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PREVENTION OF FREEZING TOGETHER OF COAL PARTICLES AND COMPOSITIONS THEREOF

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8 Claims. (Cl. 44—6)

This invention pertains to surface treatment of coal particles to prevent water-wetted surfaces from freezing together at water-freezing temperatures.

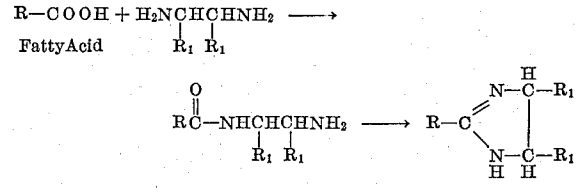
Coal particles, especially fine particles or small lumps, are known to freeze together when the surfaces are wet and are in a water-freezing environment. This freezing is objectionable because it makes difficult the unloading or dumping of railway coal cars. It also makes difficult the movement of coal out of outdoor coal storage piles in a condition for fuel or other use.

The invention provides improvements in the aforesaid surface treatment of coal particles by using as the surface treating chemical a composition comprising (1) liquid hydrocorban, which per se preferably has the effect, when applied on the surface of coal particles of the character hereinafter described more particularly, of preventing water-wetted coal particles from freezing together at mildly sub-freezing temperatures, e.g., about 15–32° F., and (2) a surface-active compound or composition in the class of substituted imidazolines. The surface-active compound has the effect of improving the antifreeze properties for coal particles of the aforesaid liquid hydrocarbon composition.

The liquid hydrocarbon composition may be one of or a composite of a wide variety of liquid aliphatic, aromatic and/or naphthenic hydrocarbons which have a freezing or solidification point at least as low as about —20° F. The aliphatic liquid hydrocarbons, straight or branched chained and saturated or olefinically-unsaturated, are preferred, especially those with eight or more carbons and the aforesaid freezing or solidification point. Composites of liquid hydrocarbons such as kerosene, diesel fuel oil, and like liquid hydrocarbon compositions may be used.

The substituted imidazolines contemplated herein embrace 2-substituted imidazolines, 2,4- or 2,5-substituted imidazolines, 1,2-substituted imidazolines, and 1,2,4- or 1,2,5-substituted imidazolines wherein the substituent in the 2-position is an aliphatic, aryl, aralkyl, or cycloalkyl group of at least 6 and not more than 35 carbons, and is preferably a hydrocarbon group consisting solely of C and H.

While the derivation of the imidazoline compounds per se does not form a part of the instant invention, a general method for preparing compounds contemplated by the instant invention is herein included for the sake of illustrating the type of imdiazolines or imidazolinium quaternary compounds which may be used in the practice of the instant invention. Imidazolines, often referred to as glyoxalidines, are heterocyclic compounds and may be derived by the dehydration of certain amides. They may be obtained by reacting polyamines and higher carboxylic acids (acids having at least 7 carbon atoms), under conditions so as to first form the amide and then dehydrating the amide to form the imidazoline. By way of illustration, the condensation of a fatty acid and alkylene polyamine proceeds according to the following scheme:



wherein R represents an alkyl or alkenyl group of monocarboxylic fatty acid having from 7–36 carbons and R_1 represents hydrogen or a lower alkyl group; see Wilkes, U.S. Patent No. 2,214,152 and Waldman et al., U.S. Patents Nos. 2,155,877 and 2,155,878.

The expression "higher molecular weight carboxy acids" is employed herein to refer to certain organic acids, particularly monocarboxy acids, having at least 7 and generally less than 36 carbons. Among the most common examples are naturally occurring acids such as fatty acids derived from hydrolysis of triglycerides, resin acids, such as abietic acid, naturally occurring petroleum acids as naphthenic acids and carboxy acids produced by the oxidation of petroleum products. While the acids falling within the term "higher molecular weight carboxy acids" differ in physical characteristics, source of origin, and/or structure, they can all be classified in this grouping for the purpose of the instant invention.

