liquefiable in a solvent than
natural forms of coal, thereby permitting recovery of
25 a liquefiable viscous product by extraction.

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
30 described in the literature. Such liquid coal mixtures
offer considerable advantages. In addition to being more

1 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
5 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-oil and coal-
aqueous mixtures and their preparation are disclosed in
U.S. Patent No. 3,762,887, U.S. Patent No. 3,617,095,
10 U.S. Patent No. 4,217,109, U.S. Patent No. 4,101,293 and
British Patent No. 1,523,193.

Regardless, however, of the form in which the coal
is ultimately employed, the coal or coal combustion products
must be cleaned because they contain substantial amounts of
15 sulfur, nitrogen compounds and mineral matter, including
significant quantities of metal impurities. During com-
bustion 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
20 must be cleaned to prevent pollution of the environment
either by cleaning the combustion products of the coal or
the coal prior to burning.

Accordingly, physical as well as chemical coal
cleaning (beneficiation) processes have been explored.
25 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
30 with the amount of fines to be treated, there is an economic
optimum in size reduction. Moreover, grinding coal even to
extremely fine sizes may not be effective in removing all

1 the impurities. 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 electri-
5 cal 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),
10 ferric salt leaching (oxidation of pyritic sulfur with
ferric sulfate), and hydrogen peroxide-sulfuric acid leaching.
Other methods are also disclosed in the above-noted refer-
ence to the Encyclopedia of Chemical Technology, Volume 6,
pages 314-322.

15 While it is obvious from the foregoing that
enormous efforts have been made to make coal a more
utilizable source of energy, further work and improvements
are still necessary and desirable before coal, coal mixtures
and other solid carbonaceous fuel sources are accepted on
20 a wide scale as primary sources of energy.

Thus, the present invention relates to a process
which comprises contacting coal in an aqueous medium with
a surface treating mixture comprising a polymerizable
monomer, a polymerization catalyst and a liquid organic
25 carrier, thereby providing a hydrophobic and oleophilic
coal product adapted to the removal of further ash and
sulfur by water separation techniques. The resultant pro-
duct is highly suitable for the formation of beneficiated
coal slurries and/or cleaned particulate coal.

30 Moreover, in a further embodiment of the present
invention an improved process for beneficiating coal is

1 provided which comprises chemically surface treating coal
in an aqueous medium to render said coal hydrophobic and
oleophilic, thereafter separating the hydrophobic and
oleophilic coal phase from the ash containing water phase
5 and recovering the hydrophobic and oleophilic coal phase,
the particular improvement comprising subjecting the chem-
ically surface treated hydrophobic and oleophilic coal to
high shear intermixing with an aqueous wash medium whereby
additional ash and other hydrophilic impurities are
10 released into the aqueous medium and a hydrophobic coal
phase floats upon and separates from a water phase.

In the accompanying figures, Fig. 1 is a flow
diagram illustrating the process of the present invention
whereby solid carbonaceous material, such as coal, is
15 beneficiated.

Fig. 2 is a flow diagram illustrating a preferred
manner by which solid carbonaceous materials, such as
coal, are beneficiated according to the present invention.

Fig. 3 is a further flow diagram depicting another
20 preferred mode by which the present invention is performed.

Fig. 4 is an illustration of a typical vessel
which may be utilized in the practice of the present invention.

In accordance with the present invention, a
highly beneficiated coal product is produced by a process
25 which involves surface treating particles of coal in an
aqueous medium with a surface treating admixture com-
prising a polymerizable monomer, a polymerization catalyst
and a liquid organic carrier, thereby rendering said coal
particles hydrophobic and oleophilic. Thus, the process
30 of this invention provides a highly beneficiated coal product
of relatively low water content which can be even further
dehydrated (dried) to a remarkable degree without the use

1 of thermal energy. The ash content of the coal prepared
by the present process is reduced to low levels and mineral
sulfur compounds present are also removed. Moreover, the final
coal product has enhanced BTU content and can be burned
5 as a solid or combined with fuel oil or water to produce
highly desirable beneficiated coal mixtures or slurries
which are readily transportable and cleanly burned.

As used herein, the term "beneficiation" is intended
to include methods for cleaning or otherwise removing impurities
10 from a substrate, such as coal and to the recovery of coal from
coal streams, such as, for example, the recovery of coal from
waste streams in coal processing operations and the con-
centration or dewatering of coal streams or slurries such as,
for example, by the removal of water in, for example, coal
15 slurry pipelines.

In one embodiment for carrying out the present
invention, wherein raw-mined coal is employed as
the feedstock, it is initially preferred to reduce raw
mined coal or other solid carbonaceous material to a fine
20 diameter size and to remove unwanted rock, heavy ash and
the like materials collected in the mining operation.
Thus, the coal is pulverized and initially cleaned, usually
in the presence of water, wherein the coal is suspended
and/or sufficiently wetted to permit fluid flow. The coal
25 is pulverized employing conventional equipment such as,
for example, ball or rod mills, breakers and the like.

It is generally desirable, although not necessary
to the present process, to employ certain water conditioning
(treating) additives in the pulverization operation. Such
30 additives assist in rendering the ash more hydrophilic,

1 which facilitates the separation thereof, in a manner
that will be discussed hereinafter. Typical additives
which are useful for purposes of this invention include
conventional inorganic and organic dispersants, surfactants,
5 and/or wetting agents. Preferred additives for this purpose
include sodium carbonate, sodium pyrophosphate, and the like.

The coal-aqueous slurry formed in the pulverization
operation is typically one having a coal to water ratio of
from about 0.5:1 to about 1:5 and preferably about 1:3
10 parts by weight, respectively. If utilized, the water
treating additives, hereinbefore described, are employed
in small amounts, usually, for example, from about 0.25 to
about 5%, based on the weight of dry coal. While it is
generally recognized that more impurities are liberated as the
15 size of the coal is reduced, the law of diminishing returns
applies in that there is an economic optimum which governs
the degree of pulverization. In any event, for the purposes
of this invention, it is generally desirable to crush
the coal to a particle size of from about 48 to about less
20 than 325 mesh, preferably about 80% of the particles being
of about a 200 mesh size (Tyler Standard Screen Size).

Any type coal can be employed in the process of
the present invention. Typically, these include, for example,
bituminous coal, sub-bituminous coal, anthracite, lignite
25 and the like. Other solid carbonaceous fuel materials,
such as oil shale, tar sands, coke, graphite, mine tailings,
coal from refuse piles, coal processing fines, coal fines
from mine ponds or tailings, carbonaceous fecal matter
and the like are also contemplated for treatment by the
30 process herein. Thus, for the purposes of this invention,
the term "coal" is also intended to include these kinds of
other solid carbonaceous fuel materials or streams.

In carrying out the beneficiation process herein, the coal-aqueous slurry, containing the pulverized coal, is contacted and admixed with a surface treating mixture comprised of a polymerizable monomer, polymerization catalyst and a small amount of a liquid organic carrier, such as fuel oil.

Any polymerizable monomer can be employed in the surface treating polymerization reaction medium. 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, butadiene, such as 1,4-butadiene, pentadiene, dicyclopentadiene, octadiene, olefinic petroleum fractions, styrene, vinyltoluene, vinylchloride, 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, anhydrides or salts thereof, particularly those included within the formula
$$\begin{array}{c} O \\ || \\ RC-OR' \end{array}$$
 wherein R is an olefinically

unsaturated organic radical, preferably containing from about 2 to about 30 carbon atoms, and R' is hydrogen, a salt-forming cation such as alkali metal, alkaline earth metal or ammonium cation, or a saturated or ethylenically un-

1 saturated hydrocarbyl radical, preferably containing from
1 to about 30 carbon atoms, either unsubstituted or sub-
stituted with one or more halogen atoms, carboxylic acid
groups and/or hydroxyl groups in which the hydroxyl hydrogens
5 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 fore-
going structural formula include unsaturated fatty acids
such as oleic acid, linoleic acid, linolenic, ricinoleic,
10 mono-, di- and tri-glycerides, and other esters of unsat-
urated fatty acids, acrylic acid, methacrylic acid, methyl-
acrylate, ethylacrylate, ethylhexylacrylate, tertiarybutyl-
acrylate, oleylacrylate, methylmethacrylate, oyleymeth-
acrylate, stearylacrylate, stearylmethacrylate, laurylmeth-
15 acrylate, vinylacetate, vinylstearate, vinylmyristate,
vinyl laurate, unsaturated vegetable seed oil, soybean oil,
rosin acids, dehydrated castor oil, linseed oil, olive oil,
peanut oil, tall oil, corn oil and the like. For the
purposes of this invention, tall oil and corn oil have
20 been found to provide particularly advantageous results. Corn
oil is especially preferred. Moreover, it is to be clearly
understood that compositions containing compounds within the
foregoing formula and in addition containing, for example,
saturated fatty acids such as palmitic, stearic, etc. are
25 also contemplated herein. Also contemplated herein as
monomers are aliphatic and/or polymeric petroleum materials.

