ABSTRACT

The invention relates to a method of lubricating the bearings of solid fuel pulverizers, for example, coal pulverizers. The method involves supplying to the bearings a lubricating composition designed to have superior performance compared to conventional coal pulverizer bearing lubricants. The invention also provides a bearing lubricant for a coal pulverizer as well as its use in coal pulverizing equipment to improve the service life and/or durability of bearings in coal pulverizing equipment. The invention also provides an additive composition for use in a bearing lubricant for a coal pulverizer, as well as the use of the additive composition to improve the service life and/or performance of the bearing lubricant.
BEARING LUBRICANTS FOR PULVERIZING EQUIPMENT

FIELD OF THE INVENTION

[0001] The invention relates to a method of lubricating the bearings of solid fuel pulverizers, for example, coal pulverizers. The method involves supplying to the bearings a lubricating composition designed to have superior performance compared to conventional coal pulverizer bearing lubricants. The invention also provides a bearing lubricant for a coal pulverizer as well as its use in coal pulverizing equipment to improve the service life and/or durability of bearings in coal pulverizing equipment. The invention also provides an additive composition for use in a bearing lubricant for a coal pulverizer, as well as the use of the additive composition to improve the service life and/or performance of the bearing lubricant.

BACKGROUND OF THE INVENTION

[0002] Pulverizers are well known for the reduction of the particle size of solid fuel to allow for combustion of the solid fuel in a furnace. A pulverizer employs some combination of impact, attrition and crushing to reduce a solid fuel to a particular particle size. Several types of pulverizer mills can be employed for the pulverization of the solid fuel, for example, coal, to a particle size appropriate for firing in a furnace. These include ball-tube mills, impact mills, attrition mills, ball race mills, and ring roll or bowl mills. Most typically, however, bowl mills with integral classification equipment are employed for the pulverization of the solid fuel to allow for transport, drying and direct firing of the pulverized fuel entrained in an air stream. There is an ongoing need to improve the mill loading and roll life of the bearings of these pulverizers.

[0003] Another factor which deteriorates roll life of the bearings in addition to increased mill loading includes solid fuel dust, such as coal dust, for example, which flows into and contaminates the bearings as well as the lubricant. Typically, pulverizers have an interface between the rotatable assembly and stationary shaft that is exposed to atmospheric conditions and a differential pressure across the assembly allows the coal dust, for example, to flow into the assembly housing the bearings. The ingress of coal at this interface, which allows the shaft to extend there through and rotate with respect to the journal assembly, contaminates the lubricant and journal bearings thus deteriorating the roll life of the journal bearings.

[0004] Some approaches involve complicated mechanical seals and expensive new equipment designed to reduce the amount of dust ingress. However, these solutions do nothing for the current equipment already in use.

[0005] Therefore, there remains a need for a method, and a lubricant, and an additive package that increases bearing roll life in these pulverisers, which facilitates increased mill loading and prevents damage from contamination of the bearings, thus allowing more effective use of existing equipment without the need for costly retfits and modifications.

SUMMARY OF THE INVENTION

[0006] The invention provides a method of lubricating the bearings of a solid fuel pulverizer. The method involved supplying to the bearings a lubricating composition designed to have superior performance compared to conventional solid fuel pulverizer bearing lubricants. The lubricating composition is designed to have improved dust loading capability, in other words, the lubricant is designed to perform better and/or last longer than conventional lubricants in the harsh conditions seen in pulverizers, including conditions related to large amounts of dust in the environment, which does get worked into the lubricant. The invention also provides a bearing lubricant for a pulverizer as well as its use in pulverizing equipment to improve the service life and/or durability of bearings in pulverizing equipment. The invention also provides an additive composition for use in a bearing lubricant for a pulverizer, as well as the use of the additive composition to improve the service life and/or performance of the bearing lubricant. In some embodiments, the solid fuel pulverizer described herein is a coal pulverizer.

[0007] The lubricating composition of the invention includes (a) an oil of lubricating viscosity, (b) a phosphorus-containing compound, and (c) a nitrogen-containing dispersant, where the phosphorus-containing compound and the nitrogen-containing dispersant work together to allow for better performance in the pulverizer bearing lubricant. In some embodiments, the compositions further include (d) a sulfur-containing compound.

[0008] In some embodiments, the invention deals with mineral base oil lubricants. In other embodiments, the invention deals with synthetic base oil lubricants.

[0009] The invention provides for various phosphorus-containing compounds including an alkyl phosphite, a phosphoric acid ester, an amine salt of a phosphoric acid ester, or some combination thereof. In some embodiments, the phosphorus-containing compound comprises an alkyl phosphite.

[0010] The invention provides for various nitrogen-containing dispersants including a polyetheramine, a borated succinimide dispersant, a non-borated succinimide dispersant, a Mannich dispersant comprising the reaction product of (i) a dialkylamine, (ii) an aldehyde and (iii) a hydrocarbyl substituted phenol, as well as any combination of the various nitrogen-containing dispersants. In some embodiments, the nitrogen-containing dispersant comprises a non-borated succinimide dispersant. The invention further provides for a lubricant containing an alkyl phosphite and a non-borated succinimide dispersant.

[0011] In any of these embodiments, the phosphorus-containing compound may be present in the lubricant composition from 0.25 or 0.5 up to 2.0 or 1.0 percent by weight and the nitrogen-containing dispersant is present in the lubricant composition from 0.1 or 0.5 up to 2.0 or 1.0 percent by weight, on an oil free basis, which may also be described herein on an active basis.

DETAILED DESCRIPTION OF THE INVENTION

[0012] Various features and embodiments of the invention will be described below by way of non-limiting illustration.

The Pulverizer and Method of Lubrication

[0013] The pulverizers suitable for use with the present invention are not overly limited. Pulverizers may generally be described as devices employable for purposes of effecting the grinding of materials. More specifically, the prior art is replete with examples of various types of apparatus that have been used to effect the grinding of many different kinds of materials. In this regard, in many instances discernible differences of a structural nature can be found to exist between individual pulverizers. The existence of such differences is, in turn,
attributable for the most part to the diverse functional requirements that are associated with the individual applications in which pulverizers are designed to be employed. For instance, in the selection of the particular type of pulverizer that is to be utilized for a specific application, one of the principal factors to consider is that of the nature of the material that is to be ground in the apparatus. Coal is one such material wherein there is a need to grind it in order to render it suitable for use in certain applications. Furthermore, fossil fuel fired power generation systems represent one such application in which it is desired to employ coal, as the source of fuel, and wherein a requirement exists to grind, i.e., pulverize, the coal to render it suitable for use for this purpose, i.e., for use in a coal-fired power generation system. Thus, in some embodiments, the pulverizers used with the invention are coal pulverizers.

