

⑫

EUROPEAN PATENT APPLICATION

⑰ Application number: 83108876.0

⑤① Int. Cl.³: **C 10 L 1/32**

⑳ Date of filing: 08.09.83

③① Priority: 10.09.82 US 416606

④③ Date of publication of application:
25.04.84 Bulletin 84/17

⑧④ Designated Contracting States:
AT BE DE FR GB IT LU NL SE

⑦① Applicant: **GULF AND WESTERN INDUSTRIES, INC.**
1, Gulf + Western Plaza
New York, N.Y. 10023(US)

⑦② Inventor: **Seymour, Mark**
4120 Bell Circle
Northampton Pennsylvania(US)

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

⑤④ **Coal-aqueous mixtures and process for preparing same.**

⑤⑦ Coal-aqueous mixture having high solids content and excellent stability are provided by an improved process involving selective mixing and other conditions.

COAL-AQUEOUS MIXTURES AND PROCESS FOR PREPARING SAME

The present invention relates to the dispersion of carbonaceous materials and more particularly to coal-aqueous coal mixtures.

Coal as an energy source is in abundant supply.

5 It is estimated that in the United States there is more energy available in coal than in petroleum, natural gas, oil shale and tar sands combined. The substitution of coal for natural gas and oil on a large scale would therefore seem a ready-made solution to our energy problems.

10 Unfortunately, however, unlike oil and gas consumption, coal use is limited not by reserves or production capacity but rather by the extraordinary industrial and regulatory difficulties of burning it in a convenient, efficient and environmentally acceptable manner.

15 A number of techniques are being explored to provide coal as a more useful energy source. One such technique employs gasification methods such as destructive distillation, to effect the conversion of coal to a low or medium Btu gas. In another approach, high pressure

20 hydrogenation is utilized to liquefy coal to make it more suited for transport, burning and the like.

Another technique suggested, and the one to which the present invention relates, is the technique whereby solid coal particles are dispersed in a fluid

25 carrier medium, such as fuel oil or water to form coal-aqueous or coal-oil mixtures.

Coal-oil and coal-aqueous mixtures, however, are distinct systems, each having its own difficulties of formulation. For example, while coal and oil are

30 relatively compatible, coal and water are not. Thus, unlike in the formulation of coal-oil admixtures, in

1 the formulation of coal-aqueous admixtures, the initial
dispersing of the coal in the continuous water phase,
especially large amounts of coal, represents a challenging
obstacle. Moreover, after dispersion, stabilizing, i.e.
5 keeping the coal from settling out of the water phase,
must be also achieved.

Such coal mixtures offer considerable advantages.
They are more readily transported than dry solid coal,
are more easily stored and are less subject to the risks
10 of explosion by spontaneous ignition, the latter being
a significant factor in handling coal. In addition,
providing coal in a fluid form can permit its burning
in apparatus normally used for burning fuel oil. This
can greatly facilitate the transition from fuel oil to
15 coal as a primary energy source, another highly desirable
result.

Various coal-oil and coal-aqueous mixtures have
been described in the literature. For example, British
Patent No. 1,523,193 discloses a mixture comprised of
20 fuel oil and from 15 to 55% by weight of finely ground
coal particles reduced in particle size to 10 microns or
finer. The effort required to grind coal to such fine
sizes, however, makes the process less economically
attractive. Moreover, the use of fuel oil as a carrier
25 medium negates the requirement of lessening our dependence
upon fuel oil.

U.S. Patent No. 4,251,229 is an example of coal-
oil mixtures stabilized with high molecular weight adducts
of alkylene oxide and an alcohol, an amine, a carboxylic
30 acid or phenol having at least three active hydrogens.
In this patent, oil is the continuous carrier phase and

1 accordingly, the stabilization of the coal, as emphasized
repeatedly therein, in the continuous oil phase, is essen-
tially the only concern.

U.S. Patent No. 4,242,098 discloses aqueous
5 coal slurry compositions containing water soluble polymers,
which are thickeners, such as xanthan gum, hydroxypropyl
guar gum or poly(ethylene oxide) having a molecular weight
over 100,000.

In United States Patent No. 3,762,887, there is
10 disclosed a dispersion of coal in an aqueous medium wherein
the coal is ground to a defined array of particle sizes,
a substantial portion of which being about 325 mesh Tyler
Standard screen or even finer. Here again, substantial
and selective grinding of the coal is required.

15 United States Patent No. 4,217,109, discloses
a technique for cleaning and dispersing coal in water
utilizing dispersing agents which by selective adsorption
impart different electrical charges to the carbon particles
and the impurities. The dispersing agents taught are
20 polyelectrolytes, such as alkali metal and ammonium salts
of polycarboxylic acids and polyphosphates.

The article titled "Development and Evaluation
of Highly-Loaded Coal Slurries" published in the 2nd Inter-
national Symposium on Coal-Oil Mixture Combustion,
25 November 27-29, 1979, teaches coal-aqueous mixtures using
coal of bimodal particle size distributions and containing
modified starches, biocides and a wetting agent such as
TRITON X, an octylphenoxy (ethyleneoxy) ethanol surfactant
of low molecular weight.

30 And according to United States Patent No. 3,617,095
a still further method is mentioned in the literature for

1 forming emulsions of bulk solids by admixing the solid,
such as coal, with water and oil in the presence of an
oxyalkylated octyl phenol emulsifying agent.

Finally, a number of further patents disclose
5 mechanical treatments and dispersants for providing coal
in a carrier medium. See, e.g., United States Patents
Nos. 4,088,453; 4,104,035; 3,620,698; 3,764,547; 3,996,026;
3,210,168; 3,524,682; 4,330,301; 4,305,729; European Patent
No. 0 050 412 and PCT International Application No. WO 81-01152.

10 While the art has attempted to provide coal in
dispersed fluid form, as evidenced by the above-described
procedures, there still remains the need for improving
these methods in order to provide coal mixtures without
undue mechanical or chemical treatment. It would be
15 highly desirable to provide coal in aqueous mixture form
wherein only minor amounts of additive materials are
needed to disperse the coal to high solids concentrations
of 70% by weight, or higher. It would be further desirable
to provide coal-aqueous mixtures wherein the coal is pre-
20 cleaned of impurities so that the resultant mixtures are
clean burning or relatively clean burning and thus more
environmentally acceptable.

U.S. Patent No. 4,358,293 dated November 9, 1982,
discloses the surprising discovery that certain polyalkylene-
25 oxide nonionic surfactants are excellent additives for
forming coal-aqueous mixtures having high coal solids
concentrations. It is also disclosed therein that polyalkyl-
eneoxide nonionic surfactants of high molecular weight
having a hydrophobic portion and a hydrophilic portion,
30 the hydrophilic portion being comprised of at least about
100 ethylene oxide repeating units, provide coal-water
dispersions having very high coal solids concentrations of

1 about 70% by weight coal, or higher, when the surfactant
is present in an amount sufficient to disperse the particu-
late coal in water. The resultant mixtures are free-
flowing and are adapted to provide coal in a form ready
5 for transport, storage and clean-burning. Surprisingly,
the surfactants employed can differ in chemical structure
so long as they are of the selected type, are of sufficient
molecular weight and are comprised of at least about 100
units of ethylene oxide.

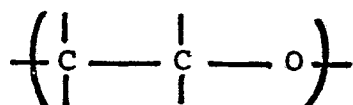
10 It has now been further surprisingly discovered
that by employing certain processing conditions, herein-
after described in detail, in the preparation of the coal-
aqueous slurries disclosed in the afore-mentioned U.S.
Patent No. 4,358,293, even more improved coal-aqueous
15 slurries are provided. For example, the coal slurries pre-
pared in accordance with the present invention are charac-
terized by high solids content, excellent long term storage
stability and other advantages which will become apparent
hereinafter.

20 The present invention relates to a method for
forming a coal-aqueous mixture by (i) admixing a polyalkyl-
eneoxide nonionic surfactant having a hydrophobic portion
and a hydrophilic portion, said hydrophilic portion being
comprised of at least about 100 units of ethylene oxide,
25 with water, under low speed agitation conditions; (ii)
admixing particulate coal with the admixture resulting from
step (i) under medium speed agitation conditions; and (iii)
agitating the resultant coal containing mixture of step
(ii) under high speed agitation. The present invention
30 also relates to a stabilized, high solids content coal-
aqueous mixture comprising particulate coal as a dispersed
solid material; water as a carrier medium; a polyalkyleneoxide

1 nonionic surfactant having a hydrophobic portion and a
hydrophilic portion, said hydrophilic portion comprising
at least about 100 units of ethylene oxide, said polyalkyl-
eneoxide nonionic surfactant being present in said mixture
5 in an amount to disperse said particulate coal in said
water carrier; and a viscosity stabilizer.

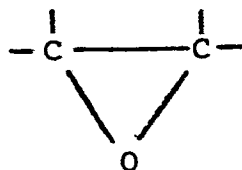
The coal-aqueous slurries of the present
invention are comprised of coal or other carbonaceous
material as the dispersed solid; water as the carrier
10 medium; and a polyalkyleneoxide nonionic surfactant,
as further described herein.

As used herein "polyalkyleneoxide nonionic
surfactant" connotes all compositions, compounds, mix-
tures, polymers, etc. having in whole or in part an
15 alkylene oxide repeating unit of the structure:



20 and having a hydrophobic portion and a hydrophilic por-
tion and which does not dissociate or ionize in solution.
These surfactants have a polymeric portion comprised of
repeating units of ethylene oxide of the general formula:

25



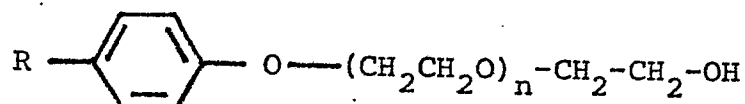
30

35

1 Moreover, the polyalkyleneoxide nonionic
 surfactant compositions employed in this invention are
 of high molecular weight, i.e., from about 4,000 or
 higher, depending on the particular surfactant employed,
 5 are hydrophilic and are comprised of at least about 100
 repeating units of the ethylene oxide monomer. In addi-
 tion, the surfactants utilized have a hydrophobic portion
 and a hydrophilic portion and are nonionic. Being
 nonionic, these compositions are generally not subject
 10 to ionization in aqueous solutions of acid or alkali.