The amount of polymerizable monomer will vary
depending upon the degree of surface treatment desired. In
general, however, monomer amounts of from about 0.005 to about
30 0.1%, by weight, of the dry coal are used.

1 The catalysts employed in the coal surface treating
beneficiation reaction of the present invention are any such
materials commonly used in polymerization reactions. These
include, for example, anionic, cationic or free radical catalysts.
5 Free radical catalysts or catalyst systems (also referred to
as addition polymerization catalysts, vinyl polymerization
catalysts or polymerization initiators) are preferred herein.
Thus, illustratively, free radical catalysts contemplated herein
include, for example, inorganic and organic peroxides such as
10 benzoyl peroxide, methylethyl ketone peroxide, tert-butyl-
hydroperoxide, hydrogen peroxide, ammonium persulfate, di-tert-
butylperoxide, tert-butyl-perbenzoate, peracetic acid and in-
cluding such non-peroxy free-radical initiators as the diazo
compounds such as 1,1'-bisazoisobutyronitrile and the like.

15 Typically, for the purposes of this invention, any
catalytic amount (e.g. 1 pound per ton of dry coal feed) of
the foregoing described catalysts can be used.

Moreover, free radical polymerization systems
commonly employ free radical initiators which function
20 to help initiate the free radical reaction. For the purposes
herein, any of those disclosed in the prior art, such as
those disclosed, for example, in U.S. Patent No. 4,033,852,
incorporated by reference herein, may be used. Specifically,
some of these initiators include, for example, water
25 soluble salts, such as sodium perchlorate and perborate, sodium
persulfate, potassium persulfate, ammonium persulfate, silver
nitrate, water soluble salts of noble metals such as platinum
and gold, sulfites, nitrites and other compounds containing the
like oxidizing anions, and water soluble salts of iron, nickel
30 chromium, copper, mercury, aluminum, cobalt, manganese,
zinc, arsenic, antimony, tin, cadmium, and the like.

1 Particularly 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
5 nitrate, $\text{Cu}(\text{NO}_3)_2$. Further initiators contemplated herein
are disclosed in copending U.S. patent application Serial
No. 230,063 filed January 29, 1981. Among others, these
initiators include metal salts of organic moities, typically
metal salts of organic acids or compositions containing
10 organic acids, such as naphthenates, tallates, octanoates,
etc. and other organic soluble metal salts, said metals
including copper, chromium, mercury, aluminum, antimony,
arsenic, cobalt, manganese, nickel, tin, lead, zinc, rare
earths, mixed rare earths, and mixtures thereof and double
15 salts of such metals. The combination of copper and cobalt
salts, particularly cupric nitrate and cobalt naphthenate,
have been found to provide particularly good and synergistic
results.

The amounts of free radical initiator contemplated
20 herein are any catalytic amount and generally are within the
range of from about 10-1000 ppm (parts per million) of the
metal portion of the initiator, preferably 10-200 ppm, based
on the amount of dry coal.

The surface treating reaction mixture of the
25 present invention also includes a liquid organic carrier.
This liquid organic carrier is utilized to facilitate
contact of the surface of the coal particles with the
polymerization reaction medium. Thus, liquid organic
carriers included within the scope of this invention are,
30 for example, fuel oil, such as No. 2 or No. 6 fuel oils,
non-fuel oil liquid organic carriers, such as hydro-
carbons including, for example, benzene, toluene,

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- 1 xylene, hydrocarbons fractions, such as naphtha and medium
boiling petroleum fractions (boiling point 100°-180°C);
dimethylformamide, tetrahydrofuran, tetrahydrofurfuryl
alcohol, dimethylsulfoxide, methanol, ethanol, isopropyl
5 alcohol, acetone, methylethyl ketone, ethyl acetate and
the like and mixtures thereof.

The amounts of liquid organic carrier, such as fuel
oil, utilized in the surface treatment reaction herein are
generally in the range of from about 0.25 to about 5% by
10 weight, based on the weight of dry coal.

The surface treatment reaction of the present
process is carried out in an aqueous medium. The amount
of water employed for this purpose is generally from about
65% to about 95%, by weight, based on the weight of coal
15 slurry.

The surface treating reaction conditions will,
of course, vary, depending upon the specific reactants
employed and results desired. Generally, however, any
polymerization conditions which result in the formation
20 of a hydrophobic or oleophilic surface on the coal can
be utilized. More specifically, typical reaction conditions
include, for example, temperatures in the range of from
about 10°C to about 90°C, atmospheric to nearly atmospheric
pressure conditions and a contact time, i.e. reaction time,
25 of from about 1 second to about 30 minutes, preferably
from about 1 second to about 3 minutes. Preferably, the
surface treatment reaction is carried out at a temperature
of from about 15°C to about 80°C and atmospheric pressure
for about 2 minutes. In general, however, the longer the
30 reaction time, the more enhanced are the results.

- 1 In the practice of the present invention, the coal can be contacted with the surface treating ingredients by employing various techniques. For example, one technique is to feed the aqueous pulverized coal slurry through a
5 spraying means, e.g. nozzle, and add the surface treating ingredients, i.e. polymerizable monomer, polymerization catalyst, initiator and liquid organic carrier to the aqueous coal spray. The resultant total spray mixture is then introduced to an aqueous medium contained in a
10 beneficiation vessel. In a preferred embodiment when this technique is used, the surface treated aqueous coal mixture now in the vessel is recycled to the same vessel by re-feeding the mixture to the vessel through at least one of said spraying means.
- 15 In a second technique, the aqueous coal slurry and surface treating ingredients, i.e. polymerizable monomer, polymerization catalyst, initiator and liquid organic carrier, are admixed in a premix tank and the resultant admixture is sprayed, e.g. through a nozzle, into an
20 aqueous medium contained in a beneficiation vessel. In another and third technique, the resultant surface treated aqueous coal mixture, formed in the beneficiation vessel in accordance with the foregoing described second technique, is recycled to the same vessel by re-feeding
25 the mixture to the vessel through at least one of said spraying means.

As the surface treating reaction is completed, the hydrophobic and oleophilic beneficiated coal particles float to the surface of the liquid mass. The ash, still
30 remaining hydrophilic, tends to settle and is removed to the water phase. Thus, the coal which results from reac-

1 tion with the hereinbefore described polymerizable surface
treating mixture is extremely hydrophobic and oleophilic
and consequently readily floats and separates from the
aqueous phase, providing a ready water washing and for high
5 recoveries of coal. The floating hydrophobic coal is also
readily seperable from the aqueous phase (for example, a skim-
ming screen may be used for the separation), which contains
ash, sulfur and other impurities which have been removed from
the coal. While it is not completely understood and while
10 not wishing to be bound to any theory, it is believed that
the surface treatment polymerization reaction involves the
formation of a polymeric organic coating on the surface of
the coal by molecular grafting of polymeric side chains on
the coal molecules.

15 In the practice of the present invention, the
surface treated coal is preferably subjected to at least
one further wash step wherein the coal phase or phases are
redispersed, with good agitation, e.g. employing high speed
mixers, as a slurry in fresh wash water. Preferably,
20 the initially surface treated coal is added to the wash
water under atomizing pressure through a spray nozzle thus
forming minute droplets in air which are directed with
force onto and into the surface of the fresh water mass.
In this manner, some air is incorporated into the system.

25 By spraying, the wash water and the treated coal
phase are intimately admixed under high speed agitation
and/or shear produced by the spray nozzle under super
atmospheric pressures. In this manner, the hydrophobic
coal particles are jetted into intimate contact with
30 the wash water through one or more orifices of the spray
nozzle thereby inducing air inclusion, both in the passage
through the nozzle as well as upon impingement upon and
into the air-water interface of the wash water bath.

1 U.S. Serial No. 230,058 and U.S. Serial No.
230,059 both filed on January 29, 1981 describe and claim
a particularly effective method and apparatus for sepa-
rating the treated coal particles from unwanted ash and
5 sulfur in the water phase utilizing an aeration spray
technique, wherein a coal froth phase is formed by spraying
or injecting the treated coal-water slurry into the surface
of the cleaning water. Briefly, according to the method
and apparatus there described, the coal slurry is injected
10 through at least one selected spray nozzle, preferably
of the hollow cone type, at pressures, for example, at from
about 15-20 psig, at a spaced-apart distance above the
water surface, into the water surface producing aeration
and a frothing or foaming of the coal particles, causing
15 these particles to float to the water surface for skimming
off.