In some embodiments, the pulverizers of the invention may include a feeder for feeding solid fuel to the pulverizer, an apparatus for pulverizing the solid fuel, a distribution system for distributing the solid fuel after the pulverization thereof, a furnace in which the solid fuel is to be burned and the requisite controls for effecting the proper operation of the solid fuel-fired power generation system. Of particular interest here is the apparatus for pulverizing the solid fuel, for example, coal.

In some embodiments, the pulverizer of the present invention is a bowl mill. A bowl mill may essentially consists of a body portion in which a grinding table is mounted for rotation, a plurality of grinding rollers that coat with the grinding table to effect the grinding of solid fuel interposed there between, solid fuel supply means for feeding to the interior of the bowl mill the solid fuel that is to be pulverized, and air supply means for supplying to the interior of the bowl mill the air required in the operation of the latter. In accordance with the mode of operation of such a bowl mill, the solid fuel, which enters the bowl mill, is pulverized by virtue of the coaction of the grinding rollers with the grinding table. After being pulverized, the solid fuel particles are thrown outwardly by centrifugal force whereby the particles are fed into a stream of air that is entering the bowl mill. The stream of air, which now contains pulverized solid fuel particles, flows through a tortuous path that is established in part by the positioning within the bowl mill of a suitably supported deflector means. As the stream of air and solid fuel particles flows along the aforementioned tortuous path, the sharp turns contained therein effects the separation of the coarse solid fuel particles from the air stream. These coarse solid fuel particles are then suitably returned to the grinding table for further pulverization while the fine solid fuel particles are carried through the bowl mill in the air stream, and exit therefrom along with the air. Each bowl mill will typically also have bearings, for example, upper bearings and lower bearings associated with the grinding rollers with the grinding table and/or their mounts.

Each pulverizer will typically also have a lubrication system for supplying lubricant to its bearings, including the upper and lower bearings of a bowl mill described, but all the various bearing that may be found in the various types of pulverizers used in the field.

The present invention provides a lubricant composition for the bearings of a solid fuel pulverizer and also provides a method of lubricating the bearings of a coal pulverizer by supplying to said bearings the described lubricant composition. The lubricant compositions useful in the invention are described below.

In some embodiments, the method of the invention involves supplying the described lubricant composition to a coal pulverizer. In some embodiments, the method of the invention involves supplying the described lubricant composition to a bowl mill pulverizer. In some embodiments, the method of the invention involves supplying the described lubricant composition to a mill coal pulverizer. In some embodiments, the method of the invention involves supplying the described lubricant composition to the lower bearings of the pulverizer. In some embodiments, the method of the invention involves supplying the described lubricant composition to the upper bearings of the pulverizer. In some embodiments, the method of the invention involves supplying the described lubricant composition to the upper and lower bearings of the pulverizer, or even all of the bearings in the pulverizer.

The Lubricant Composition

The invention includes a bearing lubricating composition made up of (a) an oil of lubricating viscosity, (b) a phosphorus-containing compound, and (c) a nitrogen-containing dispersant, wherein the phosphorus-containing compound and the nitrogen-containing dispersant work together to allow for better performance in the pulverizer bearing lubricant. The invention also provides an additive composition for use in a bearing lubricant for a pulverizer made up of (a) an optional diluent which may be an oil of lubricating viscosity or solvent, and (b) a phosphorus-containing compound, and (c) a nitrogen-containing dispersant, wherein the phosphorus-containing compound and the nitrogen-containing dispersant work together to allow for better performance in the pulverizer bearing lubricant. In some embodiments, the compositions further include (d) a sulfur-containing compound.

In some embodiments, the lubricant composition contains from 0.1 to 5.0, or from 0.25 to 5.0, or from 0.5 to 5.0, or from 0.5 to 4.0, from 0.75 to 3.0, from 0.9 to 2.0, or from 1 to 2, or even 1 or 2 percent by weight of a phosphorus-containing compound, on an actives basis (meaning no diluent oil or solvent is includes, rather the components are considered on a neat basis). In some embodiments, the lubricant composition contains a phosphorus-containing compound in an amount sufficient to deliver from 0.1 to 5.0, or from 0.25 to 0.5, or from 0.025 to 0.25, or from 0.05 to 0.1 percent by weight phosphorus to the overall lubricant composition.

In some embodiments, the lubricant composition contains from 0.01 or 0.01 to 0.25 to 10 or 5 or 4, or from 0.01 or 0.1 or 0.25 to 5, or from 0.1 to 1.0, or from 0.4 to 2.0 or 2.5, or from 0.5 to 2.0 percent by weight of a nitrogen-containing dispersant on an actives basis.

In some embodiments, the phosphorus-containing compound and the nitrogen-containing dispersant are present in the lubricant composition in a ratio from 1:10 to 10:1, or from 1:4 to 4:1, or from 1:2 to 4:1, or from 1:1 to 1:3:1, or even about 2:1, where the ratio is a weight ratio considered on an actives free basis. In some embodiments, the phosphorus-containing compound and the nitrogen-containing dispersant are present in the lubricant composition in a ratio from 0.5:1 to 4:1, or from and/or to about 0.5:1, 1:1, 1:2:1, 2:1 or 4:1, where the ratio is a weight ratio considered on an oil free basis.

The Oil of Lubricating Viscosity

One component of the compositions of the invention is an oil of lubricating viscosity, which can be present in a
major amount, for a lubricant composition, or in a concentrate forming amount, for a concentrate and/or additive composition.

[0024] Suitable oils include natural and synthetic lubricating oils and mixtures thereof. In a fully formulated lubricant, the oil of lubricating viscosity is generally present in a major amount (i.e., an amount greater than 50 percent by weight). Typically, the oil of lubricating viscosity is present in an amount of 75 to 95 percent by weight, and often greater than 80 percent by weight of the overall composition.

[0025] The base oil component generally makes up 100 parts by weight (pbw) of the overall composition with the pbw ranges for the other components being provided with this 100 pbw of base oil in mind. In other embodiments, the pbw ranges of the various components, including the base oils, are provided such that the total of the pbw of all components is 100, and thus the pbw values are equivalent to percent by weight values. The pbw ranges provided for the various components described below may be taken either way, however, in most embodiments they are to be read so as to be equivalent to percent by weight values.