Among sources of such acids may be mentioned straight chain and branched chain, saturated and unsaturated, carboxylic, aliphatic, alicyclic, fatty, aromatic, hydroaromatic, and aralkyl acids including caprylic acid, heptylic acid, capric acid, pimelic acid, sebacic acids, erucic acid, saturated and unsaturated higher molecular weight aliphatic acids, such as the higher fatty acids containing at least eight carbon atoms and including, in addition to those mentioned melissic acid, triricinoleic acid, stearic acid, oleic acid, ricinoleic acid, diricinoleic acid, polyricinoleic acid, ricinostearolic acid, ricinoleyl lactic acid, acetylricinoleic acid, chloracetyl-ricinoleic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, undecylenic acid, palmitic acid, mixtures of any two or more of the above mentioned acids or other acids, mixed higher fatty acids derived from animal or vegetable sources, for example, lard, cocoanut oil, rapeseed oil, sesame oil, palm kernel oil, palm oil, olive oil, corn oil, cottonseed oil, sardine oil, tallow soybean oil, peanut oil, castor oil, seal oils, whale oil, shark oil and other fish oils, teaseed oil, partially or completely hydrogenated animal and vegetable oils, such as those mentioned; hydroxy and alpha-hydroxy higher carboxylic, aliphatic and fatty acids, such as hydroxystearic acid, dihydroxypalmitic acid, dihydroxystearic acid, dihydroxybehenic acid, alphahydroxy capric acid, alphahydroxy stearic acid, alphahydroxy palmitic acid, alphahydroxy lauric acid, alphahydroxy myristic acid, alphahydroxy cocoanut oil mixed fatty acids, alphahydroxy margaric acid, alphahydroxy arachidic acid, and the like; fatty and similar acids derived from various waxes, such as beeswax, spermaceti, montan wax, Japan wax, concerin, and carnauba wax. Such acids include carnaubic acid, carotic acid, lacceric acid, montanic acid, psyllastearic acid, etc. As suggested, one may also employ higher molecular weight carboxylic acids derived, by oxidation and other methods, from paraffin wax, petroleum and similar hydrocarbons; resinic and hydroaromatic acids,

such as hexahydrobenzoic acid, hydrogenated naphthoic, hydrogenated carboxydiphenyl, naphthenic, and abietic acid; aralkyl and aromatic acids, such as benzoic acid, Twitchell fatty acids, naphthoic acid, carboxydiphenyl, pyridine carboxylic acid, hydroxybenzoic acid, and the like.

Other suitable acids include phenylstearic acid, benzoylnonylic acid, campholic acid, fencholic acid, cetyloxybutyric acid, cetyloxyacetic acid, chlorstearic acid, etc.

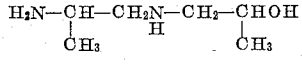
Another source of suitable acids are those commonly referred to as lac acids, such, for example, as the acids derived from shellac. Such acids include various polyhydroxy acids, for example, aleuritic acid, shelloic acid, and kerrolic acid.

As is well known, one may use substituted acids in which some other non-functional constituent enters the structure of the fatty acid. For instance, one may use aryl-, hydroxyalkoxy-, chlor-, keto-, and amino derivatives. Generally speaking, however, it is always preferable to use the unsubstituted acid, particularly free from substituents which contain either oxygen or nitrogen atoms. Generally speaking, the introduction of hydrocarbon radicals, regardless of source, has little effect, except in altering the hydrophile-hydrophobe balance.

One may also employ the blown or oxidized acids, such as blown ricinoleic acid, blown oleic, etc., or estolides derived from blown oils, such as blown castor oil, blown soybean oil, etc.

Needless to say, the acids themselves need not be employed; but one may readily employ any functional equivalent, such as the anhydride, the acyl chloride, or the like. In some instances, the esters, especially in presence of a trace or a significant amount of water, act as the acid itself, in that the acid is liberated. Unless specific reference is made to a particular isomer, one may employ any isomer or mixture of various isomers, if the acid or acids are so available.