The foregoing described washings may be carried
out with the treated coal slurry in the presence of simply
water at temperatures of, for example, about 10° to about
20 90°C, preferably about 30°C, employing from about 99 to about
65 weight percent water, based on the weight of dry coal
feed. Alternatively, additional amounts of any or all of the
heretofore described surface treating ingredients i.e. poly-
merizable monomer, catalyst, initiator, liquid organic
25 carrier, may also be added to the wash water. Moreover, the
washing conditions e.g. temperature, contact time, etc.,
utilized when these ingredients are employed can be the
same as if only water is present or the washing conditions
can be the same as those described heretofore with respect
30 to surface treatment of the coal with the surface treating
mixture. Of course, water conditioning additives may
also be utilized during the washing steps, if desired.

1 After washing and/or additional surface treatment,
the beneficiated coal may be dried to low water levels simply
by mechanical means, such as by centrifugation, pressure or
vacuum filtration etc., thus avoiding the necessity for
5 costly thermal energy to remove residual water. The
beneficiated coal prepared by the process of this invention,
as hereinbefore described, generally contains from about 0.5%
to about 10.0% by weight ash, based on the weight of dry
coal. Moreover, the sulfur content is from about 0.1% to
10 about 4% by weight, preferably about 0.3 to about 2%, based
on the weight of dry coal and the water content is from
about 2% to about 25%, preferably from about 2% to about 15%,
by weight, based on the weight of dry coal.

At this point, the beneficiated coal can be used as
15 a high energy content, ash and sulfur reduced, fuel product.
This beneficiated fuel product can be utilized in a direct
firing burner apparatus. Alternatively, the beneficiated
particulate coal can be blended with a carrier such as oil
to provide a highly stable and beneficiated coal slurry, such
20 as a coal-oil mixture (COM). Oil, preferably fuel oil, such
as No. 2, or No. 6, is blended with the beneficiated coal at
any desired ratio. These ratios typically include from
about 0.5 to about 1.5 parts by weight coal to 1 part oil.
Preferably a 1:1 weight ratio is employed.

25 It is also to be understood herein that the solid
beneficiated coal product of the present invention can also
be redispersed in aqueous systems for pumping through pipe-
lines. If desired, to provide improved stability, selected
metal ions, by way of their hydroxide or oxide, can be added
30 to the aqueous dispersion to preferably adjust the pH of
the slurry to above 7. Thus, for this purpose, alkali
and/or alkaline earth metals, each as, sodium, potassium,
calcium, magnesium, etc., hydroxide or oxides, can be used.

1 Sodium hydroxide is preferred.

It has also been discovered herein that a stabilized coal-oil mixture can be provided by the presence therein of the alkali or alkaline earth metal, e.g. (sodium, potassium, calcium, magnesium, etc.) salt of a fatty acid of the
 5 formula $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}''\text{C}-\text{OH} \end{array}$ wherein R'' is a saturated or an olefinically

unsaturated organic radical. Thus, the hereinbefore described unsaturated fatty acids, i.e., $\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOR}' \end{array}$, wherein
 10

R' is hydrogen and R is as defined before, are also intended for use herein. The presence of these fatty acid salts in the beneficiated coal-oil mixtures of this invention permits the ready dispersion of the coal in the fuel oil to produce
 15 a gel or other structure which retards settling almost indefinitely. Other metal ions, in addition to alkali or alkaline earth metals, are also useful to form stabilizing fatty acid salts. These other metals include, for example, iron, zinc, aluminum and the like.

20 Generally, the amount of fatty acid utilized in forming the stable coal-oil mixture will be from 3.0 to 0.5% by weight, based on the total weight of the mixture. The amount of alkali or alkaline earth containing compound utilized to form the gel will be sufficient to neutralize a substantial portion of the fatty acid and thus generally varies
 25 from about 0.1 to 1.0% and usually 0.1% to 0.6% by weight, based on the total weight of the coal-oil mixture. Preferably for a 50:50 coal-oil mixture, 1.5% by weight acid and 0.3% by weight of neutralizing compound are added to the mixture.

30 An alternative practice herein to form stable coal-oil mixtures is to subject the coal-oil mixture to an

1 additional surface treating reaction where additional amounts
of polymerizable monomer and polymerization catalyst are
added to a mixture of the beneficiated coal in oil. In
this case, the polymerizable monomer is again an unsaturated
5 carboxylic acid as described above, preferably tall oil, used
in amounts of 3.0 to 0.5% by weight, preferably 1.5%,
based on the total weight of the mixture. The polymerization
catalyst can be any of those described hereinbefore and is
preferably cupric nitrate, used in amounts of 2.0 to 10 ppm
10 (parts per million), preferably 5 ppm, based on the total weight
of the mixture. The polymerizable monomer and polymerization
catalyst are added to the coal-oil mixture with stirring.
Thereafter, alkali or alkaline earth metal compound, such as
sodium hydroxide, in an amount of 0.6 to 0.1%, by weight, pre-
15 ferably 0.3%, based on the total weight of the mixture is added
to the mixture. The resulting product is a preferred
stabilized coal-oil mixture.

Other processes which are suitable herein for
preparing stable beneficiated coal-oil mixtures are dis-
20 closed and claimed in U.S. Serial No. 230,055 and U.S.
Serial No. 230,064 both filed January 29, 1981. More
particularly, U.S. Serial No. 230,055 discloses and claims
a process for forming stable coal-oil mixtures by admixing
beneficiated coal with a fatty acid ester, such as tri-
25 glyceride, preferably tallow, and a base, such as sodium
hydroxide. Briefly, U.S. Serial No. 230,064 discloses and
claims a process for forming stabilized coal-oil mixtures
by initially admixing, under low shear conditions and at
an elevated temperature, coal, oil, polymerizable monomer
30 and polymerization catalyst, and immediately thereafter
subjecting the mixture to a condition of high shear agitation
at the same elevated temperature. The resultant coal-oil

1 mixture is then treated with a gelling agent, such as
a hydroxide, like sodium hydroxide, to form a stable bene-
ficiated coal-oil mixture which is in the form of a gel or
thixotropic mixture.

5 The coal fuel oil products, i.e. coal-oil
mixtures, of the present invention have unique properties.
For example, the present coal-oil mixtures are thixotropic,
have increased energy content, can utilize coal having
low ash, low sulfur and low moisture content and a wide
10 variety of coals and can provide the potential for a widely
expanded market for coal as a fluid fuel thereby assisting
in the conservation of petroleum.

 With specific reference to the drawings herein,
and particularly to Fig. 1, the process of this invention
15 is illustratively carried out, for example, by initially
pulverizing raw mined coal in pulverization zone 10 in the
presence of water, and if desired, water conditioning additives,
to form an aqueous coal slurry. This aqueous coal slurry
is mixed in line 6 with surface treating reagents and/or
20 additives, fed to line 6 from tanks 1, 2, 3, and 4 via
line 5, and the thusly treated coal-slurry is introduced
to beneficiation zone 12, as shown. Tanks 1, 2, 3 and 4 con-
tain, for example, polymerizable monomer, free radical cat-
alyst, free radical initiator and liquid organic carrier,
25 respectively. Raw mined coal is fed to zone 10 through line
23; water is fed through line 21 and water conditioning
additives may be introduced via line 25. Unwanted materials,
such as rock, are removed via line 27.

 Water is generally the principal ingredient
30 in beneficiation zone 12. Thus, the treated coal-slurry

- 20 -

1 being fed to zone 12 via line 6 is now hydrophobic and
oleophilic and after admixture with the wash water in zone 12,
for example, by high speed mixer or spray atomizer,
readily floats on the surface of the water, thereby
5 forming a coal froth phase and an aqueous phase in zone 12.
The coal froth phase in zone 12 is readily removed from
zone 12 (for example, by skimming) through line 47 to provide
a beneficiated, i.e. clean, coal product according to the
present invention having a reduced ash, sulfur and water
10 content. If desired, the clean coal from line 47 may be
further dried to remove additional water. The aqueous
phase, remaining in zone 12, contains ash, sulfur and other
hydrophilic impurities and can be removed therefrom
through line 11.

15 Alternatively, in carrying out the process of the
present invention, in accordance with Fig. 1, the surface
treating reagents and/or additives may be admixed with the
aqueous coal slurry directly in beneficiation zone 12. Thus,
these reagents and/or additives can be introduced to zone 12
20 via line 31 (monomer), 33 (free radical catalyst), 35 (free
radical initiator) 37 (water), 39 (liquid organic carrier).
The coal slurry is fed to zone 12 through line 6 and thusly
admixed with the reagents in zone 12. In another manner, as
described hereinbefore, the surface treating additives can
25 be added to the coal spray coming from line 6.