[0026] The oil of lubricating viscosity may include natural and synthetic oils, oil derived from hydrocracking, hydrotreatment, and hydrogenation, and hydrofinishing, unrefined, refined and refined oils or mixtures thereof. Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like. Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0027] Natural oils useful as the oil of lubricating viscosity include animal oils, vegetable oils (e.g., castor oil, lard oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic naphthenic types and oils derived from coal or shale or mixtures thereof.

[0028] Synthetic oils of lubricating viscosity include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylines, polypropylene, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-ocenes), poly(1-decenes), and mixtures thereof; alkyl-benzences (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated biphenyl ethers and alkylated biphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof. In some embodiments, the oil of lubricating viscosity used in the invention is a synthetic oil that includes polymerized polyisobutylene, and in some embodiments, the oil of lubricating viscosity used in the invention is a synthetic oil that includes polymerized polyisobutylene and a polyalphaolefin.

[0029] Another synthetic oil of lubricating viscosity include polyol esters other than the hydrocarbyl-capped polyol-oxalkylene polyol as disclosed herein, dicarboxylic esters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic conventional oil of lubricating viscosity also include those produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes. In one embodiment, the oil of lubricating viscosity may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0030] Oils of lubricating viscosity may further be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulfur content >0.3 percent by weight, and/or <0.5 percent by weight saturates, viscosity index 80-120); Group II (sulfur content ≤0.3 percent by weight and ≥90 percent by weight saturates, viscosity index 80-120); Group III (sulfur content ≤0.3 percent by weight and ≥90 percent by weight saturates, viscosity index ≥120); Group IV (all polyalphaolefins, or PAO, such as PAO-4, PAO-5, PAO-6, PAO-7 or PAO-8); and Group V. The oil of lubricating viscosity includes API Group I, Group II, Group III, Group IV, or Group V oil or mixtures thereof. In one embodiment, the oil of lubricating viscosity is an API Group I, Group II, Group III, Group IV or Group V oil or mixtures thereof. Alternatively, the oil of lubricating viscosity is often an API Group II, Group III or Group IV oil or mixtures thereof.

[0031] In some embodiments, the lubricating oil component of the present invention includes a Group II or Group III base oil, or a combination thereof. These are classifications established by the API (American Petroleum Institute). Group III oils contain <0.3 percent sulfur and >90 percent saturates and have a viscosity index of >120. Group II oils have a viscosity index of 80 to 120 and contain ≥0.3 percent sulfur and ≥90 percent saturates. The oil can also be derived from the hydroisomerization of wax, such as slack wax or a Fischer-Tropsch synthesized wax. Such “Gas-to-Liquid” oils are typically characterized as Group III.

[0032] The compositions of the present invention may include some amount of Group I base oils, and even Group IV and Group V base oils. Polyalphaolefins are categorized as Group IV, Group V encompasses “all others”. However, in some embodiments, the lubricating oil component of the invention contains no more than 20, 10, 5, or even 1 percent by weight Group I base oil. These limits may also apply to Group IV or Group V base oils. In other embodiments, the lubricating oil present in the compositions of the invention is at least 60, 70, 80, 90, or even 95 percent by weight Group II and/or Group III base oil. In some embodiments, the lubricating oil present in the compositions of the invention is essentially only Group II and/or Group III base oil, where small amounts of other types of base oils may be present but not in amounts that significantly impact the properties or performance of the overall composition.

[0033] In some embodiments, the compositions of the invention include some amount of Group I and/or Group II base oils. In other embodiments, the compositions of the invention are lubricating compositions where the oil of lubricating viscosity is primarily Group I and/or Group II base oils, or even essentially Group I and/or Group II base oils, or even exclusively Group I and/or Group II base oils.

[0034] In some embodiments, the compositions of the invention include some amount of Group I and/or Group II base oils. In other embodiments, the compositions of the invention are lubricating compositions where the oil of lubricating viscosity is primarily Group I and/or Group II base oils.
oils, or even essentially Group I and/or Group II base oils, or even exclusively Group I and/or Group II base oils.

[0035] The various described oils of lubricating viscosity may be used alone or in combinations. The oil of lubricating viscosity is used in the range of about 70 percent by weight to about 99 percent by weight, and in another embodiment, in the range of about 75 percent by weight to about 98 percent by weight, in another embodiment in the range of about 88 percent by weight to about 97 percent by weight of the lubricant.

The Phosphorus-Containing Compound

[0036] The compositions useful in the invention include a phosphorus-containing compound.

[0037] In some embodiments, the phosphorus-containing compound is a phosphite. Suitable phosphites include those having at least one hydrocarbyl group with 4 or more, or 8 or more, or 12 or more, carbon atoms. Typical ranges for the number of carbon atoms on the hydrocarbyl group include 8 to 30, or 10 to 24, or 12 to 22, or 14 to 20, or 16 to 18. The phosphite may be a mono-hydrocarbyl substituted phosphate, a di-hydrocarbyl substituted phosphate, or a tri-hydrocarbyl substituted phosphate.

[0038] In one embodiment, the phosphite is sulphur-free i.e., the phosphite is not a thiophosphate.

[0039] The phosphite having at least one hydrocarbyl group with 4 or more carbon atoms may be represented by the formulae:

\[
\begin{align*}
R^3 &-O-H O R^1 N/ \end{align*}
\]

\[
\begin{align*}
R^4 &-O R^3 \end{align*}
\]

\[
\begin{align*}
R^5 & R^4-2 O \end{align*}
\]

Wherein: \( R^3 \) and \( R^4 \) may be independently hydrogen or hydrocarbon typically containing 4 to 40, or 6 to 30, or 6 to 18, or 8 to 18 carbon atoms, with the proviso that at least one is a hydrocarbon group; and \( R^5 \), \( R^4 \), \( R^2 \) and \( R^3 \) may be independently hydrogen or a hydrocarbyl group, with the proviso that at least one is a hydrocarbyl group. The hydrocarbyl groups of \( R^3 \) and \( R^4 \) may be linear, branched, or cyclic.

[0042] Examples of a hydrocarbon group for \( R^3 \) and/or \( R^4 \) include straight-chain or branched alkyl groups include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl. Additional examples include 2-ethylhexyl, 4-methyl-2-pentyl, and isopropyl.

[0043] Examples of a cyclic hydrocarbon group for \( R^3 \) and/or \( R^4 \) include cyclohexyl, cycloheptyl, methylcyclohexyl, dimethylcyclohexyl, methylcyclohexyl, ethylcyclohexyl, diethylcyclohexyl, methylcyclohexyl, dimethylcyclohexyl, methylcyclohexyl, methylcyclohexyl, dimethylcyclohexyl, dimethylcyclohexyl, methylcyclohexyl, and diethylcyclohexyl.