Suitable hydrophilic polyalkyleneoxide nonionic
 surfactants for use in this invention are the commercially
 available glycol ethers of alkyl phenols of the following
 general formula I:

15

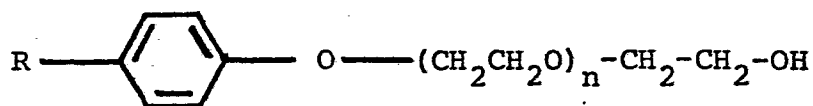


wherein R is substituted or unsubstituted alkyl of from
 20 1 to 18 carbon atoms, preferably 9 carbon atoms; sub-
 stituted or unsubstituted aryl, or an amino group and
 n is an integer of at least about 100.

These nonionic surfactants are available in
 a wide array of molecular weights depending primarily
 25 on the value of "n", i.e., the number of ethylene oxide
 repeating units. Surprisingly, it has been found that
 these surfactants of a high molecular weight of about
 4,000 or higher wherein "n" is at least 100, or higher
 are particularly effective as dispersants for forming
 30 coal-aqueous mixtures to high coal solids concentration
 requiring little if any further additives, etc., to form
 highly flowable liquids.

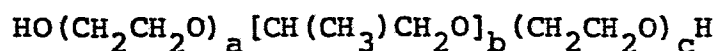
1 Procedures for the preparation of the glycol
ethers of formula I are well known and are described,
for example, in United States Patents Nos. 2,213,477
and 2,496,582, which disclosures are incorporated herein
5 by reference. Generally, the production of these compo-
sitions involves the condensation of substituted phenols
with molar porportions of ethylene oxide monomer.

Thus, polyalkyleneoxide nonionic surfactants
suitable for use in the invention include the glycol ethers
10 of alkylated phenols having a molecular weight of at least
about 4,000 of the general formula:



15 wherein R is substituted or unsubstituted alkyl of from
1 to 18 carbon atoms, preferably 9 carbon atoms; sub-
stituted or unsubstituted aryl, or an amino group, and
n is an integer of at least about 100. The substituents
20 of the alkyl and aryl radicals can include halogen, hydroxy,
and the like.

Other suitable nonionic surfactants are the
poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) or,
as otherwise described, propoxylated, ethoxylated propylene
25 glycol nonionic surfactant block polymers having a molecu-
lar weight of at least about 6,000 of the general formula:

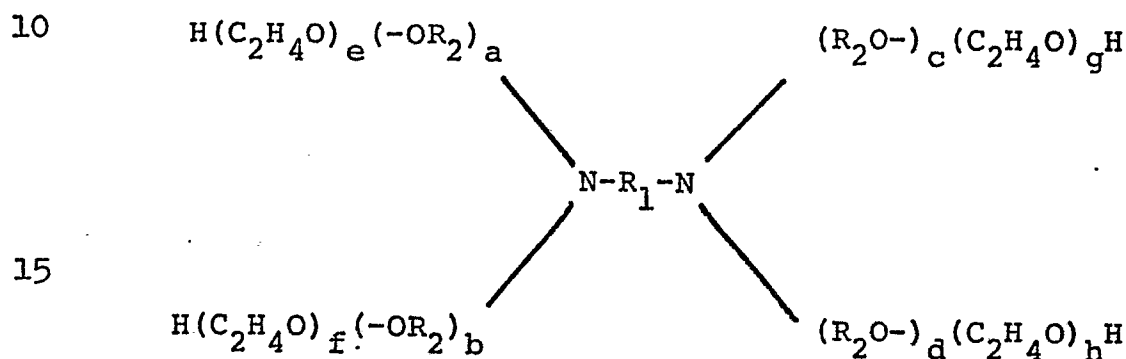


30

35

1 wherein a, b and c are whole integers and wherein a and c
total at least about 100.

Still other polyalkyleneoxide nonionic surfac-
tants suitable for use in the invention are the block
5 polymers of ethylene and propylene oxide derived from
nitrogen-containing compositions such as ethylene diamine
and having a molecular weight of at least about 14,000
of the general formula:



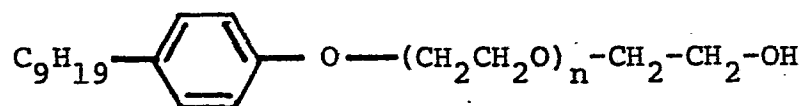
wherein R_1 is an alkylene radical having 2 to 5 carbon
atoms, preferably 2; R_2 is alkylene radical having 3 to
205 carbon atoms, preferably 3; a, b, c, d, e, f, g and h
are whole integers; and e, f, g and h total at least
about 100.

The coal-aqueous mixture compositions of the
invention herein are characterized by having a high coal solids
25 content and a relatively low viscosity of about 2,000 to
6,000 centipoise (cP) or lower as measured, e.g., in
a Brookfield viscometer, model #RVT, fitted with a number
3 spindle, at 100 r.p.m. even at solids levels of 70% by
weight, or higher, based on the total weight of the mix-
30 ture. These compositions can also include amounts of con-
ventional flow modifying materials, such as thickeners,
glues, defoaming agents, salts, etc., depending upon the
use intended.

1 The products of the invention contain only minor amounts of surfactant additives in the order of about 0.1 to 3.0 percent by weight. They further contain particulate coal as the dispersed solid in an amount from about 45 to 580 percent; water as the carrier medium in an amount of from about 19.9 to 52 percent and, if desired, from about 0.1 to 2 percent of a thickener or thickeners; about 0.01 to 2 percent of a defoaming agent and about 0.1 to 2 percent of salts, anti-bacterial agents, caustic or other
10 additive flow control agents, all of the percentages given being based on the total weight of the mixture.

 The most preferred glycol ethers of the type generally describe in formula I are the nonylphenoxy (polyethyleneoxy) ethanol compositions of the formula:

15



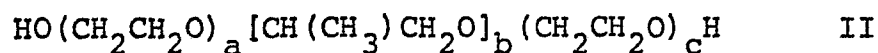
wherein n is about 100 or higher.

 Commercially available surfactants of this type
20 are supplied by the GAF Corporation under the designations IGEPAL CO-990 and IGEPAL CO-997. Other commercially available surfactants of this type are supplied by the Thompson-Hayward Chemical Co. under the designation T-Det N-100, and Whitestone Chemical Co. under the designation
25 ICONOL NP-100.

 As stated hereinbefore, another group of poly-alkyleneoxide nonionic surfactants useful in the invention are the well known poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) nonionic surfactant block poly-
30 mers. These surfactants comprise the block polymers of ethylene oxide and propylene oxide with the repeating units of propylene oxide constituting the hydrophobic

1 portion of the surfactant, and the repeating units of
ethylene oxide constituting the hydrophilic portion of
the surfactant. These block polymer compositions are
of the general formula II:

5



wherein a, b and c are whole integers and wherein a and c
total at least about 100.

These compositions can be prepared, and are
10 commercially available, in a variety of molecular weights,
depending primarily on the number of repeating units of
propylene and ethylene oxide. It has been found that
these block polymers having a molecular weight of at
least about 6,000 and comprising at least about 100
15 repeating units of ethylene oxide are excellent additives
for dispersing coal in a water carrier to the desired
high coal solids concentrations of about 45 to 80 percent,
preferably about 70 percent coal particles, based on the
weight of the total mixture. Thus, with reference to the
20 above formula II, the poly(oxyethylene)-poly(oxypropylene)-
poly(oxyethylene) nonionic surfactants suitable for use
in the invention are those wherein a, b and c are integers
and a and c total about 100 or higher.

Suitable procedures for the production of the
25 block polymers of Formula II are described in the patent
literature in, for example, United States Patents Nos.
2,674,619; 2,677,700 and 3,101,374, which are incorporated
herein by reference.

30

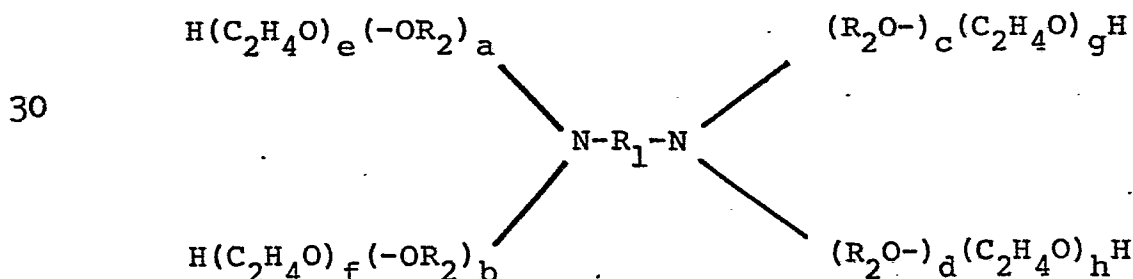
35

1 Generally, these block polymers are prepared by a controlled addition of propylene oxide to the two hydroxyl groups of propylene glycol to form the hydrophobe, followed by the controlled addition of ethylene oxide to "sandwich" in the hydrophobe between the two hydrophilic polyethyleneoxide groups.