The alkylene polyamines which may be reacted with the foregoing acids to produce the imidazolines or quaternary imidazolinium compounds herein contemplated to produce the compositions of the instant invention include those amines which have an amino group on one carbon and an amino or imino group on a contiguous carbon, that is, amines of the 1,2 series. Examples of such amines are ethylenediamine, diethylene triamine, triethylene tetramine, tetraethylenepentamine, hydroxyethyl ethylenediamine, hydroxyethyl diethylenetriamine, hydroxyethyl triethylene tetramine, beta-hydroxypropyl ethylenediamine and N-beta-hydroxypropyl propylene diamine -1,2, believed to have the formula



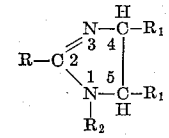
and isomers thereof.

Depending upon the amine employed, the resulting imidazoline will be a 2-substituted; a 1,2-disubstituted; a 2,4- or 2,5-disubstituted; or a 1,2,4- or 1,2,5-trisubstituted imidazoline wherein the substituent in the 2-position is the residue of the higher molecular weight carboxy acid, and the substituent in the 1-position may be hydrogen or the terminal portion of the ethylene polyamine which does not cyclize with the carboxy acid and the substituents in the 4- or 5-position, if any, are lower alkyl groups, usually methyl, on the carbons in the polyamines between the nitrogens which form the heterocyclic ring.

Thus, the imidazolines, or the corresponding quaternary imidazolinium compounds, useful in accordance with the instant invention, may vary widely in structure. The sole limiting features are that the imidazoline nucleus compounds have on at least one carbon, preferably on the carbon in the 2-position, in the heterocyclic five-membered ring an aryl, aralkyl, cycloalkyl, or aliphatic group having 6–35 carbons and that the imidazoline have in the 1-position at least one of an imino (—NH), and amino ($—NH_2$), or a hydroxy (—OH) group. The imino group

may be present in the imidazoline heterocyclic ring (an imidazoline which is unsubstituted in the 1-position of the ring) or the imino, amino, and/or hydroxy groups may exist in an organic substituent substituted in the 1-position of the ring.

By way of example, an imidazoline of the general formula



wherein R is a monovalent organic radical selected from the class consisting of aryl, aralkyl, aralkenyl, cycloalkyl, and aliphatic groups having 6–35 carbons, preferably a monovalent hydrocarbon group consisting solely of C and H, and R_1 is selected from the class consisting of hydrogen and lower alkyl groups, may have such substituents in the 1-position, shown as R_2, as —H,

$—CH_2CH_2NH_2$,$—CH_2CH_2OH$

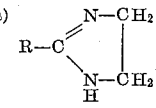
$—(CH_2CH_2NH)_xCH_2CH_2NH_2$ wherein x is a small whole number,$—CH_2CH(OH)CH_2OH$,

$—CH_2—CH_2—O—CH_2—CH_2OH$, $—CH(CH_3)CH_2NH_2$

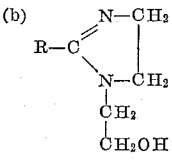
$—CH_2CH(OH)CH_3$, and the like.

Examples of imidazoline compounds which may be used are illustrated below.