[0044] In one embodiment, the phosphite may be an amine salt of a mixture of monoalkyl and dialkyl phosphoric acid esters. The monoalkyl and dialkyl groups may be linear or branched.

[0045] The amine salt of a phosphate hydrocarbon ester may be derived from an amine such as a primary amine, a secondary amine, a tertiary amine, or mixtures thereof. The amine may be aliphatic, or cyclic, aromatic or non-aromatic, typically aliphatic. In one embodiment, the amine includes an aliphatic amine such as a tertiary-aliphatic primary amine.

[0046] Examples of suitable primary amines include ethylamine, propylamine, butylamine, 2-ethylhexylamine, bis-(2-ethylhexyl)amine, octylamine, and dodecylamine, as well as such fatty amines as n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine and oleylamine. Other useful fatty amines include commercially available fatty amines such as “Armeen®” amines (products available from Akzo Chemicals, Chicago, Ill.), such as Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

[0047] Examples of suitable secondary amines include dimethylamine, diethyamine, dipropylamine, dibutylamine, dihexylamine, diheptylamine, methyl ethylamine, ethylbutylamine, N-methyl-1-amo-cyclohexane, Armeen® 2C and ethylamylamine. The secondary amines may be cyclic amines such as piperidine, piperazine and morpholine.

[0048] Examples of tertiary amines include tri-n-butylamine, tri-n-octylamine, tri-decylamine, tri-laurylamine, tri-hexadecylamine, and dimethylethylamine (Armeen® DMOD).

[0049] In one embodiment, the amines are in the form of a mixture. Examples of suitable mixtures of amines include (i)
a tertiary alkyl primary amine with 11 to 14 carbon atoms, (ii) a tertiary alkyl primary amine with 14 to 18 carbon atoms, or (iii) a tertiary alkyl primary amine with 18 to 22 carbon atoms. Other examples of tertiary alkyl primary amines include tert-butylamine, tert-hexylamine, tert-octylamine (such as 1,1-dimethylhexylamine), tert-decylamine (such as 1,1-dimethylheptylamine), tert-decylamine, tert-tetradecylamine, tert-undecylamine, tert-octadecylamine, tert-tetracontanamine, and tert-oktacosanamine.  

In one embodiment, a useful mixture of amines is "Primene® 81R" or "Primene® IMT." Primene® 81R and Primene® IMT (both produced and sold by Rohm & Haas) are mixtures of C11 to C14 tertiary alkyl primary amines and C18 to C22 tertiary alkyl primary amines respectively.  

The amine salt of a phosphate hydrocarbon ester may be prepared as is described in U.S. Pat. No. 6,468,946. Column 10, lines 15 to 63 describes phosphoric acid esters formed by reaction of phosphorus compounds, followed by reaction with an amine to form an amine salt of a phosphate hydrocarbon ester. Column 10, line 64, to column 12, line 23, describes preparative examples of reactions between phosphorus pentoxide with an alcohol (having 4 to 13 carbon atoms), followed by a reaction with an amine (typically Primene® 81-R) to form an amine salt of a phosphate hydrocarbon ester.  

Suitable phosphorus-containing compounds also include hydrocarbyl amine salts of dialkylthiodiphosphoric acid. Examples of hydrocarbyl amine salts of dialkylthiodiphosphoric acid are represented by the formula:

\[
\text{R}^{24}\text{O-S-R}^{25}\text{N} / -/ \text{N-H}\text{R}^{26}\text{R}^{23}
\]

wherein \( R^{24} \) and \( R^{25} \) are independently branched or linear alkyl groups. \( R^{26} \) and \( R^{27} \) contain about 3 to about 30, preferably about 4 to about 25, more preferably about 5 to about 20, and most preferably about 6 to about 19 carbon atoms. \( R^{24} \), \( R^{24} \), and \( R^{25} \) as described above.  

In some embodiments, the hydrocarbyl amine salts of dialkylthiodiphosphoric acid include but are not limited to the reaction product(s) of dihydrol or diocyl or dionyl dithiophosphoric acids with ethylenediamine, morpholine or Primene 81R or mixtures thereof.  

The phosphorus-containing compound may be present at 0.01 percent by weight to 5 percent by weight, or 0.1 percent by weight to 5 percent by weight, or 0.2 percent by weight to 1.5 percent by weight, or 0.25 percent by weight to 1 percent by weight, or 0.5 percent by weight to 1 percent by weight of the described composition.  

The Nitrogen-Containing Dispersant  

The compositions useful in the invention include a nitrogen-containing dispersant, which in some embodiments is a hydrocarbyl substituted nitrogen containing additive. Suitable hydrocarbyl substituted nitrogen containing additives for use in the present invention includes additives sometimes referred to as ashless dispersants. Dispersants in general are well known in the field of lubricants and fuel (though often these additives are referred to as fuel detergents when used in fuel applications). Suitable materials include primarily what is known as ashless dispersants and polymeric dispersants. Ashless dispersants are so-called because, as supplied, they do not contain metal and thus do not normally contribute to sulfated ash when added to a lubricant. However, they may, of course, interact with ambient metals once they are added to a lubricant which includes metal-containing species. Ashless dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Examples of such materials include succinimide dispersants, Mannich dispersants, and borated derivatives thereof.  

Mannich dispersants, sometimes referred to as a Mannich base dispersant or Mannich detergents, are the reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and an amine or ammonia. The hydrocarbyl substituent of the hydrocarbyl-substituted phenol can have 10 to 400, 30 to 180, 10 or 40 to 110 carbon atoms. This hydrocarbyl substituent can be derived from an olefin or a polyolefin, such as 1-decene, which is commercially available.  

The polyolefins, which can form the hydrocarbyl substituent can be prepared, for instance, by polymerizing olefin monomers by well-known polymerization methods and are also commercially available. The olefin monomers include monoolefins having 2 to 10 carbon atoms such as ethylene, propylene, 1-butene, isobutylene, and 1-decene. An especially useful monoolefin source is a C4 refinery stream having a 35 to 75 weight percent butene content and a 50 to 60 weight percent isobutene content. Useful olefin monomers also include diolefins such as isoprene and 1,3-butadiene. Olefin monomers can also include mixtures of two or more monoolefins, of two or more diolefins, or of one or more monoolefins and one or more diolefins. Useful polyolefins include polyisobutylene having a number average molecular weight of 140 to 5000, in another instance of 400 to 2500, and in a further instance of 140 or 500 to 1500. The polyisobutylene can have a vinylidene double bond content of 5 to 69%, in a second instance of 50 to 69%, and in a third instance of 50 to 95%. The polyolefin can be a homopolymer prepared from a single olefin monomer or a copolymer prepared from a mixture of two or more olefin monomers. Also possible as the hydrocarbyl substituent source are mixtures of two or more homopolymer, two or more copolymers, or one or more homopolymers and one or more copolymers. The foregoing description of suitable hydrocarbyl groups or polyolefin groups is also applicable to the hydrocarbyl substituent of the succinimide dispersant, described in detail below.  