The nonionic surfactants of this type (Formula II) having the requisite number of at least 100 units of ethylene oxide are available from the BASF-Wyandotte Corporation under the PLURONIC designation, Series Nos. F-77, F-87, F-68, F-88, F-127, F-98, and F-108. These compositions have at least 100 ethylene oxide units, as per the following table of these PLURONIC surfactants:

15 PLURONIC F	Mol. Wt.	% Ethylene Oxide	Number of Ethylene Oxide Units
F-77	6,600	70	105
F-87	7,700	70	120
F-68	8,350	80	151
20 F-88	10,800	80	195
F-127	12,500	70	200
F-98	13,000	80	235
F-108	14,000	80	255

As also described hereinbefore, a further group of polyalkyleneoxide nonionic surfactants suitable as coal dispersants herein are the nitrogen containing block polymers of the general formula III:



1 wherein R_1 is an alkylene radical having 2 to 5 carbon
atoms, preferably 2; R_2 is an alkylene radical having
3 to 5 carbon atoms, preferably 3; a, b, c, d, e, f, g
and h are whole integers; and e, f, g and h total at
5 least about 100.

These materials are prepared by the addition
of a C_3 to C_5 alkylene oxide to an alkylene diamine under
conditions to add two polyoxyalkylene groups to each of
the nitrogen groups in the presence of a catalyst so as
10 to polymerize the oxyalkylene groups into the desired
long-chained polyoxyalkylene radicals. After the desired
addition and polymerization of the C_3 to C_5 alkylene oxide
group has been completed, ethylene oxide is introduced
and is added to the polyoxyalkylene groups to impart the
15 desired hydrophilic characteristics to the compound.
The preparation of these materials from commercially
available alkylene diamines and alkylene oxides is known
in the art.

In general, the agents are prepared by mixing
20 the C_3 to C_5 alkylene oxide with the alkylene diamine at
atmospheric or elevated pressures, at temperatures between
about 50 to 150° centigrade and in the presence of an
alkaline catalyst such as an alkali metal hydroxide or
alcoholate. The degree of polymerization or the size
25 of the hydrophobic group is controlled by the relative
proportions of C_3 to C_5 alkylene oxide and alkylene dia-
mine; the alkylene oxide being introduced in a sufficient
quantity to obtain a hydrophobic base weight of about 2000
to 3600 units although other weights can be provided.

30

35

1 These surfactants (Formula III) having the
requisite number of at least 100 ethylene oxide repeating
units are available from the BASF Wyandotte Chemicals Corp-
oration under the TETRONIC designations Series Nos. 1107;
5 1307; 908 and 1508. These compositions have at least 100
ethylene oxide units, as per the following table of these
TETRONIC surfactants.

10	TETRONIC	Mol. Wt.	% Ethylene Oxide	Number of Ethylene Oxide Repeating Units
	1107	14,500	70	230
	1307	15,500	70	245
	908	16,500	80	300
15	1508	17,000	80	309

Any of a wide array of coals can be used to form
the coal-aqueous mixtures of the invention, including anthra-
cite, bituminous, sub-bituminous, mine tailings, fines,
20 lignite and the like. Other finely divided solid carbona-
ceous materials may also be used, e.g., coke, prepared either
from coal or from petroleum.

To form the coal-aqueous mixtures, coal is pul-
verized to approximately 90% finer than a 200 mesh Tyler
25 Standard screen size, although courser or finer particle
sizes can be employed, if desired.

Advantageously, according to the invention, the
untreated pulverized raw coal, is beneficiated, i.e.,
cleaned of amounts of ash and sulfur. The art will appre-
30 ciate that mixtures formed of beneficiated coal offer con-
siderable advantage. They are clean burning or relatively
clean burning, and are more suited for burning in apparatus
for powering utilities, home burners and the like without
undue burdensome and expensive cleaning apparatus.

1 Any of a wide array of beneficiating treatments
can be employed in preparing the particulate coals, includ-
ing conventional heavy-media separations, magnetic separa-
tion and the like. The preferred method for providing the
5 beneficiated coal particles is by a chemical treatment
process such as described in U.S. Patent No. 4,304,573.

 Generally, according to the preferred chemical
beneficiation treatment method, raw as-mined coal is
10 ground in the presence of water to a particle size of
about 200 mesh. The ground coal is treated in an aqueous
medium with a monomeric compound, generally an unsaturated
polymerizable composition such as readily available tall
oil fatty acids in the presence of a metal initiator such
15 as cupric nitrate; and minor amounts of fuel oil, all in
an aqueous phase are also present. The ground coal so
treated is made hydrophobic and oleophilic and is separated
from the unwanted ash and sulfur by a froth flotation
technique.

20 The cleaned coal recovered from the preferred
chemical treatment process, now in the form of beneficiated
coal particles, is suited for the coal-aqueous mixtures of
the invention. These coal particles are characterized by
having an ash content reduced to levels of about 0.5 to
25 6.0% and a sulfur content reduced to levels of about 0.5
to 2.0%.

30

35

1 As in said U.S. Patent No. 4,358,293 it is
preferred herein to form the coal-aqueous mixture by
first adding the surfactant to water together with other
additives such as conventional defoaming agents, if de-
5 sired. This admixing can be done with stirring at con-
ditions of atmospheric or nearly atmospheric temperature
and pressure. Thereafter, the particulate coal, preferably
beneficiated coal particles, is added to the mixture to
produce a coal-aqueous mixture of high coal solids content
10 of about 45 to 80% by weight coal, based on the total
weight of the mixture at atmospheric or nearly atmospheric
temperatures and pressures. If desired, thickeners can
then be added to further stabilize the mixture to assist
in preventing the coal particles from settling when the
15 mixture is to be stored for extended periods. Caustic
soda or other bases can also be added at this point. As
will be apparent, adding thickeners in or near the final
stage is preferred so that the stirring requirements
are kept at a minimum. The coal-aqueous mixtures can be
20 prepared in a batch operation or in the continuous mode.
In continuous production, the coal can be admixed with
water in a first stage along with other flow control agents
such as the surfactant. The compositions of the first
stage can then be transferred continuously to a second
25 stage wherein the thickener is added. Again, adding the
thickener at the later stage results in reduced stirring
requirements.

30

35

1 In accordance with the discovery of the pre-
sent invention, it has now been found that further speci-
fic processing conditions provide for a more improved
coal-aqueous product, as well as, avoiding certain problems,
5 such as deleterious foaming and flocculation during pro-
cessing. More particularly, in preparing the coal-aqueous
compositions of the present invention, the surfactant and
other additives, such as conventional defoaming agents, if
desired, are first added to water and mixed, under low speed
10 agitation conditions, such as at from about 500 rpm to about
1500 rpm, preferably about 1000 rpm, for a time of from about
30 seconds to about 3 minutes, preferably about 1 minute.
Thereafter, the particulate coal, preferably beneficiated coal
particles, is added to the mixture and admixed therein under
15 moderate or medium agitation conditions, for example, at
an rpm in the range of from about 1000 rpm to about 3000 rpm,
preferably about 2000 rpm for a time sufficient to provide a
wetted out admixture. Usually this time is in the range of
from about 5 minutes to about 20 minutes. At this time, the
20 agitation of the admixture is increased to a high speed, for
example, from above about 3000 rpm to about 6000 rpm, preferably
about 4000 rpm for a time sufficient to disperse the coal,
usually from about 5 minutes to about 15 minutes, preferably
about 10 minutes. If desired, thickeners are then added to
25 the slurry under the afore-described high speed agitation con-
ditions, e.g. 4000 rpm, for a further time of from about 1
minute to about 3 minutes, preferably about 2 minutes. In
the preparation of a most preferred formulation, other ingre-
dients, such as viscosity stabilizers and antibacterial agents
30 are then added to the formulation at high speed agitation
for a further time of from about 1 minute to about 3 minutes,
preferably about 2 minutes. By wetted out or wet as used herein,
it is meant that the surface of each coal particle is covered
water.

1 Typical mixing or dispersing apparatus employed
herein include for example Premier Mill Co.'s Hi-Vispersator
High-Speed Disperser.

5 It is to be understood that the above indicated
residence times, temperatures, mixing speeds, etc. may vary
according to specific process requirements such as the
volume of ingredients, size of apparatus, mixing efficiency,
etc. Thus, for example, depending on the scale of the
operation, e.g. pilot plant, plant, etc., these process
10 conditions of the present invention may be adjusted accord-
ingly.

 It has been found that by employing these afore-
described specific conditions of the present invention, the
coal is allowed to be dispersed in a surfactant/antifoam
15 solution at relatively low viscosity, while the surfactant
is orienting at the coal-water interface. The anti-foam
agent controls the level of foam caused by the surfactant
being agitated in solution. The thickeners are added after
the coal is adequately dispersed to impart the desired
20 rheological and suspension properties from flocculating
by forming a protective colloid.

 As indicated above, additives that can be added
to the coal-aqueous mixture include defoaming agents, thick-
eners, salts, bases, other flow modifying agents and com-
25 binations of these materials.

 Generally, the defoaming agents that can be
used are conventional and include both silicon and non-
silicon containing compositions. A commercially available
defoaming agent suitable for use in the mixtures is COLLOID
30 691, supplied by Colloids, Inc. This composition generally
comprises a mixture containing mineral oil, amide and an
ester.

1 Thickeners can also be added to the mixture. They
are added to increase the non-settling characteristics of
the composition. Suitable thickeners include, for example,
xanthan gum, guar gum, glue and the like. Other thickeners
5 include, for example, alkali soluble acrylic polymers (e.g.
ACRYSOL ICS-1 sold by the Rohm and Haas Company). Combina-
tions of these thickeners are also contemplated herein.
For the purposes herein, the thickeners are generally used
in amounts ranging from about 0.01 to about 3.0% by weight,
10 based on the total weight of the mixture.

 In preparing the compositions containing the
preferred 70% by weight coal, based on the weight of the
total mixture, the polyalkyleneoxide nonionic surfactants
are preferably mixed with water in a proportion of about
15 0.3 part by weight surfactant to 29.3, parts by weight,
water at atmospheric or nearly atmospheric temperatures
and pressures. A defoaming agent is also added to the
water in an amount of about 0.03, part by weight, to
assist in processing. The pulverized coal is then mixed
20 with the water in a proportion of 70 parts by weight coal
to 29.3 parts by weight of water to obtain a flowable
liquid. If desired, to the mixture can then be added
about 0.12 to about 0.15, part by weight, of thickener
or thickeners to provide protection against settling.
25 Other additives such as salts or bases, antibacterial
agents such as formaldehyde, and the like, viscosity
stabilizers, such as ammonia, etc. can also be added in
about 0.2 to about 0.3, part by weight, of the total
mixture to further assist in dispersing the coal and
30 providing the other obvious advantages.