With specific reference to Fig. 2, the process of
this invention is illustratively continuously carried out
beginning with raw mined coal and ending with a coal-oil
mixture, although as indicated above other feedstocks and
30 products, such as beneficiated particulate coal and coal-water
mixtures are also contemplated herein. Thus, referring to
Fig. 2, raw coal is initially pulverized in pulverization
zone 10A in the presence of water and, if desired, water
conditioning additives, to form an aqueous coal slurry. This

- 2 / -

1 aqueous coal slurry is fed to mix zone 11, through line 9,
and admixed in zone 11 with surface treating reagents/
additives transported from reagent and/or additive tanks
1A, 2A and 3A and 4A, via line 8. Tanks 1A, 2A, 3A and
5 4A contain, for example, polymerizable monomer, free radical
catalyst, free radical initiator and liquid organic carrier,
respectively. Raw mined coal is fed to zone 10A through
line 23A; water is fed through line 21A and water condi-
tioning additives may be introduced to zone 10A via line
10 25A. The resultant admixture in mix zone 11 which contains
the initial chemically treated hydrophobic and oleophilic
coal, is then introduced to a first beneficiation zone
12A through line 29.

Alternatively, surface treating additives (or addi-
15 tional surface treating additives) i.e., polymerizable monomer,
polymerization catalyst, liquid organic carrier, hereinbefore
described, may be added directly to zone 12A (or zones 14 and
16), for example, through line 31A (monomer), 33A (free
radical catalyst), 35A (free radical initiator), 37A (water),
20 39A (liquid organic carrier), or they can be admixed before-
hand along with the pulverized coal slurry in lines leading
to the beneficiation zones or vessels in the zones. In the
case where the surface treating reagents/additives are added
directly to zone 12A, the coal slurry from zone 10A may be
25 added directly to zone 12A via lines 9A and 29. In addition,
as described before, the coal slurry in the beneficiation vessel
can be recycled within each particular vessel to achieve
greater mixing and separation.

The coal in zone 12A is extremely hydrophobic and
30 oleophilic and after good agitation with, for example, a high

1 speed mixer or spray atomizer, a coal froth phase ensues which is recovered. A screen may be advantageously used for the separation and recovery of the flocculated coal. If desired, the recovered coal can be introduced, via lines
5 47 and 49 to a further sequence of wash steps, (e.g. zones 14 and 16) wherein with further agitation of the recovered hydrophobic coal froth from zone 12A, provided by high speed mixers, or other means, such as a spray atomizer, additional ash is released to the water phase.

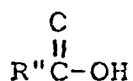
10 The water-wetted ash suspension phase, which is also formed in zone 12A, can be recovered and can be sent to waste and water recovery, after which the water can be recycled for reuse in the process as shown in Fig. 2.

Alternatively, as indicated above, additional ash
15 and sulfur is removed from the beneficiated coal froth phase by a series of counter-current water-wash steps, i.e. the water phase in the wash zones 14 and 16 can be recycled to a previous wash zone, as also illustrated in Fig. 2.

As indicated hereinbefore, in addition to water, zones 12A,
20 14 and 16 may also contain any or all of the foregoing chemical surface treatment additives. The finally washed and surface treated coal exiting zone 16 via line 57 can be dried to a very low water level by, for example, centrifugation. The water which is taken off in the centrifuge
25 may also be recycled in the process as shown. The recovered dry beneficiated coal product can be used directly as such as a solid fuel or can be blended with a carrier to form a highly desirable beneficiated coal slurry, such as a coal-oil-liquid fuel mixture.

30 In the preparation of the coal-oil mixture, Fig. 2

1 illustrates that the dry beneficiated surface treated coal is fed to a coal-oil dispersion mixer, wherein, preferably hereinbefore identified



5 or naphthenic acid, may be added along with alkali metal hydroxide, such as sodium or calcium hydroxide, to form a stable dispersion. If desired, further surface treatment of the coal may be carried out in the coal-oil dispersion mixer by adding a polymerizable monomer and polymerization catalyst to the admixture, as described above, with or without subsequent addition of alkali or alkaline earth hydroxide. Illustratively, coal-fuel dispersion can be carried out, either continuously or batchwise, in, for example, conventional paint grinding equipment, wherein heavy, small
15 grinding media are used to shear the dispersion into a non-settling flowable coal-fuel product of thixotropic nature.

It is to be understood herein that while the coal-oil admixture process illustrated herein utilizes coals beneficiated as described herein, any coal, e.g. raw coal,
20 coal beneficiated by processes not herein described and the like, can also be employed to form stable coal-oil mixtures in accordance with the process of the present invention.

Fig. 3 illustrates a further preferred mode by which the present invention may be performed. With specific
25 reference thereto, raw mined coal is introduced to pulverization zone 70, through line 103 and pulverized therein in the presence of water which is added via line 101. The water preferably contains a conditioning or treating additive such as an inorganic or organic surfactant, wetting agent, dispersant or the like which enhances the effectiveness of the
30 water. Typical organic surfactants (such as Triton X-100)

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1 include anionic, cationic and nonionic materials. Sodium
pyrophosphate is a preferred additive for the purposes of
this invention. Conditioning ingredients can be fed to zone
70 through line 105, for example. The aqueous coal slurry
5 in zone 70 is sent to mix zone 82 via line 81 and admixed
therein with reagents/additives from tanks 1B, 2B, 3B and
4B containing polymerizable monomer, free radical catalyst,
free radical initiator and liquid organic carrier, respectively,
for example.

10 The aqueous chemically treated hydrophobic and
oleophilic coal slurry admixture formed in zone 82 is fed
to a first water wash zone 72 through line 107 and through
high shear nozzle D, whereby the velocity of the stream
and the shearing forces are believed to break up the coal
15 phase stream into fine droplets which in turn can pass
through an air interface within wash zone 72 and impinge
downwardly upon and forcefully jet into the mass of the
continuous water in, e.g. a tank or tanks, contained therein.
If desired, further surface treating reagents, and/or addi-
20 tives, hereinbefore identified, may be added to zone 72,
(and/or zones 74 and 76), for example, through lines 109
(polymerizable monomer), 111 (free radical catalyst), 113
(free radical initiator), 115 (water), 117 (liquid organic
carrier). The hydrophobic and oleophilic coal phase, which
25 ensues in zone 72, is then preferably, as shown, fed to a
further sequence of wash zones, via line 47.

Without intending to be limited to any theory
or reaction mechanism, it is believed to be helpful to discuss
the phenomena thought to provide some of the advantageous
30 results achieved by the process herein. Thus, the high shear-
ing forces created in mixing, such as in nozzle D, are believed

1 to assist in breaking up the coal-oil water flocs as the dispersed particles forcefully enter the surface of the water in the tank, thereby water-wetting and releasing ash and other impurities from the interstices between the coal flocs. .

5 The coal flocs are thereby broken up so that the trapped ash and other impurities are freed and introduced to the aqueous phase and thus separated from the coal particles. The finely divided coal particles, whose surfaces are now believed surrounded by polymer and liquid organic carrier, such as

10 fuel oil, also now contain (occluded) air sorbed in the atomized particles as a result of the shearing effects of the nozzle. The combination of surface treatment and sorbed air causes the flocculated coal to decrease in apparent density and to float on the surface of the water,

15 as a distinct coal froth phase. Thus, the coal particles assume a density less than water, repel water by virtue of their increased hydrophobicity and quickly float to the surface of the water.

By the foregoing technique, not only is ash

20 substantially removed from the treated coal product, but the entrapped air and the more hydrophobic and oleophilic coal surfaces provide for a marked increase in the yield of total beneficiated treated coal, which is ultimately recovered.

The still hydrophilic ash remains in the bulk

25 aqueous phase and tends to settle downward in the tank by gravity and is withdrawn from zone 72 in an ash-water stream 119 from the base of the vessel. Some small amount of fine coal which may not be separated completely can be transferred with the aqueous phase (withdrawn ash-water stream) to a fine

30 coal recovery zone 121, as shown in Fig. 3. Recovered coal

1 fines can be recycled via line 123 to the aqueous coal slurry
in zone 70.

The wash process carried out in zone 72 can be repeated, employing a counter-current wash system, whereby the
5 coal progresses to a cleaner state through sequential introduction to beneficiation zones 74 and 76, via lines 47 and 49, as illustrated in Fig. 3. Concomitantly, clean wash water becomes progressively loaded with water soluble and water wetted solid impurities extracted by the wash water.

10 As described before, the intimately admixed ash-water suspension coming from zone 72, containing some small amounts of particulate coal, is forwarded to fine coal recovery zone 121 where high ash-low water solids are recovered and expelled for removal from the process and
15 the fine coal is recycled, as shown. The wash water can be further treated, at 125, to control the condition of the recovered water prior to recycle. The cleaned water is recycled to the original aqueous coal slurry or such other make-up as the overall process may require to balance material
20 flow.

As shown in Fig. 3, the coal froth phases resulting in zones 72 and 74 can be introduced for further washings via nozzles E and F, respectively. In this manner, the coal particles are again atomized. The velocity and high shear
25 created by nozzles E and F once again permit wash water contact with any ash still retained in the interstices of the coal flocs, thereby assisting, in each wash step, to release ash to the aqueous phase. The aqueous phases in zones 72, 74 and 76 float the flocculated coal-oil-air mass to the
30 top of the respective tanks.