The hydrocarbyl-substituted phenol which is used to prepare the Mannich dispersant can have 1 to 10 carbon atoms, and is generally formaldehyde or a reactive equivalent thereof such as formalin or paraformaldehyde.  

The amine used to form the Mannich dispersant can be a monoamine or a polyamine, including those materials described below for the succinimide dispersants, including alkanolamines having one or more hydroxyl groups. Useful amines include ethanamine, diethanolamine, methyamine, dimethylamine, ethylenediamine, diethylaminopropylamine, diethylaminoamine and 2-(2-amino-ethyl)amin) ethanol. The Mannich dispersant can be prepared by reacting
a hydrocarbyl-substituted phenol, an aldehyde, and an amine as described in U.S. Pat. No. 5,697,988. In one embodiment, the Mannich reaction product is prepared from an allylphenol derived from a polyisobutenyl, formaldehyde, and an amine that is a primary monoamine, a secondary monoamine, or an alkylenediamine, in particular, ethylenediamine or dimethylamine. In one embodiment, the allylphenol may be prepared from a high-vinylidene polyisobutenylene having, e.g., greater than 50, greater than 70 or greater than 75 percent terminal vinylidene groups (i.e., such percentage of polyisobutenylene molecules having vinylidene end groups.) The foregoing description of the amine is also applicable to the description of the amine used in preparing the succinimide dispersant, described below.

[0061] In one embodiment, the Mannich dispersant comprises the reaction product of a hydrocarbyl-substituted phenol, formaldehyde or a reactive equivalent of formaldehyde, and a primary or secondary amine. In one embodiment, the Mannich dispersant comprises the reaction product of a polyisobutenyl-substituted phenol, formaldehyde or a reactive equivalent of formaldehyde, and dimethylamine.

[0062] As used herein, the term “hydrocarbyl substituent” or “hydrocarbyl group” is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include hydrocarbon substituents, including aliphatic, alicyclic, and aromatic substituents; substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain. A more detailed definition of the term “hydrocarbyl substituent” or “hydrocarbyl group” is found in paragraphs [0137] to [0141] of published application US 2010/0197536.

[0063] Another suitable hydrocarbyl substituted nitrogen containing additive is a succinimide dispersant, which may also be referred to as a succinimide fuel detergent. In one embodiment, the succinimide dispersant is a condensation product of hydrocarbyl-substituted succinimine hydride or a reactive equivalent thereof (e.g., an anhydride, ester, or acid halide), with an amine such as a polyethylene polyamine. Succinimide dispersants may generally be viewed as comprising a variety of chemical structures including typically

![Chemical Structure](attachment:image.png)

where each R₁ is independently an alkyl group, frequently a polyisobutenylene group with a molecular weight (Mₘ) of 500-5000 based on the polyisobutenylene precursor, and R₂ is alkylene groups, commonly ethylene (CH₂)ₙ groups. Such molecules are commonly derived from reaction of an allyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure shown above, including a variety of amides and quaternary ammonium salts. In the above structure, the amine portion is shown as an alkyiene polyamine, although other aliphatic and aromatic mono- and polyamines may also be used, including those described above and below. Also, a variety of modes of linkage of the R₂ groups onto the imide structure are possible, including various cyclic linkages. The ratio of the carbonyl groups of the acylating agent to the nitrogen atoms of the amine may be 1.05 to 1.3, and in other instances 1:1 to 1:2.75 or 1:1.5 to 1:2.5. Succinimide dispersants are more fully described in U.S. Pat. Nos. 4,234,435 and 3,172,892 and in EP 0355895.

[0064] Succinimide dispersants may also be described as being prepared from hydrocarbyl-substituted succinimine acylating agent which are, in turn, prepared by the so-called “chlorine” route or by the so-called “thermal” or “direct alkylation” route. These routes are described in detail in published application US 2005-0202981, paragraphs 0014 through 0017. A direct alkylation or low-chlorine route is also described in U.S. Pat. No. 6,077,909; refer to column 6 line 13 through col. 7 line 62 and column 9 lines 10 through col. 10 line 11. Illustrative thermal or direct alkylation processes involve heating a polyolefin, typically at 180 to 250°C, with maleic anhydride under an inert atmosphere. Either reactant may be in excess. If the maleic anhydride is present in excess, the excess may be removed after reaction by distillation. These reactions may employ, as the polyolefin, high vinylidene polyisobutylene, that is, having greater than 50, 70, or 75% terminal vinylidene groups, in some embodiments alpha vinylidene end groups. In certain embodiments, the succinimide dispersant may be prepared by the direct alkylation route. In other embodiments, it may comprise a mixture of direct alkylation and chlorine-route dispersants.

[0065] Any of these additives may be post-treated with any of a variety of agents to impart desirable properties thereto. Such post-treatment includes reaction with urea, thiourea, dimercaptopropaniazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitrides, epoxides, boron compounds such as boric acid, phosphorus compounds, or mixtures thereof. References detailing such treatment are listed in U.S. Pat. No. 4,654,403.

[0066] Additional suitable hydrocarbyl substituted nitrogen containing additives include acylated amines, hydrocarbyl substituted amines, or mixtures thereof.

[0067] Suitable acylated amines include reaction products of one or more carboxylic acylating agent and one or more amine. The carboxylic acylating agents include C₆₋₂₀ fatty acids, C₁₈₋₄₀ isosaliciphatic acids, C₁₅₋₄₄ dimer acids, addition dicaarboxylic acids, trimer acids, addition tricarboxylic acids, and hydrocarbyl substituted carboxylic acylating agents, including those described above. Dimer acids are described in U.S. Pat. Nos. 2,482,760, 2,482,761, 2,731,481, 2,793,219, 2,964,545, 2,978,468, 3,157,681, and 3,256,304. Suitable amines may be any of those described above, in some embodiments a polyamine, such as an alkenylenepolyamine or a condensed polyamine. Acylated amines, their intermediates and methods for preparing the same are described in U.S. Pat. Nos. 3,219,666; 4,234,435; 4,952,328; 4,938,881; 4,957,649; 4,904,401; and 5,053,152.