 The following examples will further illustrate
the invention:

1

EXAMPLE 1Preparation of a coal-aqueous mixture.

5

A coal-aqueous mixture using unbeneficiated particulate coal is prepared of the following composition.

10	<u>Component</u>	<u>Weight %</u>
	Particulate Coal ¹	70.00
	Water ²	29.37
	Salt ³	0.60
	Defoaming Agent ⁴	0.30
15	Polyethyleneoxide nonionic surfactant having 100 ethylene oxide repeating units and a molecular weight of 4680 ⁵	0.57

-
- 20 1 - Pocohontas seam coal
2 - Industrial water
3 - Industrial grade sodium chloride
4 - COLLOID 691 from Colloids, Inc., Newark, N.J.
5 - IGEPAL CO-997 from the GAF Corporation, N.Y., N.Y.

25

The coal is ground to about 90 percent finer than 200 mesh Tyler Standard screen size. The surfactant defoaming agent, and salt in the amounts specified are added to the 29.37 grams of water in a Hi-Vispersator high-speed disperser available from the Premium Mill Co.,
30 equipped with a 1 3/4 inches Cowles-type blade operating at 2000 r.p.m. The disperser is operated at atmospheric temperature and pressure. The particulate coal is then added to the mixture with continued mixing.

35

1 The mixture is seen to disperse the entire 70%
by weight coal and is observed to be free flowing.

EXAMPLE 2

5

Preparation of a coal-aqueous mixture.

 A coal-aqueous mixture using another unbene-
ficiated particulate coal is prepared of the following
10 composition.

	<u>Component</u>	<u>Weight %</u>
	Pariculate Coal ¹	70.00
15	Water ²	29.03
	Salt ³	0.60
	Defoaming Agent ⁴	0.03
	Polyethyleneoxide nonionic surfactant having 245 ethylene oxide repeating units and a molecular weight of 15,500 ⁵	0.34
20		

1 - Pocohontas seam coal

2 - Industrial water

3 - Industrial grade sodium chloride

25 4 - COLLOID 691 from Colloids, Inc., Newark N.J.

5 - TETRONIC 1307 from BASF Wyandotte Chemicals, Corp.,
Parsippany, N.J.

 The coal is ground to about 90% finer than 200
30 mesh Tyler Standard screen size. The surfactant, defoaming
agent, and salt in the amounts specified are added to the
29.46 grams of water in a high speed disperser equipped
with a 1 3/4 inches Cowles-type blade operating at 2000
r.p.m. The particulate coal is then added to the mixture

35

- 1 with continued mixing. The vessel is operated at atmospheric temperatures and pressure.

The mixture is seen to disperse the entire 70% by weight coal and is observed to be free flowing.

5

EXAMPLE 3

Preparation of particulate cleaned coal.

- 10 200 grams of Pittsburgh seam coal having 6.3% ash content and a 1.5% sulfur content based on the weight of dry coal was pulverized in the presence of water to a 200 mesh Tyler Standard size using a ball mill grinding unit. The coal was then transferred to a mixing vessel.
- 15 Into this vessel was also introduced 0.03 gram of corn oil, 5.0 grams of No. 2 fuel oil, 1.0 cubic centimeter of a 5% solution of hydrogen peroxide in water; 2.0 cubic centimeters of a 5.0% solution of cupric nitrate in water and 200 grams of the 200 mesh coal. The mixture was stirred and heated to 86°F. for 2 minutes. The mixture was sprayed into the water surface and a frothing ensued. Coal, in the froth phase, having a 3.4% ash and 0.9% sulfur based on the weight of dry coal was skimmed from the surface of the water and recovered. The water phase containing large amounts of ash and sulfur was discarded.
- 25

The recovered coal was slightly dried using a Buchner filter drying unit.

30

35

1

EXAMPLE 4

Preparation of a coal-aqueous mixture.

5

Beneficiated coal, treated in accordance with the procedure of Example 3, was formed into a coal-aqueous mixture of the following composition.

	<u>Component</u>	<u>Weight %</u>
10	Particulate Coal ¹	70.21
	Water ²	29.04
	Xanthan gum ³	0.06
	Guar gum ⁴	0.03
15	Salt ⁵	0.06
	Defoaming Agent ⁶	0.03
	Polyethyleneoxide nonionic surfactant having about 100 repeating units of ethylene oxide and a molecular weight of about 4680 ⁷	0.57
20		

1 - Pocohontas seam coal cleaned in accordance with the teachings of Example 3. The weight percent given being on a moisture free basis.

25 2 - Industrial water

3 - BIOZAN SPX-5423, Hercules Inc., Wilmington, Delaware

4 - GUAR THKX-225, Hercules Inc., Wilmington, Delaware

5 - Industrial grade sodium chloride

30 6 - COLLOID 691 from Colloids, Inc., Newark, N.J.

7 - IGEPAL CO-997 from the GAF Corporation, N.Y., N.Y.

35

1 The surfactant, defoaming agent and salt in
the amounts specified were added to the 29.04 grams of
water in a high speed disperser equipped with a 1 3/4
5 inches Cowles-type blade operated at 2000 r.p.m. The
disperser was operated at atmospheric temperature and
pressure. The particulate coal was then added to the
mixture with continued mixing at 4500 r.p.m. To the
mixture was then added the xanthan gum and guar gum
thickeners with mixing at 4500 r.p.m.

10 The mixture was observed to disperse the
entire 70.21 wt.% coal particles and was observed to
be free flowing. The viscosity was measured with a
Brookfield viscometer model #RVT and found to be 2000
cP at 100 r.p.m. using a #6 spindle.

15

20

25

30

35

1

EXAMPLE 5

Preparation of a coal-aqueous mixture.

5

Beneficiated coal, treated in accordance with the procedure of Example 3, was formed into a coal-aqueous mixture of the following composition.

	<u>Component</u>	<u>Weight</u>
10	Particulate Coal ¹	70.00
	Water ²	29.56
	Xanthan gum ³	0.06
	Guar gum ⁴	0.03
15	Amino-hydroxy material ⁵	0.05
	Defoaming Agent ⁶	0.03
	Polyethyleneoxide nonionic surfactant having about 245 repeating units of ethylene oxide and a molecular weight of about 15,500 ⁷	0.30

20

1 - Pocohontas seam coal cleaned in accordance with the teachings of Example 3. The weight percent given being on a moisture free basis.

2 - Industrial water

25

3 - KELZAN, Kelco Co., division of Merck & Co., Inc., San Diego, California

4 - GUAR THKX-225, Hercules Inc., Wilmington, Delaware

5 - AMP-95 International Minerals & Chemical Corp.,

30

Des Plains, Illinois

6 - COLLOID 691 from Colloids, Inc., Newark, N.J.

7 - TETRONIC 1307 from BASF Wyandotte Chemicals, Corp., Parsippany, N.J.

35

1 The surfactant and defoaming agent in the amounts
specified were added to the 29.56 grams of water in a high
speed disperser equipped with a 1 3/4 inches Cowles-type
blade operated at 2000 r.p.m. The disperser was operated
5 at atmospheric temperature and pressure. The particulate
coal was then added to the mixture with continued stirring
at 4500 r.p.m. To the mixture was then added the xanthan
gum and guar gum thickeners while mixing at 4500 r.p.m.

 The mixture was observed to disperse the entire
10 70.00 wt.% coal particles and was observed to be free
flowing. The viscosity was measured with a Brookfield
viscometer model #RVT and found to be 2000 cP at 100 r.p.m.
using a #6 spindle.

15 EXAMPLES 6-14

 These examples compare mixtures which can be
prepared to high coal solids concentrations utilizing
polyalkyleneoxide nonionic surfactants having a high
molecular weight and at least 100 repeating units of
20 ethylene oxide with compositions which do not disperse
the coal to high solid levels using similar surfactants,
but which do not have the required 100 repeating units
of ethylene oxide and high molecular weight.

 In each example the same or substantially the
25 same amounts of particulate coal, water, thickeners, salt
and defoaming agents were used and a similar surfactant
was used, i.e., a poly(oxyethylene)-poly(oxypropylene)-
poly(oxyethylene) surfactant, except that the different
surfactants tested had different molecular weights and a
30 different number of ethylene oxide repeating units.

1 The mixtures were each prepared in accordance
with the procedures of Example 4. The surfactant, defoam-
ing agent, and salt in the amount specified were added
to water in a high speed disperser equipped with a 1 3/4
5 inches Cowles-type blade operated at 2000 r.p.m. The
disperser was operated at atmospheric temperature and
pressure. The particulate coal was then added to the
mixture with continued mixing. To the mixture was then
added the xanthan gum and guar gum thickeners in the stated
10 amounts with mixing.

 The following table A tabulates the results of
Examples 6-14 showing that coal dispersions of high solid
concentrations were prepared utilizing the poly(oxyethy-
lene)-poly(oxypropylene)-poly(oxyethylene) surfactants
15 having the requisite 100 repeating units of ethylene
oxide and a molecular weight in excess of 6000, whereas,
the same amount or substantially the same amount of coal
was not fully dispersed utilizing surfactants not having
the requisite 100 repeating units of ethylene oxide and
20 high molecular weight.