The final coal froth phase in zone 76 is fed to a centrifuge, via line 57, for drying. The beneficiated, clean

- 27 -

1 coal phase is thereby remarkably dried without the necessity
for thermal energy, which is believed due to the reduced
attraction for water between the large coal-oil surfaces and
the water physically occluded therebetween in the flocculated
5 dry coal recovered from the mechanical drying step. 0

The dry hydrophobic cleaned coal can be used
advantageously at this point as a higher energy content, ash
and sulfur reduced solid fuel, which is referred to herein as
Product I. This solid fuel can be utilized in direct firing
10 or to form beneficiated coal slurries as described above.

As indicated above in another embodiment of this
invention, a liquid fuel mixture, which is easily pumped
as a liquid, but which is of such rheological quality as to
form a thixotropic liquid, can also be provided. A
15 thixotropic liquid is one that has "structure" or tends to
become viscous and gel-like upon standing quiescently,
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
20 pumping processes or by heating.

In the practice of this invention, as illustrated
by Fig. 3, the dry, beneficiated coal Product I is mixed
with a quantity of fuel oil (illustratively 1:1 by weight
and preferably heated to reduce viscosity especially in
25 instances wherein the fuel oil is of a heavy viscosity grade)
in a mix tank to provide a pumpable fluid mixture.

Alternatively, the fuel-oil coal mixture in the
mix zone may be subjected to an additional surface
treatment step, in line with the general reaction procedure
30 employed in the initial surface treatment beneficiation,
hereinbefore described. For this purpose, any of the herein-

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1 before identified polymerizable monomers, such as tall oil,
corn oil, and the like may be used and added to the mix
zone along with any of the hereinbefore identified polymer-
ization catalysts and/or initiators. Moreover, the saturated
5 carboxylic acids hereinbefore described may be used alone
or in combination with the unsaturated acids, if desired.
In the case wherein saturated acids are used alone, initiators
and catalysts need not be employed. Naphthenic acids are
illustrative of saturated acids which may be used.

10 • The admixture of surface treated coal, fuel oil
and carboxylic acid can then be substantially neutralized,
with a water soluble alkali metal, such as from a hydroxide,
like sodium hydroxide, calcium hydroxide or mixtures thereof
as indicated above to form a stable coal-oil mixture. A
15 liquid clean coal-oil fuel mixture (Product II), having no
tendency to settle out, is storable recovered to provide a
flowable high energy source for a wide variety of end uses.

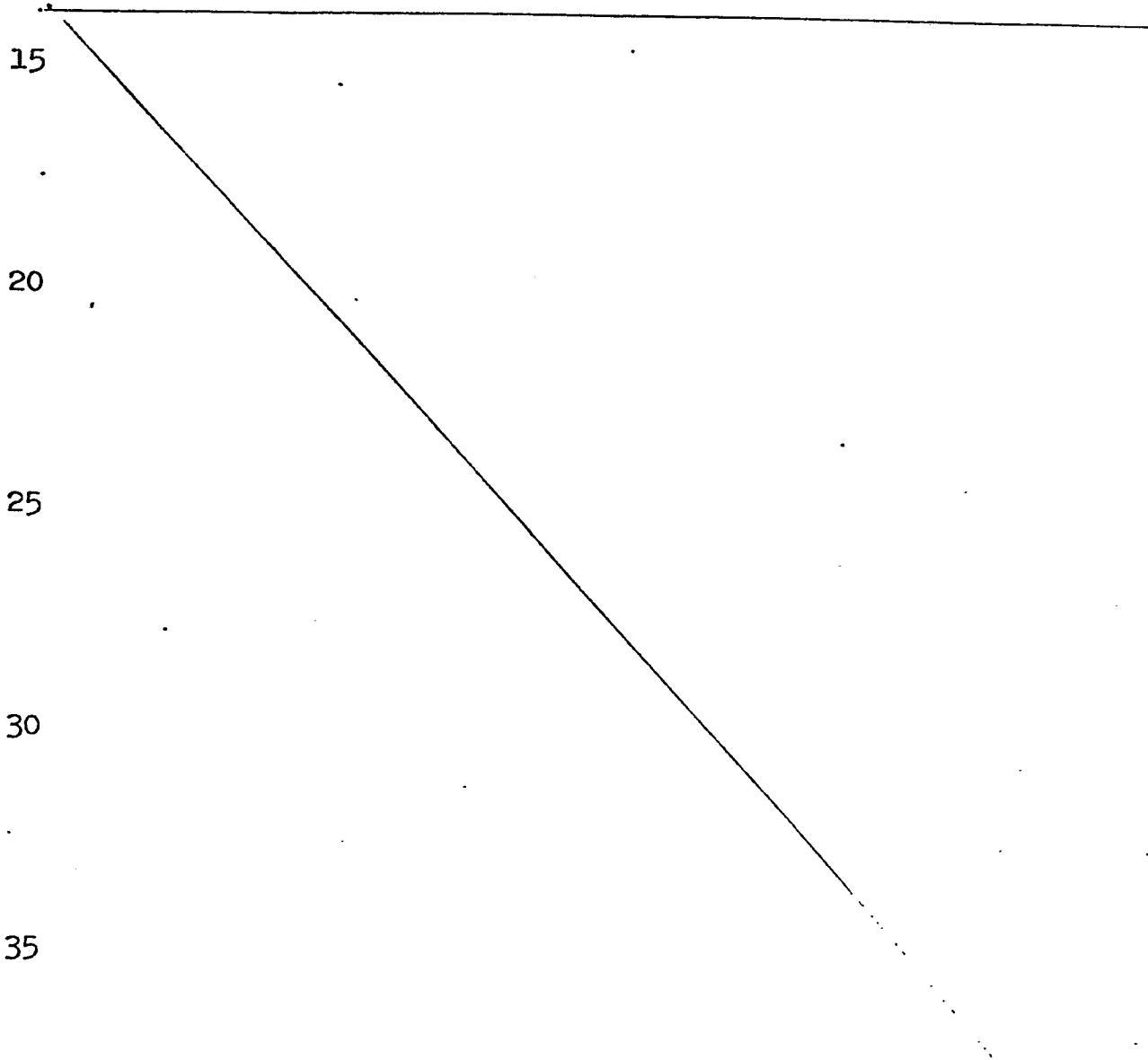
Alternatively, the beneficiated coal product I can
be slurried with water to provide coal-aqueous slurries or
20 mixtures:

Fig. 4 illustrates a unit 55 which is suitable as
a froth flotation vessel useful in any of the wash and/or
beneficiation zones employed in the present process. In
this unit, the aqueous coal slurry i.e. admixture of coal,
25 water and preferably surface treating reagents/additives,
is sprayed into the vessel through lines 29 and through
spray nozzles 61. Additional surface treating reagents/
additives or any other desired ingredients may also be
added via lines 31, 33, 35, 37 and 39. In this vessel the
30 coal froth is skimmed off from the main portion of the

1 vessel into a collector compartment and can be introduced to the next zone via line 147, for example. The aqueous-ash phase in the main portion of the vessel is removed through line 41, for example.

5 It is to be understood herein that any of the zones illustrated in Figures 1-3 may comprise a single vessel or zone or any number of vessels or zones arranged in a manner suitable and in accordance with carrying out the invention as described herein.

10 In order that those skilled in the art may better understand how the present invention may be practiced, the following examples are given by way of illustration and not by way of limitation.



EXAMPLE 1

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200 grams of Pittsburgh seam coal having an initial ash content of 6.2% and initial sulfur content of 1.5% is pulverized in the presence of 400 grams of water to a 5 200 mesh size using a ball mill grinding unit. The coal is transferred to a mixing vessel. Into this vessel containing the coal is also introduced 0.05 grams of corn oil, 2.0 grams of #2 fuel oil, 1.0cc. of a 5.0% solution of hydrogen peroxide in water and 2.0cc. of a cupric nitrate solu-
10 tion in water. The mixture is stirred and heated to about 30°C for about 2 minutes. The resultant mixture is sprayed into a vessel containing clean water and a frothing ensues. The coal, in the coal froth phase, is skimmed from the water surface. The water phase containing large amounts of hydro-
15 philic ash and sulfur is discarded.

The cleaning procedure is repeated two further times using clean water and skimming the frothed coal from the water surface. The particulate coal is then dried to a water content of 15%, based on the weight of dry coal,
20 using a laboratory Buchner funnel. The ash content of the final particulate product is reduced to 1.5% and the sulfur content is reduced to 0.8%.

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EXAMPLE 2

The procedure of Example 1 is repeated using equivalent amounts of (a) coker gasoline; (b) oleic acid; and (c) tall oil, each substituted for the corn oil. A cleaned coal particulate product is produced having an ash content of about 3% and a moisture content of about 15%, based on the weight of the dry coal.