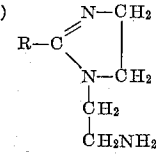
(a)



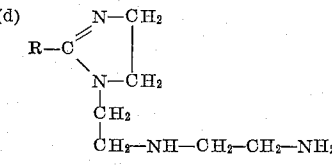
(b)



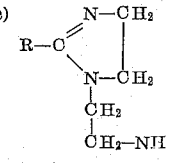
(c)



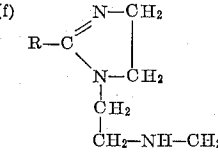
(d)



(e)



(f)



A class of 1,2-substituted imidazolines which as proven very effective in the invention includes the 1,2-substituted imidazolines which may be described as the reaction product of a tall oil fatty acid mixture containing at least 70% by weight of fatty acids having a molecular weight of the range of 235–280 and a polyalkylene polyamine mixture consisting essentially of 75–90% diethylenetriamine, 5–15% triethylenetetramine and 5–10% tetraethylene pentamine. The said reaction product is prepared by heating the tall oil fatty acids and the polyalkylene polyamine mixture at 160–190° C. for 60–90 minutes, then at 190–225° C. for 210 to 360 minutes and finally at 225–250° C. for 210–270 minutes. The resulting product is essentially a 1,2-substituted imidazoline, the substituent in the 2-position being a hydrocarbon radical consisting of the hydrocarbon residue of the tall oil fatty acids and the substituent in the 1-position being the residue of the polyalkylene polyamine which has not been reacted to form the heterocyclic imidazoline ring. The final reaction product must analyze 85–99% glyoxalidine ring closure and 88–99% total titratables, hereinafter defined.

The acid components of tall oil fatty acid mixtures consist essentially of 14–18 carbon acids. The unsaturated acids, oleic and linoleic acids, are the predominant acid components. Myristic acid, palmitic acid, heptade-

canoic acid, stearic acid, and linolenic acid are usually present as the minor constituents. The rosin acids, if any, are present only in small amounts. The tall oil fatty acids may contain neutrals up to 30% by weight of the total acid mixture.

The polyalkylene polyamines employed in the instant invention are commercial mixtures of polyalkylene polyamines and may contain minor amounts of ethylene diamine, the latter preferably not exceeding 5%. The polyalkylene polyamines are preferably those having 3–5 amino groups (diethylenetriamine, triethylenetetramine and tetraethylenepentamine) in which the diethylenetriamine content is at least 75% of the total. Hence, the predominating constituent of the polyalkylene polyamine mixture is diethylenetriamine.

A specific embodiment of such 1,2-substituted imidazoline is illustrated below.

Example I

About 0.5 gram mol of Pamak Light Ends tall oil fatty acids, Hercules Powder Company, having the following typical analysis:

Acid number		159.2
Rosin acids	percent	0.6
Fatty acids	do	79.8
Saponification number		162.2
Saponifiables (AOCS)	percent	21.0
Neutrals	do	21.5
Specific gravity, 25/25		0.9140
Iodine number		150.0
Acid analysis:		
Stearic acid	percent	1.6
Oleic acid	do	40.1
Myristic acid	do	0.4
Palmitic acid	do	13.8
Heptadecanoic acid	do	2.7
Linolenic acid	do	0.3
Linoleic acid	do	31.2

and 1.0 gram mol of a polyalkylene polyamine mixture consisting of 1.0% ethylene diamine, 80% diethylenetriamine, 12% triethylenetetramine, and 7% tetraethylenepentamine were mixed and heated at steadily increasing temperatures for a total of 9¼ hours. The aqueous distillate was removed from the reaction vessel and collected, the total amount being 21.5 grams. The observations made during the reaction are as follows:

TABLE I

Minutes	Temp., ° C.	Aqueous Distillate, cc.
0	159	0.0
10	167	0.8
15	175	5.5
35	183	8.5
55	188	10.0
70	191	11.0
0	191	0.0
20	201	1.8
40	207	3.5
80	212	4.5
130	215	5.0
250	228	8.0
0	228	8.0
50	230	8.0
80	234	9.0
160	237	10.5
205	247	0
235	247	0

The product obtained had a 99% ring closure and a neutralization equivalent of 230 (theoretical 211).