25

30

35



TABLE A

Components (grams)	Mol. Ethylene Oxide									
	Wt. Repeating Units									
Examples	6	7	8	9	10	11	12	13	14	
Particulate coal ¹	272.0	272.0	272.0	272.0	272.0	272.0	272.0	272.0	272.0	
Water ²	74.0	74.0	74.0	74.0	74.0	74.0	74.0	74.0	74.0	
Xanthan gum ³	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	
Guar gum ⁴	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
Salt ⁵	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	
Defoaming Agent ⁶	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
PLURONICS - L35	2.0	-	-	-	-	-	-	-	-	1,900
" F38	-	2.0	-	-	-	-	-	-	-	5,000
" F77	-	-	1.1	-	-	-	-	-	-	6,500
" F87	-	-	-	1.1	-	-	-	-	-	7,700
" F68	-	-	-	-	1.1	-	-	-	-	8,350
" F88	-	-	-	-	-	1.1	-	-	-	10,800
" F127	-	-	-	-	-	-	1.1	-	-	12,500
" F98	-	-	-	-	-	-	-	1.1	-	13,000
" F108	-	-	-	-	-	-	-	-	1.1	14,000

Mixture viscosity
in CP at 100 r.p.m.
using a #3 spindle.

N.I.

N.I.

5400

3850

5900

3800

3500

3600

3000

1

TABLE A (cont'd)

- 1 - Pocohontas seam coal cleaned in accordance with
the teachings of Example 3 and containing 10%
moisture
- 2 - Industrial water
- 3 - BIOZAN SPX-5423, Hercules Incorporated, Wilmington,
Delaware
- 4 - GUAR THKX-225, Hercules Incorporated, Wilmington,
Delaware
- 5 - Industrial grade sodium chloride
- 6 - COLLOID 691 from Colloids, Inc., Newark, N.J.
- N.I. - The amount of coal specified was not fully incor-
porated into the water.

20

25

30

35

1

EXAMPLES 15-21

5 These examples compare mixtures which can be prepared to high coal solid concentrations utilizing poly-alkyleneoxide nonionic surfactants having a high molecular weight and at least 100 repeating units of ethylene oxide with compositions which do not disperse the coal to high solid levels using similar surfactants but which do not have the required 100 repeating units of ethylene
10 oxide and high molecular weight.

In each example the same amounts or substantially the same amounts of particulate coal, water, thickeners, salt and defoaming agents were used and a similar surfactant was used, i.e., nitrogen containing
15 block polymers of propylene and ethylene oxide, except that the different surfactants tested had different molecular weights and a different number of ethylene oxide repeating units.

The mixtures were each prepared in accordance
20 with the procedures of Example 4. The surfactant, defoaming agent, and salt in the amount specified were added to water in a high speed disperser equipped with a 1 3/4 inches Cowles-type blade operated at 4500 r.p.m. The disperser was operated at atmospheric temperature
25 and pressure. The particulate coal was then added to the mixture with continued mixing. To the mixture was then added the xanthan gum and guar gum thickeners in the stated amounts with mixing.

The following table B tabulates the results of
30 Examples 15-21 showing that coal dispersions of high solid concentrations were prepared utilizing the nitrogen

35

1 containing propylene and ethylene oxide block polymer
surfactants having the requisite 100 repeating units of
ethylene oxide and a molecular weight in excess of 14,000
whereas, the same amount of coal was not dispersed utiliz-
5 ing surfactants not having the requisite 100 repeating
units of ethylene oxide and high molecular weight.
Tetronics 1107, 1307, 908, 1508 have a higher ratio of
ethylene oxide to propylene oxide, i.e. ethylene oxide con-
tent greater than propylene oxide content, while tetronics
10 304, 504 and 704 have a higher ratio of propylene oxide
to ethylene oxide, i.e. propylene oxide content greater
than ethylene oxide.

15

20

25

30

35

TABLE B

Examples	Components (grams)						Mol. Wt.	Ethylene Oxide Repeating Units
	15	16	17	18	19	20		
particulate coal ¹	272.0	272.0	272.0	272.0	272.0	272.0		
water ²	74.0	74.0	74.0	74.0	74.0	74.0		
Kaithan gum ³	0.2	0.2	0.2	0.2	0.2	0.2		
guar gum ⁴	0.1	0.1	0.1	0.1	0.1	0.1		
Salt ⁵	0.2	0.2	0.2	0.2	0.2	0.2		
Defoaming Agent ⁶	0.1	0.1	0.1	0.1	0.1	0.1		
PETRONIC -- 304	1.3	-	-	-	-	-	1,650	15
" 504	-	1.3	-	-	-	-	3,400	30
" 704	-	-	1.3	-	-	-	5,500	50
" 1107	-	-	-	1.3	-	-	14,500	230
" 1307	-	-	-	-	1.3	-	15,500	245
" 908	-	-	-	-	-	1.3	16,500	300
" 1508	-	-	-	-	-	1.3	17,000	309

Mixture viscosity
in CP at 100 r.p.m.
using a #3 spindle

N.I.

N.I.

N.I.

3100

3700

3200

2750

1

TABLE B (cont'd)

1 - Pocohontas seam coal cleaned in accordance
with the teachings of Example 3 and containing 10%
5 moisture

2 - Industrial water

3 - BIOZAN SPX-5423, Hercules Incorporated, Wilmington,
Delaware

10 4 - GUAR THKX-225, Hercules Incorporated, Wilmington,
Delaware

5 - Industrial grade sodium chloride

6 - COLLOID 691 from Colloids, Inc., Newark, N.J.

15 N.I. - The amount of coal specified was not fully
incorporated into the water.

20

25

30

35

1

EXAMPLES 22-28

These examples compare mixtures which can be prepared to high coal concentrations utilizing polyalkyleneoxide nonionic surfactants having a high molecular weight and at least 100 repeating units of ethylene oxide with compositions which do not disperse the coal to high solid levels using similar surfactants but which do not have the required 100 repeating units of ethylene oxide and high molecular weight.

In each example the same amounts or substantially the same amounts of particulate coal, water, thickeners, salt and defoaming agents were used and a similar surfactant was used, i.e., a glycol ether of an alkylated phenol, except that the different surfactants tested had different molecular weights and a different number of ethylene oxide repeating units.

The mixtures were each prepared in accordance with the procedures of Example 4. The surfactant, defoaming agent, and salt in the amount specified were added to water in a high speed disperser equipped with a 1 3/4 inches Cowles-type blade operated at 4500 r.p.m. The disperser was operated at atmospheric temperature and pressure. The particulate coal was then added to the mixture continued mixing. To the mixture was then added the xanthan gum and guar gum thickeners in the stated amounts with mixing.

The following table C tabulates the results of Examples 22-28 showing that coal dispersions of high solid concentrations were prepared utilizing the glycol ether of alkylated phenol surfactants having the requisite

35

- 1 100 repeating units of ethylene oxide and a molecular weight in excess of 4000, whereas, the same amount or substantially the same amount of coal was not fully dispersed utilizing surfactants not having the requisite 100
- 5 repeating units of ethylene oxide and high molecular weight.

10

15

20

25

30

35

TABLE C

Examples	22	23	24	25	26	27	28	Mol. Wt.	Ethylene Oxide Repeating Units
<u>Components (grams)</u>									
Particulate coal ¹	272.0	272.0	272.0	272.0	272.0	272.0	272.0		
Water ²	74.0	74.0	74.0	74.0	74.0	74.0	74.0		
Xanthan gum ³	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
Guar gum ⁴	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
Salt ⁵	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
Defoaming Agent ⁶	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
IGEPAL - CO-630	1.4	-	-	-	-	-	-	720	10
" CO-730	-	1.4	-	-	-	-	-	940	15
" CO-850	-	-	1.4	-	-	-	-	1,160	20
" CO-887	-	-	-	2.0	-	-	-	1,600	30
" CO-897	-	-	-	-	2.0	-	-	2,040	40
" CO-977	-	-	-	-	-	2.0	-	2,480	50
" CO-997	-	-	-	-	-	-	2.0	4,680	100

Mixture viscosity
in cP at 100 r.p.m
using a #3 spindle

N.I. N.I. N.I. N.I. N.I. N.I. N.I. 2000

Mixture viscosity
in cP at 100 r.p.m.
using a #3 spindle

N.I.

N.I.

N.I.

N.I.

N.I.

N.I.

2000

1

TABLE C (cont'd)

- 1 - Pocohontas seam coal cleaned in accordance with
the teachings of Example 3 and containing 10%
5 moisture
- 2 - Industrial water
- 3 - BIOZAN SPX-5423, Hercules Incorporated, Wilmington,
Delaware
- 10 4 - GUAR THKX-225, Hercules Incorporated, Wilmington,
Delaware
- 5 - Industrial grade sodium chloride
- 6 - COLLOID 691 from Colloids, Inc., Newark, N.J.
- 15 N.I. - The amount of coal specified was not fully incor-
porated into the water.

As the Examples show, coal-aqueous mixtures
are provided having high coal solids content. The
20 resultant mixtures are stable, have low viscosity and
incorporate large amounts of solid coal particles,
typically 70% by weight coal or higher. Examples 6-14
demonstrate that polyalkylene oxide nonionic surfactants
of high molecular weight of at least 6000 and having at
25 least 100 repeating units of ethylene oxide units are
excellent dispersants for forming coal-aqueous mixtures.
Examples 6 to 14 further demonstrate that for the sur-
factants of the same basic structure, i.e., block poly-
mers of propylene and ethylene oxide, advantageous
30 results are achieved by employing the composition of a
molecular weight of 6000 or higher having at least 100
repeating units of ethylene oxide.

1 Similarly, Examples 15 to 21 demonstrate that
for the polyalkyleneoxide nonionic surfactants of the
block polymer type derived from nitrogen containing com-
positions such as ethylene diamine, compositions of
5 14,000 molecular weight or higher having 100 repeating
units of ethylene oxide provide the same or nearly the
same advantageous results. Similarly, as Examples 22-28
show the glycol ether of alkylated phenol surfactants
having the 100 repeating units of ethylene oxide and
10 high molecular weight also are excellent coal dispersants.

15

20

25

30

35

1

EXAMPLE 29

The following formulation is used to prepare an aqueous coal slurry in accordance with the improvement of the present invention.