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EXAMPLE 3

1 The process of Example 1 is repeated using (a)
Kittanning seam coal; (b) Illinois #6 seam coal; and (c)
lower Freeport seam coal in lieu of the Pittsburgh seam
5 coal. A cleaned coal product having an ash content of
about 3.0% and a moisture concentration of 15%, based on
the weight of the dry coal, is provided.

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EXAMPLE 4

200 grams, Illinois #6 coal reduced to about 1/4" size lumps and having an ash content of 19.9%, is crushed to a particle size of about 28 mesh and then pulverized to 200 mesh in a laboratory ball mill in the presence of water to form a coal-aqueous liquid slurry. The liquid phase of the slurry contains about 65% water based on the total weight of the slurry.

50 mg. tall oil, 10 gms. of fuel oil, 250 milligrams sodium pyrophosphate, 100 milligrams of cupric nitrate and 1.0 gms. H_2O_2 (5% solution in water) are added to the above coal-aqueous slurry at about 30-40°C. The hydrophobic, surface treated coal phase which ensues is recovered by removing it from the surface of the aqueous phase on which it floats. The aqueous phase contains the hydrophilic ash and is discarded.

Subsequent to several re-dispersions in clean soft water, containing sodium pyrophosphate, at about 30°C, the surface treated coal is recovered. After filtering through a Buchner funnel, the water content of the coal is about 15%. (Conventionally processed coal, i.e., without chemical surface treatment, customarily retains from about 20-50% water when ground to the same mesh size).

The recovered, mechanically dried, treated, beneficiated coal is admixed with 160 grams of fuel oil and an additional 5.0 gms. of tall oil is added thereto. After thorough admixing at 85°C, caustic soda, equivalent to the acid value of the admixture, is added thereto and further admixed therewith.

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

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EXAMPLE 5

The process of Example 4 is repeated, except that gram equivalent amounts of the following polymerizable monomers are substituted for the tall oil used in Example 4:

(a) coker gasoline and (b) oleic acid.

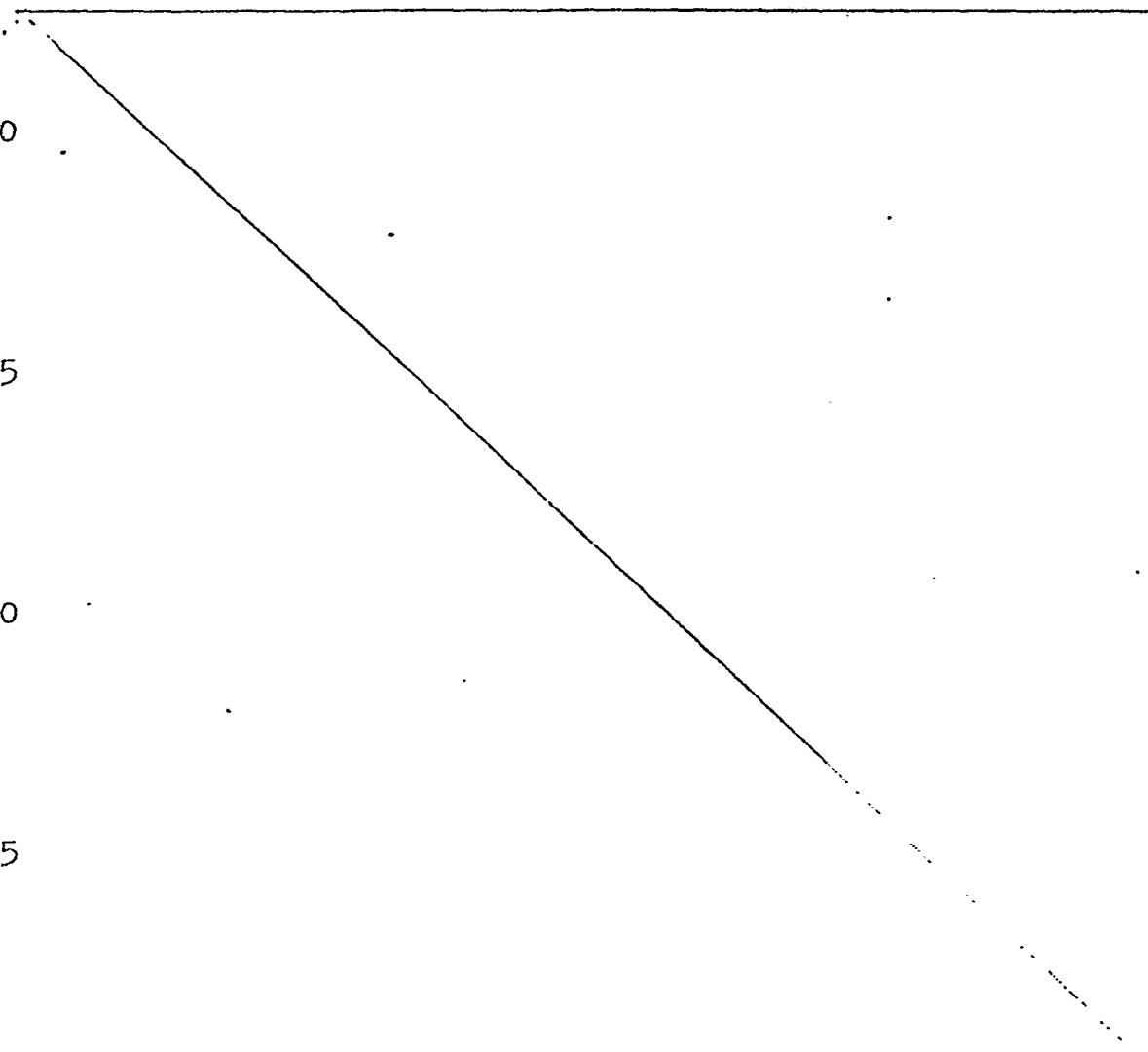
The surface of the pulverized coal is similarly altered to result in strongly hydrophobic coal particles which are processed similar to Example 4. In each case, the same amount of tall oil is admixed with the recovered beneficiated coal, after drying. Acidity is neutralized with caustic and similar coal-oil liquid suspensions are prepared, which all exhibit thixotropic quality depending upon the metal ion selected to displace the sodium ion of the sodium hydroxide originally added. No settling is observed over several weeks observation, independent of the monomer used in the surface treatment reaction.

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EXAMPLE 6

1 The process of Example 4 is repeated except that
2 grams of benzoyl peroxide are used in place of the hydrogen
peroxide. Moreover, 2 grams of Triton-X-100 surfactant
5 and 25 grams of sodium pyrophosphate are present in the
original slurry water. The ash in the resulting aqueous
phase is filtered out after treating with lime. The ash con-
tent of the treated coal is reduced from about 19.9% to about
4.7% after five separate washings, wherein the water also
10 contains Triton-X-100 and sodium pyrophosphate. The tall
oil used in the surface treatment reaction and the tall oil
employed in the formation of the stable coal-oil
mixture, is neutralized first with caustic soda and sub-
sequently treated with an equivalent amount of calcium
15 hydroxide. The viscosity of the coal-oil mixture is of a
thixotropic gel-like nature, indicating no settling is to be
expected upon extended standing.

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EXAMPLE 7

235 grams of beneficiated coal having a 15% moisture content prepared in accordance with Example 1 is placed in a vessel in which a stabilized coal-fuel oil mixture is formed by the addition to said coal of 200 gms of #2 fuel oil, 6.0 gms. tall oil, 1.0 gms. of a 0.1% solution of H_2O_2 (or benzoyl peroxide) in water (toluene), and 2.0 gms. of a 0.1% aqueous solution of cupric nitrate. The mixture is stirred for about 1.0 minute at about 85°C. 1.5 gms. of sodium hydroxide is added thereto and stirred for 5.0 minutes at about 65°C. The resultant coal-oil mixture is a stabilized gel and remains so indefinitely.

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

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1 1. A process for beneficiating coal comprising
admixing coal in an aqueous medium with a surface treating
mixture comprising a polymerizable monomer, a polymerization
catalyst and a liquid organic carrier, thereby rendering
5 said coal hydrophobic and oleophilic.

2. The process according to claim 1 further
comprising subjecting the surface treated hydrophobic and
oleophilic coal to at least one water washing to remove
quantities of selected impurities and recovering the resul-
10 tant beneficiated coal product.

3. The process according to claim 1 or 2 wherein
said liquid organic carrier is a non-fuel oil liquid organic
carrier.

4. The process according to any of claims 1 to 3
15 wherein said liquid organic carrier is selected from the
group consisting of benzene, toluene, xylene, naptha and
medium boiling petroleum fractions, dimethylformamide,
tetrahydrofuran, tetrahydrofurfuryl alcohol, dimethylsul-
foxide, methanol, ethanol, isopropyl alcohol, acetone,
20 methylethyl ketone, ethyl acetate and mixtures thereof.

5. The process according to any of claims 2 to 4
wherein said surface treated hydrophobic and oleophilic
coal is subjected to said at least one water washing by
subjecting said chemically treated coal to high shear inter-
25 mixing with at least one aqueous wash medium.