The analysis for ring closure, expressed as percent glyoxalidine, is conducted by weighing two samples, by difference, to the nearest milligram into 250 milliliters glass stoppered Erlenmeyer flasks. The sample size should be between 1.8 and 2.0 grams. Fifty milliliters of anhydrous isopropanol (99%+) is added to each flask containing the weighed sample and the contents and are swirled to dissolve the sample. The flasks are then placed in an ice bath and cooled to 0°±5° C. To the cooled solution is added 25 milliliters of chilled, diluted phenyl isothiocyanate in anhydrous isopropanol (one part by volume phenyl isothiocyanate to 19 parts by volume anhydrous isopropanol). The samples are allowed to stand at 0°±5° C. for 30 minutes, after which to each flask is added 10 drops of thymol blue indicator. The samples are titrated immediately with standard 0.1 N HCl in anhydrous isopropanol to the first permanent red end-point. The exact end-point, which may be obscured by the color of the sample, may be obtained by comparison with a suitable solution of the original material.

A similar titration is run on a series of blanks and the average milliliters of the standard HCl to bring the samples to the first permanent red end-point is determined. The total glyoxalidine, expressed as percent by weight, of the product is calculated by subtracting the milliliters of HCl required for blank from the milliliters of HCl required for the sample and multiplying the difference by the normality of the HCl times the quotient of the molecular weight of the imidazoline divided by 1,000 times 100, the total product being divided by the weight of the sample in grams.

The total titratables are determined in a similar manner to the foregoing ring closure analysis, with the exception that the phenyl isothiocyanate is not added to the samples. The percent titratables is calculated by the difference between the milliliters of HCl required for the sample and average milliliters HCl required for the blank and thereafter multiplying this difference by the normality of the HCl times the quotient of the molecular weight of the imidazoline divided by 1,000 times 100, the total product being divided by the weight of the sample in grams. The "total titratables" analysis consists of a titration with alcoholic HCl. Using this data and the molecular weight of the desired imidazoline, a calculation is made which gives the percent of imidazoline which would be present if all of the titratables were imidazoline. This figure is called total titratables and preferably should be close to 100%. The ring closure analysis involves the tying up of the primary and secondary amines with phenyl isothiocyanate. The thio ureas produced are not titratable. Therefore, only tertiary amines are left to be titrated. As the imidazoline is the only tertiary amine present, a titration at this point gives the quantity of imidazoline present. This percentage is called "ring closure."

The liquid hydrocarbon selected is one in which the particular substituted imidazoline is miscible, soluble or at least dispersible. The amount of substituted imidazoline is in the order, on a weight basis, of about 300–8000 p.p.m., preferably about 500–2000 p.p.m., of the imidazoline, based on the liquid hydrocarbon. The coal is sprayed or otherwise surface treated with about 0.5–5 gallons of the liquid hydrocarbon-imidazoline composition per ton of coal.

The freezing problems of coal particles are not particularly critical in coal with lump sizes wherein the smallest dimension of the particles or lumps is in the order of about 2 inches or more. Even if such particles or lumps freeze together, they can generally be broken apart relatively easily. Coal particles such as stoker coal and industrial screenings present freezing problems, however. Stoker coal generally has lump sizes of about 1½ to 2 inches while industrial screenings generally embrace particle sizes as low as about 100 mesh and as high as about 1½ inches, and may include coal fines known as coal dust.

This invention applies especially to coal of the character of stoker coal or industrial screenings.

Embodiments illustrating practice of the invention and the advantages thereof are described below.

Example II

A liquid hydrocarbon marketed and used per se as a coal de-dusting and anti-freezing composition and marketed as Shell's D-Dust H, which is effective per se as a coal anti-freezing composition down to about 15° F. when surface-applied on coal particles such as stoker coal and industrial screenings, was combined with varying concentrations therein of an imidazoline as prepared essentially per the procedure of Example I. Coal particles were sprayed therewith at an application temperature of about 130° F. The surface treated coal particles were placed in various sub-freezing environments in 800 ml. beakers. After allowing sufficient time to permit freezing, if any, the beakers were inverted to ascertain whether the particles would fall out of or remain in the beaker.