5

<u>Ingredient</u>	<u>Material</u>	<u>Parts by Weight</u>
1	Water	29.236
10 2	Tetronic 1307	.34
3	Colloid 691	.03
4	Cleancoal	70.00
5	Kelzan	.014
6	Guar THIX	.10
15 7	37% Formaldehyde	.14
8	28% Ammonia	.14
		<u>100.00</u>

20

1. Industrial Water
2. Surfactant - BASF Wyandotte Corp.
3. Anti-foam Agent - Colloids, Inc.
4. Pocahontas Clean Coal
5. Xanthan Gum - Kelco Division, Merck & Co., Inc.
6. Guar Gum - Hercules, Inc.
- 25 7. Formaldehyde Solution- Borden Chemicals
8. Ammonium Hydroxide - Fischer Scientific

25

Slurry Properties

30

Solids	- 70.0 $\pm$ 1.0
pH	- 8.0 $\pm$ 1.0
Brookfield Viscosity, cp	
10 rpm	- 14,000 $\pm$ 4,000
100 rpm	- 6,500 $\pm$ 1,500
Settling (spatula probe)	
6 weeks	- None
8 weeks	- Slight amount of soft sediment

35

1 The ingredients are added in the order listed.
A high-speed disperser, namely a High-Vispersator is
used to stir, mix and disperse the materials into a
stable homogeneous slurry. Ingredients 1, 2 and 3 are
5 stirred together for one minute at low speed (1,000 rpm).
The coal is added to this solution at medium speed (2000
rpm) for a sufficient time to wet the coal particles and
disperse the coal in ingredients 1, 2 and 3. Then the speed
of the disperser is increased to high speed (4000 rpm)
10 for 10 minutes to further disperse the coal particles.
Ingredients 5 and 6 are then added with the disperser
at high speed. After two minutes ingredients 7 and 8
are added and the batch is considered complete after
an additional two minutes of mixing at high speed. All
15 mixing is carried out at atmospheric temperatures and
pressures.

20

25

30

35

1

EXAMPLE 30

The following formulation is used to prepare
 an aqueous coal slurry in accordance with the improvement
 5 of the present invention.

	<u>Ingredient</u>	<u>Material</u>	<u>Parts by Weight</u>
	1	Water	29.236
10	2	Tetronic 908	.34
	3	Colloid 691	.03
	4	Cleancoal	70.00
	5	Kelzan	.014
	6	Guar THIX	.10
15	7	37% Formaldehyde	.14
	8	28% Ammonia	.14
			<u>100.00</u>

- | | | |
|----|---------------------------|-------------------------------------|
| | 1. Industrial Water | |
| | 2. Surfactant | - BASF Wyandotte Corp. |
| 20 | 3. Anti-foam Agent | - Colloids, Inc. |
| | 4. Pocahontas Clean Coal | |
| | 5. Xanthan Gum | - Kelco Division, Merck & Co., Inc. |
| | 6. Guar Gum | - Hercules, Inc. |
| 25 | 7. Formaldehyde Solution- | Borden Chemicals |
| | 8. Ammonium Hydroxide | - Fischer Scientific |

Slurry Properties

	Solids	- 70.0 $\pm$ 1.0
30	pH	- 8.0 $\pm$ 1.0
	Brookfield Viscosity, cp	
	10 rpm	- 14,000 $\pm$ 4,000
	100 rpm	- 6,500 $\pm$ 1,500
	Settling (spatula probe)	
	6 weeks	- None
35	8 weeks	- Slight amount of soft sediment

1 The ingredients are added in the order listed.
A high-speed disperser, namely a High-Vispersator is
used to stir, mix and disperse the materials into a
stable homogeneous slurry. Ingredients 1, 2 and 3 are
5 stirred together for one minute at low speed (1,000 rpm).
The coal is added to this solution at medium speed (2,000
rpm) for a sufficient time to wet the coal particles and ..
disperse the coal in ingredients 1, 2 and 3. Then the
speed of the disperser is increased to high speed (4,000
10 rpm) for 10 minutes to further disperse the coal particles.
Ingredients 5 and 6 are then added with the disperser at
high speed. After two minutes ingredients 7 and 8 are added
and the batch is considered complete after an additional
two minutes of mixing at high speed. All mixing is carried
15 out at atmospheric temperatures and pressures.

20

25

30

35

EXAMPLE 31

The following formulation is used to prepare an aqueous coal slurry in accordance with the improvement of the present invention.

	<u>Ingredient</u>	<u>Material</u>	<u>Parts by Weight</u>
	1	Water	29.236
10	2	Tetronic 1508	.34
	3	Colloid 691	.03
	4	Cleancoal	70.00
	5	Kelzan	.014
	6	Guar THIX	.10
15	7	37% Formaldehyde	.14
	8	28% Ammonia	.14
			<u>100.00</u>

1. Industrial Water
2. Surfactant - BASF Wyandotte Corp.
- 20 3. Anti-foam Agent - Colloids, Inc.
4. Pocahontas Clean Coal
5. Xanthan Gum - Kelco Division, Merck & Co., Inc.
6. Guar Gum - Hercules, Inc.
- 25 7. Formaldehyde Solution- Borden Chemicals
8. Ammonium Hydroxide - Fischer Scientific

Slurry Properties

	Solids	- 70.0 $\pm$ 1.0
30	pH	- 8.0 $\pm$ 1.0
	Brookfield Viscosity, cp	
	10 rpm	- 14,000 $\pm$ 4,000
	100 rpm	- 6,500 $\pm$ 1,500
	Settling (spatula probe)	
	6 weeks	- None
35	8 weeks	- Slight amount of soft sediment

1 The ingredients are added in the order listed.
A high-speed disperser, namely a High-Vispersator is
used to stir, mix and disperse the materials into a
stable homogeneous slurry. Ingredients 1, 2 and 3 are
5 stirred together for one minute at low speed (1,000 rpm).
The coal is added to this solution at medium speed (2,000
rpm) for a sufficient time to wet the coal particles and
disperse the coal in ingredients 1, 2 and 3. Then the
speed of the disperser is increased to high speed (4,000
10 rpm) for 10 minutes to further disperse the coal particles.
Ingredients 5 and 6 are then added with the disperser at
high speed. After two minutes ingredients 7 and 8 are added
and the batch is considered complete after an additional
two minutes of mixing at high speed. All mixing is carried
15 out at atmospheric temperatures and pressures.

20

25

30

35

1

EXAMPLE 32

The following formulation is used to prepare
 an aqueous coal slurry in accordance with the improvement
 5 of the present invention.

	<u>Ingredient</u>	<u>Material</u>	<u>Parts by Weight</u>
	1	Water	29.236
10	2	Pluronic-F-98	.34
	3	Colloid 691	.03
	4	Cleancoal	70.00
	5	Kelzan	.014
	6	Guar THIX	.10
15	7	37% Formaldehyde	.14
	8	28% Ammonia	.14
			<u>100.00</u>

1. Industrial Water
2. Surfactant - BASF Wyandotte Corp.
- 20 3. Anti-foam Agent - Colloids, Inc.
4. Pocahontas Clean Coal
5. Xanthan Gum - Kelco Division, Merck & Co., Inc.
6. Guar Gum - Hercules, Inc.
- 25 7. Formaldehyde Solution- Borden Chemicals
8. Ammonium Hydroxide - Fischer Scientific

Slurry Properties

	Solids	- 70.0 $\pm$ 1.0
30	pH	- 8.0 $\pm$ 1.0
	Brookfield Viscosity, cp	
	10 rpm	- 14,000 $\pm$ 4,000
	100 rpm	- 6,500 $\pm$ 1,500
	Settling (spatula probe)	
	6 weeks	- None
35	8 weeks	- Slight amount of soft sediment

1 The ingredients are added in the order listed.
A high-speed disperser, namely a High-Vispersator is
used to stir, mix and disperse the materials into a
stable homogeneous slurry. Ingredients 1, 2 and 3 are
5 stirred together for one minute at low speed (1,000 rpm).
The coal is added to this solution at medium speed (2,000
rpm) for a sufficient time to wet the coal particles and
disperse the coal in ingredients 1, 2 and 3. Then the
speed of the disperser is increased to high speed (4,000
10 rpm) for 10 minutes to further disperse the coal particles.
Ingredients 5 and 6 are then added with the disperser at
high speed. After two minutes ingredients 7 and 8 are added
and the batch is considered complete after an additional
two minutes of mixing at high speed. All mixing is carried
15 out at atmospheric temperatures and pressures.

20

25

30

35

1

EXAMPLE 33

5

The following formulation is used to prepare an aqueous coal slurry in accordance with the improvement of the present invention.

	<u>Ingredient</u>	<u>Material</u>	<u>Parts by Weight</u>
	1	Water	29.236
10	2	Pluronic-F-108	.34
	3	Colloid 691	.03
	4	Cleancoal	70.00
	5	Kelzan	.014
	6	Guar THIX	.10
15	7	37% Formaldehyde	.14
	8	28% Ammonia	.14
			<u>100.00</u>

1. Industrial Water
2. Surfactant - BASF Wyandotte Corp.
- 20 3. Anti-foam Agent - Colloids, Inc.
4. Pocahontas Clean Coal
5. Xanthan Gum - Kelco Division, Merck & Co., Inc.
6. Guar Gum - Hercules, Inc.
- 25 7. Formaldehyde Solution- Borden Chemicals
8. Ammonium Hydroxide - Fischer Scientific

Slurry Properties

	Solids	- 70.0 $\pm$ 1.0
30	pH	- 8.0 $\pm$ 1.0
	Brookfield Viscosity, cp	
	10 rpm	- 14,000 $\pm$ 4,000
	100 rpm	- 6,500 $\pm$ 1,500
	Settling (spatula probe)	
	6 weeks	- None
35	8 weeks	- Slight amount of soft sediment

1 The ingredients are added in the order listed.
A high-speed disperser, namely a High-Vispersator is
used to stir, mix and disperse the materials into a
stable homogeneous slurry. Ingredients 1, 2 and 3 are
5 stirred together for one minute at low speed (1,000 rpm).
The coal is added to this solution at medium speed (2,000
rpm) for a sufficient time to wet the coal particles and
disperse the coal in ingredients 1, 2 and 3. Then the
speed of the disperser is increased to high speed (4,000
10 rpm) for 10 minutes to further disperse the coal particles.
Ingredients 5 and 6 are then added with the disperser at
high speed. After two minutes ingredients 7 and 8 are added
and the batch is considered complete after an additional
two minutes of mixing at high speed. All mixing is carried
15 out at atmospheric temperatures and pressures.