6. The process according to claim 5 wherein said
high shear intermixing of said chemically treated coal
with said aqueous wash medium is carried out by jetting
said coal into said aqueous wash medium under atomizing
30 pressure through a spray nozzle.

1 7. The process according to any of claims 1 to 6
wherein the polymerizable monomer is selected from tall oil,
corn oil or mixtures thereof and said polymerization catalyst
is comprised of a free radical catalyst and a free radical
5 initiator selected from inorganic water soluble metal salts,
organic metal salts or mixtures thereof, wherein the metal
is selected from iron, zinc, antimony, arsenic, copper,
tin, cadmium, silver, gold, platinum, chromium, mercury,
aluminum, cobalt, nickel or lead.

10 8. The process according to any of claims 1 to 7
wherein the polymerizable monomer is corn oil, the catalyst
is hydrogen peroxide and the free radical initiator is
cupric nitrate.

15 9. The process according to any of claims 2 to 8
wherein at least one of the water washings is carried out
in the presence of a member selected from a polymerizable
monomer, a polymerization catalyst, a liquid organic carrier
or mixtures thereof.

20 10. The process according to claims 1 or 2
wherein said polymerization catalyst is selected from
the group consisting of an anionic catalyst and a
cationic catalyst.

25 11. A beneficiated coal product comprising sur-
face treated, hydrophobic and oleophilic coal having a
reduced ash content within the range of from about 0.5 to
about 10% by weight based on the weight of dry coal.

 12. A coal oil mixture comprised of an intimate
blend of the beneficiated coal product of any of the
preceding claims and fuel oil.

30 13. A coal slurry comprising a mixture of the
beneficiated coal product of any of the preceding claims
and a carrier.

1 14. The coal slurry according to claim 13
wherein the carrier is water.

5 15. A process for forming coal-oil mixture comprising admixing pulverized coal with a member selected from a polymerizable monomer, a saturated fatty carboxylic acid or mixtures thereof, and an alkali or alkaline earth hydroxide in the presence of fuel oil.

10 16. The process of claim 15 wherein said polymerizable monomer is tall oil and said hydroxide is selected from the group consisting of sodium hydroxide and calcium hydroxide.

15 17. A process for forming coal-oil mixtures comprising admixing pulverized coal with a polymerizable monomer and a polymerization catalyst in the presence of fuel oil.

20 18. A process for forming coal-oil mixtures comprising admixing pulverized coal with a polymerizable monomer and a polymerization catalyst in the presence of a fuel oil to form a coal-oil mixture and thereafter introducing a hydroxide to said coal-oil mixture to form a stabilized coal-oil mixture.

25 19. The process of claim 18 wherein said polymerizable monomer is tall oil, said polymerization catalyst is comprised of a mixture of a free radical catalyst and free radical initiator, and said hydroxide is sodium hydroxide.

20 20. The process of claim 19 wherein said free radical catalyst is hydrogen peroxide and said free radical initiator is cupric nitrate.

30 21. A stabilized aqueous coal mixture comprised of an intimate admixture of the beneficiated coal product of claim 11, water and a sufficient amount of an alkali or alkaline earth metal hydroxide or oxide to provide said aqueous coal mixture with a pH of above 7.

1 22. The stabilized aqueous coal mixture of claim
21 wherein said alkali hydroxide is sodium hydroxide.

 23. The process of claim 17 wherein said poly-
merization catalyst is selected from the group consisting
5 of an anionic catalyst and a cationic catalyst.

 24. An arrangement for producing a beneficiated
coal product, said arrangement comprising in sequential
combination:

 coal pulverization means;
10 means for feeding pulverized coal from said coal
pulverization means to a surface treatment reaction zone;
 a surface treatment reaction zone having means
for introducing measured amounts of chemical reactants for
providing surface treatment of said coal in an aqueous
15 medium;

 means for introducing surface treated coal from
said surface treatment reaction zone to a water wash zone;
and

 at least one water wash zone having means for
20 admixing ingredients introduced or contained therein under
high shear agitation.

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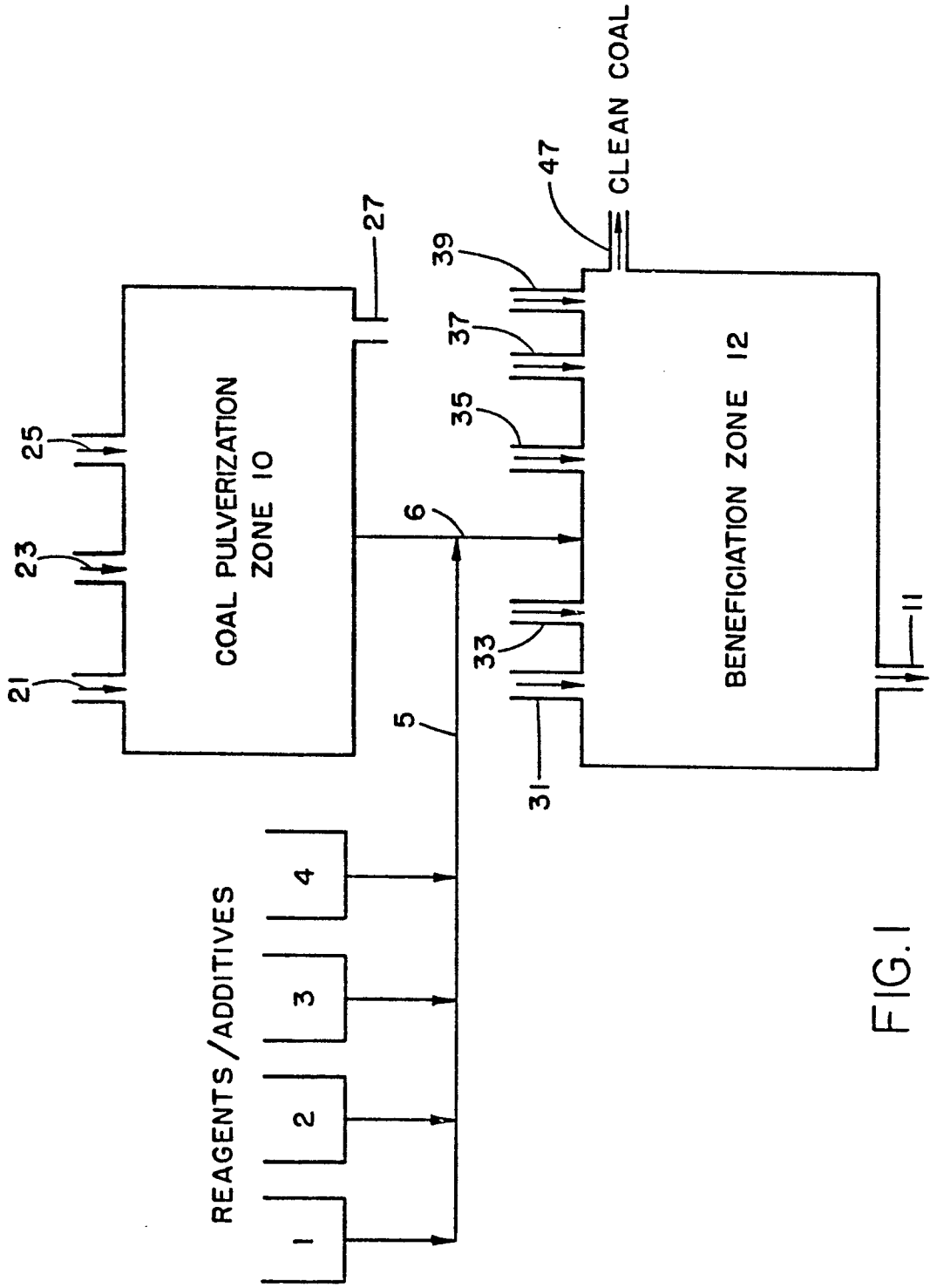