Data observed and recorded was as follows:

TABLE II

[Domestic stoker coal, 1" x ⅜"]

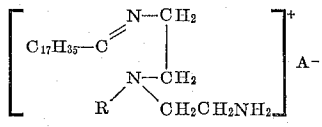
Freezing Temp.	Hydrocarbon	PPM of Imidazoline	Dosage	Fall Out
+10° F.	None	None	None	No.
+10° F.	D-Dust H	None	2 gal./ton	No.
+10° F.	do	500	2 gal./ton	No.
+10° F.	do	1,000	2 gal./ton	Yes.
+10° F.	do	2,000	2 gal./ton	Yes.
+10° F.	do	5,000	2 gal./ton	Yes.
+10° F.	do	5,000	1 gal./ton	No.
−10° F.	None	None	None	No.
−10° F.	D-Dust H	None	2 gal./ton	No.
−10° F.	do	500	2 gal./ton	No.
−10° F.	do	1,000	2 gal./ton	Yes.
−10° F.	do	2,000	2 gal./ton	Yes.
−10° F.	do	5,000	2 gal./ton	Yes.
−10° F.	do	5,000	1 gal./ton	No.

The above domestic stoker coal has an inherent moisture content of 8% and a surface moisture content of 7% or a total moisture content of 15%. The "Yes" and "No" under the Fall Out heading mean, respectively, that the coal sample had not frozen solid, and thereby had fallen out, or had frozen solid, and thereby had not fallen out of the inverted beaker.

Example III

Stoker coal having 5% inherent moisture content and 11% surface moisture content was sprayed at 130° F. at an application dosage of 2 gallons per ton coal with D-Dust H, and D-Dust H containing both 25 p.p.m. and 5000 p.p.m. of a 1,2-substituted imidazoline prepared essentially per the procedure of Example I. The coal particles sprayed with D-Dust H were frozen together at 13° F., and even vigorous jarring did not break them loose. The coal particles sprayed with D-Dust H plus 25 p.p.m. behaved similarly, showing that such small concentration is ineffective. The coal particles sprayed with D-Dust H plus 5000 p.p.m. of the imidazoline were placed in a −6° F. environment. The free water had frozen, but, with a slight amount of jarring, the coal particles broke free from the walls of the container and the coal particles broke free from themselves. The ice formed was frost-like and not hard or large crystals and was less than the amount formed in the D-Dust H treatment.

If desired, the previously described imidazolines may be used in the form of the quaternary salts thereof. The quaternary imidazolinium compounds are derived by combining the 1-substituted imidazolines with an appropriate agent such as dimethyl sulfate; diethyl sulfate; organic halo compounds such as benzyl chloride; alkyl monochlorides such as 1-chloroethane, 1-chloropropane, 1-chlorobutane; alkyl dichlorides such as 1,2-dichloroethane, 1,4-dichlorobutane; epichlorohydrin; and the like so as to form the quaternary derivative thereof. This is accomplished by heating the quaternizing compound and the imidazoline in an organic solvent in a manner well known in the art. The resulting quaternary imidazolinium compound may be illustrated by the following formula wherein the imidazoline is shown, by way of example, as being 2-heptadecyl 1-aminoethyl imidazoline. It will be understood that the other imidazoline compounds having substituents in the 1-, 4-, or 5-positions will have similar formulae.



wherein R is an organic substituent such as alkyl, chloroalkyl, benzyl, etc., and A is an anion such as a halide anion or a methyl or ethyl sulfate anion.

The following are additional examples of combinations of carboxylic acids and polyamines which may be reacted to form imidazolines which are useful in the practice of the invention.