[0068] The hydrocarbyl substituted nitrogen containing additive may also be a hydrocarbyl-substituted amine. These hydrocarbyl-substituted amines are well known to those skilled in the art. These amines are disclosed in U.S. Pat. Nos.
Examples of hydrocarblyl substituted amines include ethylene polyamines such as diethylelenetriamine; poly(propylene)amine; N,N-dimethyl-N-propylene)amine, (50:50 mole ratio of monomers); polybutene amine; N,N-di(hydroxyethyl)-N-polybutene amine; N-(2-hydroxypropyl)-N-polybutene amine; N-polybutene-nitrite; N-poly(N-butene)ethylene diamine; N-poly(propylene)trimethylene diamine; N-poly(butene)diethylelenetriamine; N,N,N',N'-tetrakis(2-hydroxypropyl)ethylene diamine; N,N-dimethyl-N,N'-poly(propylene)-1,3-propylenediamine and the like.

In one embodiment, the boron compound is a borated dispersant. Typically, the borated dispersant contains from about 0.1% to about 5%, or from about 0.5% to about 4%, or from 0.7% to about 3% by weight boron. In one embodiment, the borated dispersant is a borated acylated amine, such as a borated succinimide dispersant. Borated dispersants are described in U.S. Pat. Nos. 3,000,916; 3,087,936; 3,254,025; 3,282,955; 3,313,727; 3,491,025; 3,533,945; 3,666,662 and 4,925,983. In one embodiment, the boron compound contains one or more alkali or mixed alkali metal and alkaline earth metal borate. These metal borates are generally hydrated particulate metal borates which are known in the art. Alkali metal borates include mixed alkali and alkaline metal borates. These metal borates are available commercially. Representative patents disclosing suitable alkali and alkaline earth metal and alkaline earth metal borates and their methods of manufacture include U.S. Pat. Nos. 3,997,454; 3,819,521; 3,853,772; 3,907,601; 3,955,474; and 4,089,790.

Hydrocarblyl substituted nitrogen containing additives described above can also be post-treated by reaction with any of a variety of agents besides borating agents. Among these are urea, thiourea, dimercaptotriazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, and phosphorus compounds. References detailing such treatment are listed in U.S. Pat. No. 4,654,403.

The amines used in the preparation of the hydrocarblyl substituted nitrogen containing additives described above may be polyamines. Suitable polyamines include aliphatic, cyclic, aliphatic, heterocyclic, and aromatic polyamines. Examples of the polyamines include alkylene polyamines, hydroxy containing polyamines, aryl polyamines, and heterocyclic polyamines.

Alkylene polyamines are represented by the formula:

\[(H)_{m}(R_1)\overline{N-(Alkyene-N)}_{n-1}(R_2)_{(R_3)}\]

wherein n has an average value from 1, or about 2 to about 10, or to about 7, or to about 5, and the “Alkyene” group has from 1, or about 2 to about 10, or to about 6, or to about 4 carbon atoms. Each R₂ is independently hydrogen, or an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms.

[0075] Such alkylenepolyamines include methylenepolyamines, ethylenepolyamines, butylenepolyamines, propylenepolyamines, pentylenepolyamines, etc. The higher homologs and related heterocyclic amines such as piperazines and N-aminoalkyl-substituted piperazines are also included. Specific examples of such polyamines are ethylenediame, diethylenetriamine (DETA), triethylenetetramine (TETA), tri-(2-aminoethyl)amine, propylenediamine, trimethylene diamine, tripropylenetetramine, tetraethylenepentamine, hexa-ethylenediamine, pentaethylenhexamine, etc.

[0076] Higher homologs obtained by condensing two or more of the above-noted alkylen amines are similarly useful as are mixtures of two or more of the aforesaid polyamines.

[0077] Ethylenepolyamines, such as those mentioned above, are useful. Such polyamines are described in detail under the heading Ethylene Amines in Kirk Othmer’s “Encyclopedia of Chemical Technology”, 2d Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Such polyamines are most conveniently prepared by the reaction of ethylene dichloride with ammonia or by reaction of an ethylene amine with a ring opening reagent such as water, ammonia, etc. These reactions result in the production of a complex mixture of polyalkylenepolyamines including cyclic condensation products such as the aforesaid piperezines. Ethylenepolyamine mixtures are also useful.

[0078] Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave as residue what is often termed “polyamine bottoms”. In general, alkylenepolyamine bottoms can be characterized as having less than two, usually less than 1% (by weight) material boiling below about 200°C. A typical sample of such ethylene polyamine bottoms obtained from the Dow Chemical Company of Freeport, Tex. designated “E-100” has a specific gravity of 1.078. A percent nitrogen by weight of 33.15 and a viscosity at 40°C of 121 centistokes. Gas chromatography analysis of such a sample contains about 0.93% “Light Ends” (most probably DETA), 0.72% TETA, 21.74% tetraethylenepentamine and 76.61% pentaethylenhexamine and higher (by weight). These alkylenepolyamine bottoms include cyclic condensation products such as piperezine and higher analogs of diethylenetriamine, triethylenetetramine and the like. These alkylenepolyamine bottoms can be reacted solely with the acylating agent or they can be used with other amines, polyamines, or mixtures thereof.

[0079] Another useful polyamine is a condensation reaction between at least one hydroxy compound with at least one polyamine reactant containing at least one primary or secondary amino group. The hydroxy compounds are in some embodiment’s polyhydric alcohols and amines. The polyhydric alcohols are described above. In some embodiments, the hydroxy compounds are polyhydric amines. Polyhydric amines include tri-(hydroxypropyl)amine, tri-(hydroxymethyl) amino methane, 2-amino-2-methyl-1,3-propanediol, N,N,N', N'-tetrais(2-hydroxypropyl)ethylene diamine, and N,N,N'...
N'-tetrakis(2-hydroxyethyl)ethylenediamine, and in some embodiments tris(hydroxymethyl)aminomethane (THAM).

[0080] In another embodiment, the polyamines are hydroxy-containing polyamines. Hydroxy-containing polyamine analogs of hydroxymonoamines, particularly alkoxyalkyl alkylene polyamines (e.g., N,N,N-diehtanol)ethylenediamine) may also be used. Such polyamines may be made by reacting the above-described alkylene polyamines with one or more of the above-described alkylene oxides. Similar alkylene oxide-alkanolamine reaction products may also be used such as the products made by reacting the above-described primary, secondary or tertiary alkanolamines with ethylene, propylene or higher epoxides in a 1:1 to 1:2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art.