FIG. 1

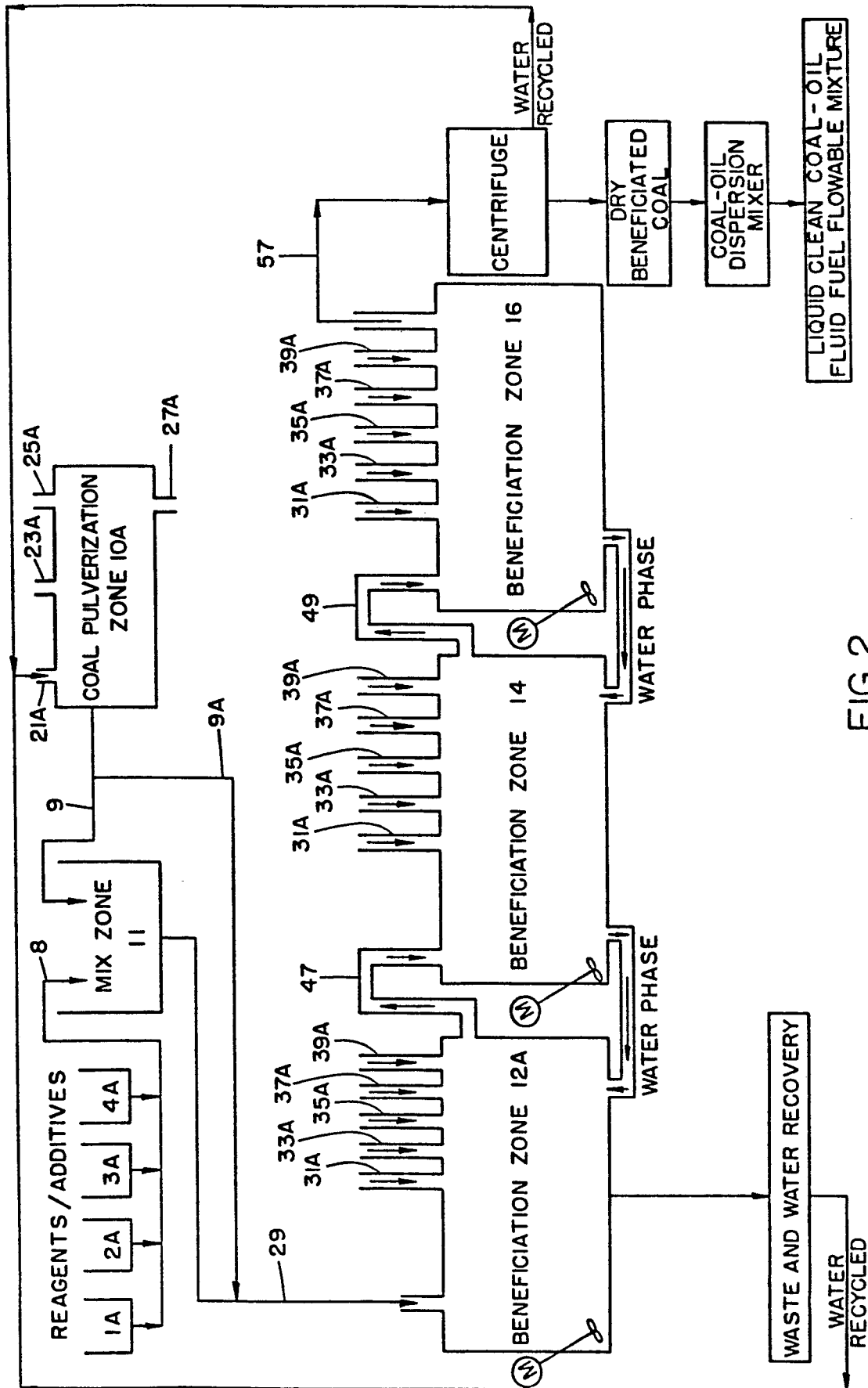
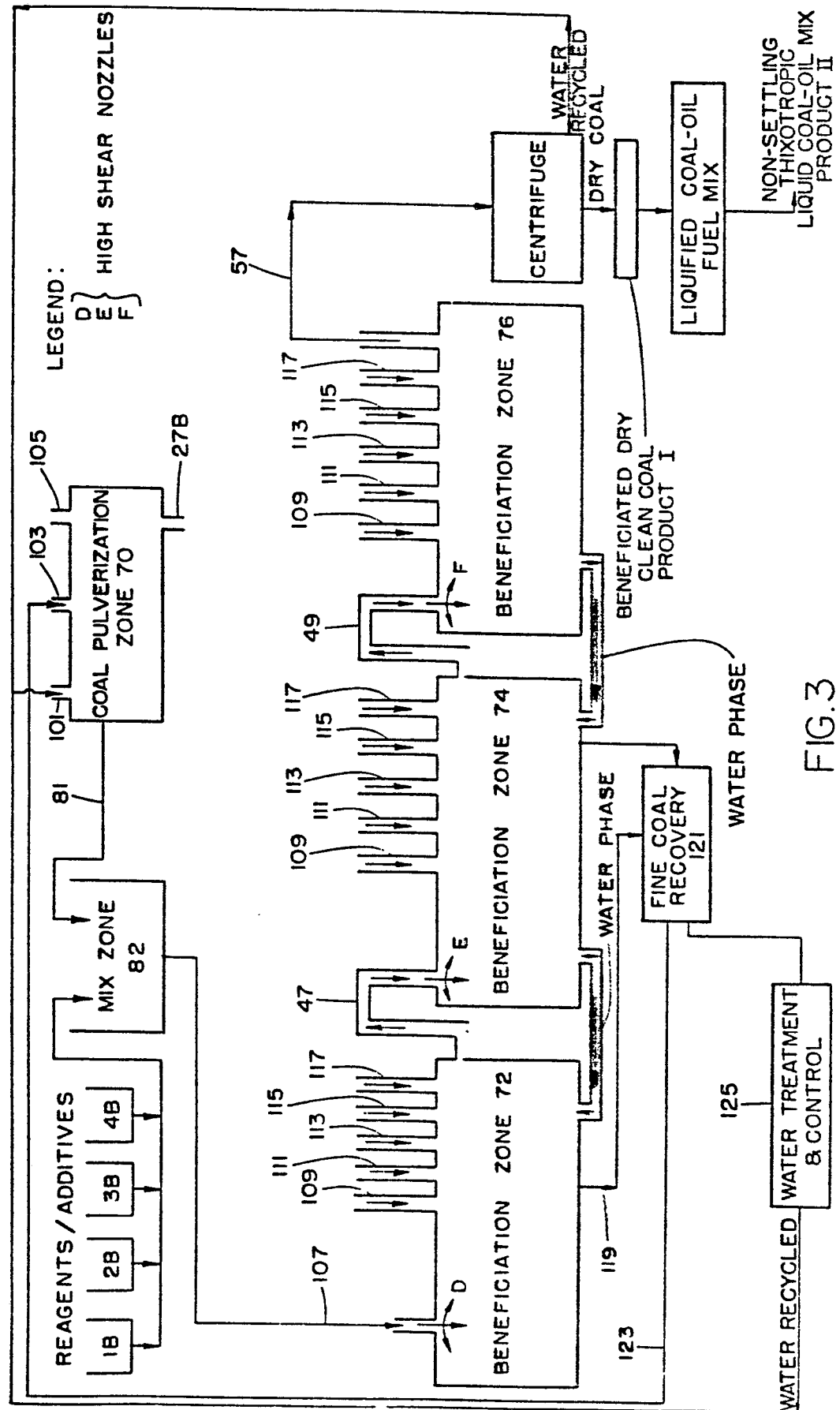


FIG. 2



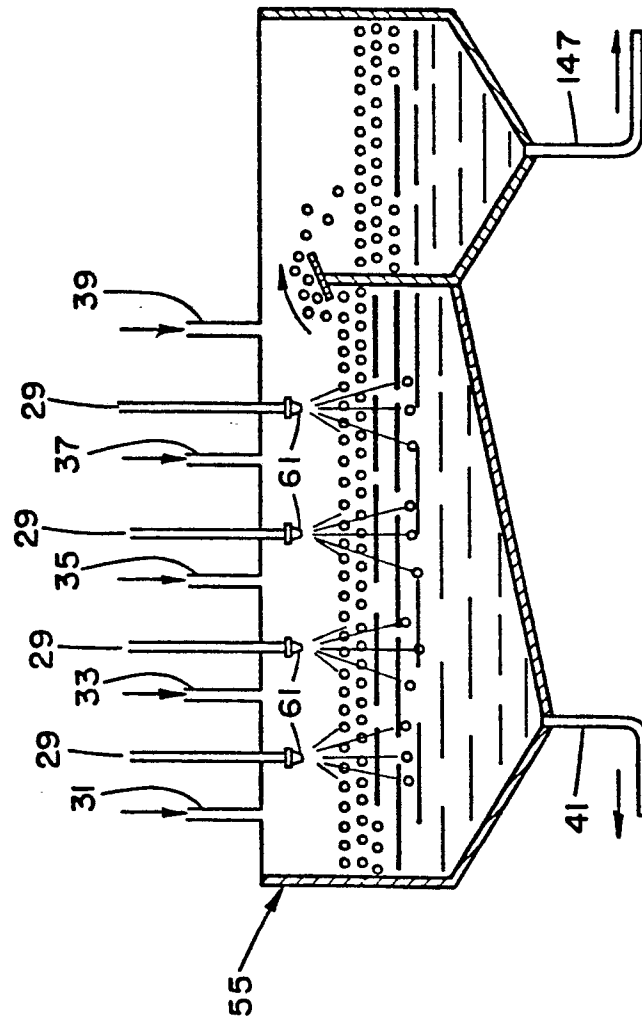


FIG. 4