20

25

30

35

1

EXAMPLE 34

The following formulation is used to prepare
an aqueous coal slurry in accordance with the improvement
5 of the present invention.

	<u>Ingredient</u>	<u>Material</u>	<u>Parts by Weight</u>
	1	Water	29.236
10	2	Pluronic-F-127	.34
	3	Colloid 691	.03
	4	Cleancoal	70.00
	5	Kelzan	.014
	6	Guar THIX	.10
15	7	37% Formaldehyde	.14
	8	28% Ammonia	.14
			<u>100.00</u>

1. Industrial Water
2. Surfactant - BASF Wyandotte Corp.
- 20 3. Anti-foam Agent - Colloids, Inc.
4. Pocahontas Clean Coal
5. Xanthan Gum - Kelco Division, Merck & Co., Inc.
6. Guar Gum - Hercules, Inc.
- 25 7. Formaldehyde Solution- Borden Chemicals
8. Ammonium Hydroxide - Fischer Scientific

Slurry Properties

	Solids	- 70.0 $\pm$ 1.0
30	pH	- 8.0 $\pm$ 1.0
	Brookfield Viscosity, cp	
	10 rpm	- 14,000 $\pm$ 4,000
	100 rpm	- 6,500 $\pm$ 1,500
	Settling (spatula probe)	
	6 weeks	- None
35	8 weeks	- Slight amount of soft sediment

1 The ingredients are added in the order listed.
A high-speed disperser, namely a High-Vispersator is
used to stir, mix and disperse the materials into a
stable homogeneous slurry. Ingredients 1, 2 and 3 are
5 stirred together for one minute at low speed (1,000 rpm).
The coal is added to this solution at medium speed (2,000
rpm) for a sufficient time to wet the coal particles and
disperse the coal in ingredients 1, 2 and 3. Then the
speed of the disperser is increased to high speed (4,000
10 rpm) for 10 minutes to further disperse the coal particles.
Ingredients 5 and 6 are then added with the disperser at
high speed. After two minutes ingredients 7 and 8 are added
and the batch is considered complete after an additional
two minutes of mixing at high speed. All mixing is carried
15 out at atmospheric temperatures and pressures.

20

25

30

35

1

EXAMPLE 35

The following formulation is used to prepare
 an aqueous coal slurry in accordance with the improvement
 of the present invention.

	<u>Ingredient</u>	<u>Material</u>	<u>Parts by Weight</u>
	1	Water	29.176
10	2	Igepal CO-990	0.40
	3	Colloid 691	.03
	4	Cleancoal	70.00
	5	Kelzan	.014
	6	Guar THIX	.10
15	7	37% Formaldehyde	.14
	8	28% Ammonia	.14
			<u>100.00</u>
	1.	Industrial Water	
	2.	Surfactant - GAF Corp.	
20	3.	Anti-foam Agent - Colloids, Inc.	
	4.	Pocahontas Clean Coal	
	5.	Xanthan Gum - Kelco Division, Merck & Co., Inc.	
	6.	Guar Gum - Hercules, Inc.	
25	7.	Formaldehyde Solution- Borden Chemicals	
	8.	Ammonium Hydroxide - Fischer Scientific	

Slurry Properties

	Solids	- 70.0 $\pm$ 1.0
30	pH	- 8.0 $\pm$ 1.0
	Brookfield Viscosity, cp	
	10 rpm	- 14,000 $\pm$ 4,000
	100 rpm	- 6,500 $\pm$ 1,500
	Settling (spatula probe)	
	6 weeks	- None
35	8 weeks	- Slight amount of soft sediment

1 The ingredients are added in the order listed.
A high-speed disperser, namely a High-Vispersator is
used to stir, mix and disperse the materials into a
stable homogeneous slurry. Ingredients 1, 2 and 3 are
5 stirred together for one minute at low speed (1,000 rpm).
The coal is added to this solution at medium speed (2,000
rpm) for a sufficient time to wet the coal particles and
disperse the coal in ingredients 1, 2 and 3. Then the
speed of the disperser is increased to high speed (4,000
10 rpm) for 10 minutes to further disperse the coal particles.
Ingredients 5 and 6 are then added with the disperser at
high speed. After two minutes ingredients 7 and 8 are added
and the batch is considered complete after an additional
two minutes of mixing at high speed. All mixing is carried
15 out at atmospheric temperatures and pressures.

20

25

30

35

1

EXAMPLE 36

The following formulation is used to prepare
 an aqueous coal slurry in accordance with the improvement
 5 of the present invention.

	<u>Ingredient</u>	<u>Material</u>	<u>Parts by Weight</u>
	1	Water	29.176
10	2	T-Det-N-100	.40
	3	Colloid 691	.03
	4	Cleancoal	70.00
	5	Kelzan	.014
	6	Guar THIX	.10
15	7	37% Formaldehyde	.14
	8	28% Ammonia	.14
			<u>100.00</u>

1. Industrial Water
2. Surfactant - Thompson Haywood Chemical Co.
- 20 3. Anti-foam Agent - Colloids, Inc.
4. Pocahontas Clean Coal
5. Xanthan Gum - Kelco Division, Merck & Co., Inc.
6. Guar Gum - Hercules, Inc.
- 25 7. Formaldehyde Solution- Borden Chemicals
8. Ammonium Hydroxide - Fischer Scientific

Slurry Properties

	Solids	- 70.0 ± 1.0
30	pH	- 8.0 ± 1.0
	Brookfield Viscosity, cp	
	10 rpm	- 14,000 ± 4,000
	100 rpm	- 6,500 ± 1,500
	Settling (spatula probe)	
	6 weeks	- None
35	8 weeks	- Slight amount of soft sediment

1 The ingredients are added in the order listed.
A high-speed disperser, namely a High-Vispersator is
used to stir, mix and disperse the materials into a
stable homogeneous slurry. Ingredients 1, 2 and 3 are
5 stirred together for one minute at low speed (1,000 rpm).
The coal is added to this solution at medium speed (2,000
rpm) for a sufficient time to wet the coal particles and
disperse the coal in ingredients 1, 2 and 3. Then the
speed of the disperser is increased to high speed (4,000
10 rpm) for 10 minutes to further disperse the coal particles.
Ingredients 5 and 6 are then added with the disperser at
high speed. After two minutes ingredients 7 and 8 are added
and the batch is considered complete after an additional
two minutes of mixing at high speed. All mixing is carried
15 out at atmospheric temperatures and pressures.

20

25

30

35

1

EXAMPLE 37

The following formulation is used to prepare
 an aqueous coal slurry in accordance with the improvement
 5 of the present invention.

	<u>Ingredient</u>	<u>Material</u>	<u>Parts by Weight</u>
	1	Water	29.176
10	2	NP-100	.40
	3	Colloid 691	.03
	4	Cleancoal	70.00
	5	Kelzan	.014
	6	Guar THIX	.10
15	7	37% Formaldehyde	.14
	8	28% Ammonia	.14
			<u>100.00</u>

1. Industrial Water
2. Surfactant - Whitestone Chemical
- 20 3. Anti-foam Agent - Colloids, Inc.
4. Pocahontas Clean Coal
5. Xanthan Gum - Kelco Division, Merck & Co., Inc.
6. Guar Gum - Hercules, Inc.
- 25 7. Formaldehyde Solution- Borden Chemicals
8. Ammonium Hydroxide - Fischer Scientific

Slurry Properties

	Solids	- 70.0 $\pm$ 1.0
30	pH	- 8.0 $\pm$ 1.0
	Brookfield Viscosity, cp	
	10 rpm	- 14,000 $\pm$ 4,000
	100 rpm	- 6,500 $\pm$ 1,500
	Settling (spatula probe)	
	6 weeks	- None
35	8 weeks	- Slight amount of soft sediment

1 The ingredients are added in the order listed.
A high-speed disperser, namely a High-Vispersator is
used to stir, mix and disperse the materials into a
stable homogeneous slurry. Ingredients 1, 2 and 3 are
5 stirred together for one minute at low speed (1,000 rpm).
The coal is added to this solution at medium speed (2,000
rpm) for a sufficient time to wet the coal particles and
disperse the coal in ingredients 1, 2 and 3. Then the
speed of the disperser is increased to high speed (4,000
10 rpm) for 10 minutes to further disperse the coal particles.
Ingredients 5 and 6 are then added with the disperser at
high speed. After two minutes ingredients 7 and 8 are added
and the batch is considered complete after an additional
two minutes of mixing at high speed. All mixing is carried
15 out at atmospheric temperatures and pressures.

20

25

30

35

1

EXAMPLE 38

The following formulation is used to prepare
an aqueous coal slurry in accordance with the improvement
5 of the present invention.