[0081] Specific examples of alkoxyalkyl alkylene polyamines include N-(2-hydroxyethyl)ethylenediamine, N,N-bis(2-hydroxyethyl)ethylenediamine, 1-(2-hydroxyethyl)piperazine, mono(hydroxypropyl)substituted tetraethylenepentamine, N-(3-hydroxybutyl)tetraethylenediamine, etc. Higher homologs obtained by condensation of the above-illustrated hydroxy-containing polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the aforesaid polyamines are also useful.

[0082] In another embodiment, the amine is a heterocyclic polyamine. The heterocyclic polyamines include aziridines, azetidines, azolines, pyridines, pyrroles, indoles, piperidines, imidazoles, pyrazines, isindolines, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkylpiperazines, N,N'-di aminoalkylpiperazines, azepines, azocines, azirines, azecines and tetra-, di- and perhydro derivatives of each of the above and mixtures of two or more of these heterocyclic amines. In some embodiments, the heterocyclic amines are the saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, piperidines, and the like. Piperidine, N-aminoalkyl-substituted piperidines, piperazine, N-aminoalkyl-substituted piperazines, morpholine, aminoalkyl-substituted morpholines, pyrrolidine, and N-aminoalkyl-substituted pyrrolidines. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminoalkylpyrrolidine, N-aminoethylpiperazine, and N,N'-dimethylethylpiperazine. Hydroxy heterocyclic polyamines are also useful. Examples include N-(2-hydroxyethyl)cyclo-

[0083] The amines used in the preparation of the hydroxy-substituted nitrogen containing additives described above may also be amines having at least 4 aromatic groups, at least one —N-H functional group, and at least 2 secondary or tertiary amino groups.

[0084] Suitable amines having at least 3 aromatic groups, at least one —N-H functional group, and at least 2 secondary or tertiary amino groups may be represented by the formula:

\[
\begin{align*}
\text{H} & \quad \text{N} \\
& \quad \text{R} \\
& \quad \text{R'} \quad \text{R} \\
& \quad \text{N} \\
& \quad \text{R} \\
& \quad \text{H}
\end{align*}
\]

wherein independently each variable may be defined as follows: R' may be hydrogen or a C₁₋₅ alkyl group (typically hydrogen); R² may be hydrogen or a C₁₋₅ alkyl group (typically hydrogen); U may be an aliphatic, alicyclic or aromatic group, with the proviso that when U is aliphatic, the aliphatic group may be linear or branched alkylene group containing 1 to 5, or 1 to 2 carbon atoms; and w may be 1 to 10, or 1 to 4, or 1 to 2 (typically 1).

[0085] Suitable amines having at least 3 aromatic groups, at least one —N-H functional group, and at least 2 secondary or tertiary amino groups may be represented by the formula:

\[
\begin{align*}
\text{H} & \quad \text{N} \\
& \quad \text{R} \\
& \quad \text{R'} \quad \text{R} \\
& \quad \text{N} \\
& \quad \text{R} \\
& \quad \text{H}
\end{align*}
\]

wherein independently each variable may be defined as follows: R¹ may be hydrogen or a C₁₋₅ alkyl group (typically hydrogen); R² may be hydrogen or a C₁₋₅ alkyl group (typically hydrogen); U may be an aliphatic, alicyclic or aromatic group, with the proviso that when U is aliphatic, the aliphatic group may be linear or branched alkylene group containing 1 to 5, or 1 to 2 carbon atoms; and w may be 1 to 10, or 1 to 4, or 1 to 2 (typically 1).

[0086] Alternatively, the amines may also be represented by the formula:

\[
\begin{align*}
\text{H} & \quad \text{N} \\
& \quad \text{R} \\
& \quad \text{R'} \quad \text{R} \\
& \quad \text{N} \\
& \quad \text{R} \\
& \quad \text{H}
\end{align*}
\]

wherein each variable U, R¹, and R² are the same as described above and w is 0 to 9 or 0 to 3 or 0 to 1 (typically 0).

[0087] Examples of suitable amines having at least 3 aromatic groups may be represented by any of the following formulae:
In one embodiment, the amine having at least 3 aromatic groups may include mixtures of compounds represented by the formulae disclosed above. A person skilled in the art will appreciate that these compounds may also react with the aldehyde described below to form acridine derivatives. In addition to such compounds, a person skilled in the art will also appreciate that other acridine structures may be possible where the aldehyde reacts with other benzyl groups bridged with the >NH group. Any or all of the N-bridged aromatic rings are capable of such further condensation and perhaps aromatization.

Examples of suitable amines having at least 3 aromatic groups may be bis[p-(aminophenyl)phenyl]-methane, 2-(7-amino-acridin-2-ylmethyl)-N-4-[4-(4-aminophenylamino)-benzyl]-phenyl]-benzene-1,4-diamine, N-[4-(4-aminophenylamino)-benzyl]-phenyl]-benzene-1,4-diamine, N-[4-(7-amino-acridin-2-ylmethyl)-phenyl]-benzene-1,4-diamine, or mixtures thereof.

In one embodiment, the amine having at least 3 aromatic groups may be bis[p-(aminophenyl)phenyl]-methane, 2-(7-amino-acridin-2-ylmethyl)-N-4-[4-(4-aminophenylamino)-benzyl]-phenyl]-benzene-1,4-diamine or mixtures thereof.

The amine having at least 3 aromatic groups may be prepared by a process comprising reacting an aldehyde with an amine (typically 4-aminophenylamine). The resultant amine may be described as an alkylene coupled amine having at least 3 aromatic groups, at least one —NH₂ functional group, and at least 2 secondary or tertiary amino groups.

In some embodiments, the hydrocarbyl substituted nitrogen containing additives are succinimide dispersants. In some embodiments, the hydrocarbyl substituted nitrogen containing additives are non-borated succinimide dispersants. In some embodiments, the succinimide dispersants are derived from an alkyl aryl amine, polyethylene polyamines, or some combination thereof. In some embodiments, the succinimide dispersants are derived from a hydrocarbyl-substituted succinic anhydride or acid (a reactive equivalent thereof e.g., an ester, acid halide, etc.) where the hydrocarbyl-substituted succinic anhydride contains a polyisobutylene group with a molecular weight from 500 to 3000, or from 1600 to 3000, or from 1000 to 2000.