Example	Carboxylic Acid	Polyamine
IV	Refined tall oil	Aminoethylethanolamine.
V	Hydrogenated tallow fatty acids.	Diethylenetriamine.
VI	Tall oil	Do.
VII	Mixture of capric and caprylic acids.	Do.
VIII	Refined tall oil	Do.
IX	Hydrogenated tallow fatty acids.	Aminoethyl ethanolamine.
X	Oleic acid	Diethylene triamine.
XI	do	Aminoethylethanolamine.
XII	Coconut oil fatty acids	Do.
XIII	do	Diethylene triamine.

It will be appreciated that other specific embodiments of imidazolines within the foregoing generic definition may be used in the practice of the invention as hereinafter claimed.

The invention is hereby claimed as follows:

1. A process for anti-freeze treatment of coal which comprises surface-coating small coal particles with about 0.5 to 5 gallons per ton of coal of a liquid hydrocarbon having a solidification point at least as low as −20° F. and containing a small amount in the order of 300–8000 p.p.m. of a member selected from the group consisting of (a) imidazolines having on a ring carbon a hydrocarbon substituent with 6–35 carbons and (b) quaternary salts of said imidazolines.

2. A process for anti-freeze treatment of coal which comprises surface-coating small coal particles with about 0.5 to 5 gallons per ton of coal of a liquid hydrocarbon having a solidification point at least as low as −20° F. and containing a small amount in the order of 500–2000 p.p.m. of an imidazoline substituted in the 2-position with a hydrocarbon substituent having 6–35 carbons.

3. A process for anti-freeze treatment of coal which comprises spraying small coal particles with about 0.5 to 5 gallons per ton of coal of a liquid hydrocarbon having a solidification point at least as low as −20° F. and containing a small amount in the range of 300 to 8000 p.p.m. of a member selected from the group consisting of (a) imidazolines having on a ring carbon a hydrocarbon substituent with 6–35 carbons and (b) quaternary salts of said imidazolines.

4. A process as claimed in claim 1 wherein said coal is stoker coal.

5. A process as claimed in claim 1 wherein said coal is industrial screenings.

6. A process for anti-freeze treatment of coal which comprises surface-coating small coal particles with about 0.5 to 5 gallons per ton of coal of a liquid hydrocarbon having a solidification point at least as low as −20° F. and containing a small amount in the order of 3000–8000 p.p.m. of an imidazoline of a tall oil fatty acid mixture containing at least 70% by weight of fatty acids having a molecular weight in the range of 235–280 and a polyalkylene polyamine mixture consisting essentially of 75–

90% diethylenetriamine, 5–15% triethylenetetramine, and 5–10% tetraethylenepentamine, said imidazoline analyzing 85–99% glyoxalidine ring closure and 88–99% total titratables.

7. A body of small coal particles in which said particles are surface-coated with about 0.5 to 5 gallons per ton of coal of a liquid hydrocarbon having a solidification point at least as low as —20° F. and containing a small amount in the order of 300–8000 p.p.m. of a member selected from the group consisting of (a) imidazolines having on a ring carbon a hydrocarbon substituent with 6–35 carbons and (b) quaternary salts of said imidazolines.

8. A body of small coal particles in which said particles are surface-coated with about 0.5 to 5 gallons per ton of coal of a liquid hydrocarbon having a solidification point at least as low as —20° F. and containing about 300–8000 p.p.m. of an imidazoline of a tall oil fatty acid mixture containing at least 70% by weight of fatty acids

having a molecular weight in the range of 235–280 and a polyalkylene polyamine mixture consisting essentially of 75–90% diethylenetriamine, 5–15% triethylenetetramine, and 5–10% tetraethylenepentamine, said imidazoline analyzing 85–99% glyoxalidine ring closure and 88–99% total titratables.

References Cited by the Examiner

UNITED STATES PATENTS

2,116,682	5/1938	Kleinicke et al.	44—6
2,973,254	2/1961	Schmidt	44—1
3,098,727	7/1963	Hamer et al.	44—56
3,115,397	12/1963	Fareri et al.	44—56

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