	<u>Ingredient</u>	<u>Material</u>	<u>Parts by Weight</u>
	1	Water	29.176
10	2	Tetronic 908	.40
	3	Colloid 691	.03
	4	Coal(non-beneficiated)	70.00
	5	Kelzan	.014
	6	Guar THIX	.10
15	7	37% Formaldehyde	.14
	8	28% Ammonia	.14
			<u>100.00</u>

- | | | | |
|----|----|------------------------|-------------------------------------|
| | 1. | Industrial Water | |
| | 2. | Surfactant | - BASF Wyandotte Corp. |
| 20 | 3. | Anti-foam Agent | - Colloids, Inc. |
| | 4. | Pocahontas Coal | |
| | 5. | Xanthan Gum | - Kelco Division, Merck & Co., Inc. |
| | 6. | Guar Gum | - Hercules, Inc. |
| 25 | 7. | Formaldehyde Solution- | Borden Chemicals |
| | 8. | Ammonium Hydroxide | - Fischer Scientific |

Slurry Properties

	Solids	- 70.0 ± 1.0
30	pH	- 8.0 ± 1.0
	Brookfield Viscosity, cp	
	10 rpm	- 14,000 ± 4,000
	100 rpm	- 6,500 ± 1,500
	Settling (spatula probe)	
	6 weeks	- None
35	8 weeks	- Slight amount of soft sediment

1 The ingredients are added in the order listed.
A high-speed disperser, namely a High-Vispersator is
used to stir, mix and disperse the materials into a
stable homogeneous slurry. Ingredients 1, 2 and 3 are
5 stirred together for one minute at low speed (1,000 rpm).
The coal is added to this solution at medium speed (2,000
rpm) for a sufficient time to wet the coal particles and
disperse the coal in ingredients 1, 2 and 3. Then the
speed of the disperser is increased to high speed (4,000
10 rpm) for 10 minutes to further disperse the coal particles.
Ingredients 5 and 6 are then added with the disperser at
high speed. After two minutes ingredients 7 and 8 are added
and the batch is considered complete after an additional
two minutes of mixing at high speed. All mixing is carried
15 out at atmospheric temperatures and pressures.

20

25

30

35

1 From the foregoing it will be seen that coal-
aqueous mixtures are readily provided having significantly
high solid concentrations. The mixtures can be provided
in a clean form ready for burning in utility burners,
5 home burners and the like with little if any need for
additional cleaning to remove ash and sulfur.

10

15

20

25

30

35

Claims

1. A method for forming a coal-aqueous mixture, said method comprising the steps of:

- 5 (i) admixing a polyalkyleneoxide nonionic surfactant having a hydrophobic portion and a hydrophilic portion, said hydrophilic portion being comprised of at least about 100 units of ethylene oxide, with water, under low speed agitation conditions;
- 10 (ii) admixing particulate coal with the admixture resulting from step (i) under medium speed agitation conditions; and
- (iii) agitating the resultant coal containing mixture of step (ii) under high speed agitation.

15 2. The method of Claim 1 wherein said medium speed agitation in step (ii) is carried out for a time sufficient to wet the coal particles and said high speed agitation is carried out for a time sufficient to disperse the coal.

20 3. The method of Claim 1 or 2 wherein an anti-foam agent is added to the mixture during step (i).

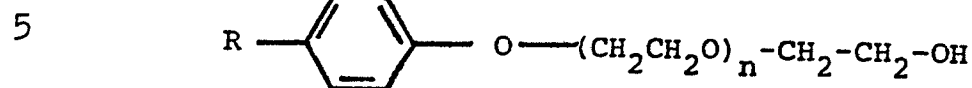
 4. The method of Claim 3 wherein said anti-foam agent is comprised of a mixture of mineral oil, amide and polyethylene glycol oleate ester.

25 5. The method of any of Claims 1 to 4 wherein the particulate coal is added in an amount from about 45 to 80 percent; the water is added in an amount from about 19.9 to 52 percent; and the polyalkyleneoxide nonionic surfactant is added in an amount from about 0.1 to 3.0 percent based on the total weight of the mixture.

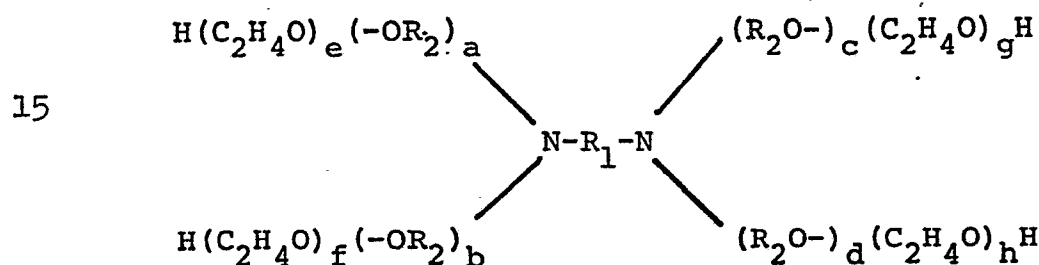
30

0106130

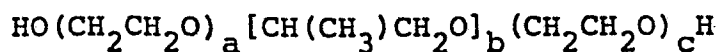
- 1 6. The method of any of Claims 1 to 5 wherein
the polyalkyleneoxide nonionic surfactant comprises a
composition of the formula



- wherein R is substituted or unsubstituted alkyl of from
1 to 18 carbon atoms; substituted or unsubstituted aryl
10 or an amino group, and n is an integer of at least about
100 or a composition of the formula



- 20 wherein R_1 is an alkylene radical having 2 to 5 carbon
atoms; R_2 is an alkylene radical having 3 to 5 carbon
atoms; a, b, c, d, e, f, g, and h are whole integers and
e, f, g, and h total at least about 100 or a composition
25 of the formula



- 30 wherein a, b and c are whole integers and a and c total
at least about 100.

1 7. The method of any of Claims 1 to 6 wherein
said polyalkyleneoxide nonionic surfactant has a molecular
weight of at least about 4000.

 8. The method of Claim 6 wherein R_1 is an alkylene
5 radical having 2 carbon atoms and R_2 is an alkylene radical
having 3 carbon atoms and R is nonyl.

 9. The method of any of Claims 1 to 8 including
the further steps of:

 (iv) admixing a thickening agent under high
10 speed agitation conditions, to the admixture
resulting from step (iii).

 10. The method of Claim 9 wherein said thickening
agent is xanthan gum, guar gum, cellulose gum, glue or
alkali soluble acrylic polymer.

15 11. The method of Claims 9 or 10 including the
further step of:

 (v) admixing an anti-bacterial agent, a
viscosity stabilizer or mixtures thereof
to the mixture resulting from step (iv),
20 under high speed agitation.

 12. The method of Claim 11 wherein said vis-
cosity stabilizer is ammonia.

 13. The method of any of Claims 1 to 12 wherein
said particulate coal is characterized by having a sulfur
25 content of from 0.5 to 2.0 percent by weight, an an ash
content of from about 0.5 to 6.0 percent, based on the
weight of dry coal and is about 200 mesh in tyler standard
screen size.

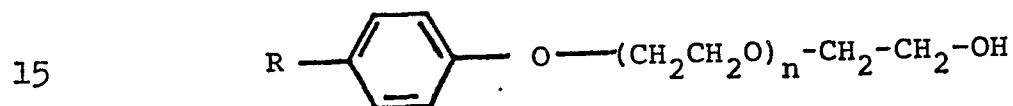
 14. A stabilized, high solids content coal-
30 aqueous mixture comprising particulate coal as a dispersed
solid material; water as a carrier medium; a polyalkylene-
oxide nonionic surfactant having a hydrophobic portion and

0106130

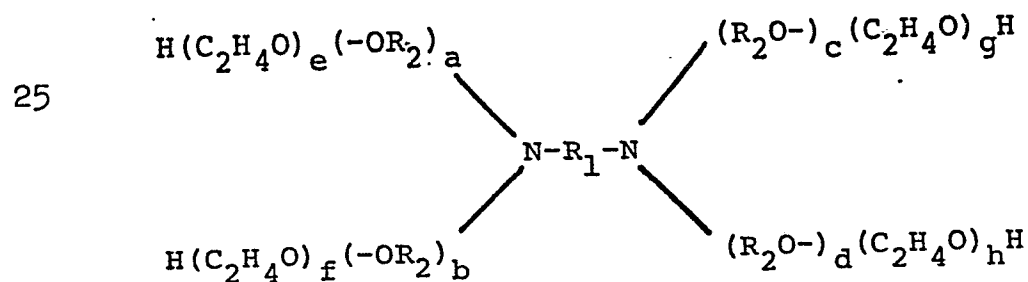
1 a hydrophilic portion, said hydrophilic portion comprising
at least about 100 units of ethylene oxide, said polyalkyl-
eneoxide nonionic surfactant being present in said mixture
in an amount to disperse said particulate coal in said water
5 carrier; and a viscosity stabilizer.

15. The stabilized, high solids content coal-
aqueous mixture of Claim 14 further comprising a thickening
agent and/or an anti-foam agent.

16. The stabilized, high solids content coal-
10 aqueous mixture of Claim 14 or 15 wherein said polyalkyl-
eneoxide nonionic surfactant comprises a composition
of the formula



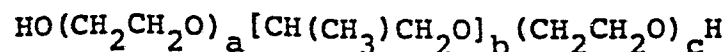
wherein R is substituted or unsubstituted alkyl of from
1 to 18 carbon atoms; substituted or unsubstituted aryl
20 or an amino group, and n is an integer of at least about
100 or a composition of the formula



30

35

- 1 wherein R_1 is an alkylene radical having 2 to 5 carbon atoms; R_2 is an alkylene radical having 3 to 5 carbon atoms; a, b, c, d, e, f, g and h are whole integers and e, f, g and h total at least about 100 or a composition
5 of the formula



wherein a, b and c are whole integers and a and c total at least about 100.

- 10 17. The stabilized, high solids content coal-aqueous mixture of Claim 16 wherein R_1 is an alkylene radical having 2 carbon atoms and R_2 is an alkylene radical having 3 carbon atoms and R is nonyl.

- 15 18. The stabilized, high solids content coal-aqueous mixture of any of Claims 14 to 17 the polyalkylene-oxide nonionic surfactant has a molecular weight of at least about 4000.

19. The stabilized, high solids content coal-aqueous mixture of any of Claims 14 to 18 wherein the
20 viscosity stabilizer comprises ammonia.

25

30

35