Suitable hydrocarbyl substituted nitrogen containing additives also include quaternary ammonium salts, also referred to as quaternary ammonium salt detergents and/or dispersants. Examples of suitable quaternary ammonium salts include (i) imide quaternary ammonium salts, (ii) Mannich quaternary ammonium salts, (iii) polyalkene substituted amine quaternary ammonium salts, (iv) amide quaternary ammonium salts, (v) ester quaternary ammonium salts, (vi) polyester quaternary ammonium salts, or (vii) any combination thereof.

These various types of quaternary ammonium salts may be prepared in any number of ways but generally are prepared by reacting a non-quaternized nitrogen-containing compound with a quaternizing agent. Each of the different types of quaternary ammonium salts described uses a different non-quaternized nitrogen-containing compound in its preparation, but generally the non-quaternized nitrogen-containing compound contains a tertiary nitrogen capable of being quaternized (or a primary or secondary nitrogen atom that can be alkylated to a tertiary nitrogen that can then be quaternized) and a hydrocarbyl substituent group. The non-quaternized compounds are typically detergents and/or dispersants themselves, put once converted to quaternary ammonium salts, can provide improved performance.

The hydrocarbyl substituent groups of the quaternary ammonium salt detergents and/or dispersants, and/or of the non-quaternized nitrogen-containing compounds from which they are prepared, are not overly limited and may be any of the hydrocarbyl substituent groups derived herein.

Each of the quaternary ammonium salts described above is prepared using a quaternizing agent. Suitable quaternizing agents are not overly limited so long as they are able to convert the tertiary nitrogen of the non-quaternized precursor to a quaternized nitrogen. Suitable quaternizing agents include dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl epoxides, esters of certain polycarboxylic acids, or mixtures thereof. Any of these agents, including the hydrocarbyl epoxides and hydrocarbyl
substituted carbonates, may be used in combination with an acid, for example acetic acid. Suitable acids include carboxylic acids, such as acetic acid, propionic acid, 2-ethylhexanoic acid, and the like. In some embodiments, including, for example, the amide quaternary ammonium salts, the quaternizing agent, including the hydrocarbyl epoxides and hydrocarbyl substituted carbonates, are used without the addition of such an acid. In some embodiments, particularly when no acid is used, some amount of water is present during the reaction.

In some embodiments, the quaternizing agent can be a hydrocarbyl epoxides, as represented by the following formula:

![Formula Image]

wherein R15, R16, R17 and R18 can be independently H or a C1-50 hydrocarbyl group. Examples of suitable hydrocarbyl epoxides include: styrene oxide, ethylene oxide, propylene oxide, butylene oxide, styrene oxide, C2-50 epoxides, or combinations thereof.

With regards to the amide quaternary ammonium salt described above, the presence of the amide group and its impact on the rest of the structure allows for the salt to be “self-salting” and thus not requiring of a separate cation assuming the structure also includes at least one other acid group. For example, when hydrocarbyl substituted succinic anhydrides, and similar materials are used to prepare the non-quaternized nitrogen-containing compounds, the resulting quaternary ammonium salt can have an amide group and an acid group, where the acid group becomes the counter anion for the quaternized nitrogen or the resulting amide quaternary ammonium salt. These materials may be described as betaines. The preparation of these quaternary ammonium salts is typically marked by the use of an alkylene oxide quaternizing agent, or a similar agent, without the addition of a separate acid.

In another embodiment, the quaternizing agent can be an ester of a carboxylic acid or an ester of a polycarboxylic acid. In some embodiments, the quaternizing agent includes dimethyl oxalate, methyl 2-nitrobenzoate and methyl sulfonylate.

In some embodiments, the quaternary ammonium salt is a quaternized polymer formed by polymerizing the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing the acylating agent wherein the condensation product has at least one tertiary amino group, or even polymerizing the hydrocarbyl-substituted acylating agent which is then reacted with a compound having an oxygen or nitrogen atom. One or more of the tertiary amino groups on the polymer may then be quaternized using the methods described herein resulting in a quaternized polymer.

Any of the quaternary ammonium salts described above may be derived in the presence of a protic solvent. In some embodiments, the process used to prepare these additives is substantially free of to free of methanol. In one embodiment, the protic solvent includes compounds that contain 1 or more hydroxyl functional groups, and may include water. In some embodiments, the protic solvent is water.


The nitrogen containing dispersant may be a polyetheramine. In some embodiments, the polyetheramine can include compounds having two or more consecutive ether groups and at least one primary, secondary or tertiary amine group where the amine nitrogen has some basicity. The polyetheramines of this invention can include poly(oxyalkylene) amines having a sufficient number of repeating oxyalkylene units to render the poly(oxyalkylene)amine soluble in a normally liquid fuel, such as, in hydrocarbons boiling in a gasoline or diesel fuel range and blends of hydrocarbon fuel with non-hydrocarbon fuel. Generally, poly(oxyalkylene)amines having at least 5 oxyalkylene units are suitable for use in the present invention.

Poly(oxyalkylene)amines can include: hydrocarbyl(poly(oxyalkylene)-amines, hydrocarbyl/poly(oxyalkylene)polyamines, hydrocarbyl/poly(oxyalkylene)-amines, hydrocarbyl (oxyalkylene)polyamines, and derivatives of polyhydric alcohols having at least two poly(oxyalkylene)amine and/or poly(oxyalkylene) polycrylamide chains on the molecule of the derivative.

In one embodiment, the poly(oxyalkylene)amine for use in the invention is represented by the formula:

\[ R^n \text{O}[\text{A}_1\text{O}_{m-1}\text{R}^n]\text{R}^m \]

wherein R^n is a hydrocarbyl group of 1 to 50 carbon atoms, or 8 to 30 carbon atoms; A^2 is an alkylene group having 2 to 18 carbon atoms and in some embodiments 2 to 6 carbon atoms; m is a number from 1 to 50; R^7 is an alkylene group having 2 to 18 carbon atoms or in some embodiments 2 to 6 carbon atoms; and R^n and R^m are independently hydrogen, a hydrocarbyl group or —[R(nR''=)R(m)]^x wherein R^n is an alkylene group having 2 to 6 carbon atoms, R^m and R'' are independently hydrogen or a hydrocarbyl group, and n is a number from 1 to 7.

In another embodiment, the poly(oxyalkylene)amine of the present invention can be represented by the formula:

\[ R^n\text{O}[\text{C}_{n+1}\text{CH}_{(n+1)}\text{CH}]=\text{CH}_{(n+1)}\text{CH} (\text{CH}_{(n+1)}\text{CH})_2 \text{CH} (\text{CH}_{(n+1)}\text{CH})_2 \text{NH}_2 \]

wherein R^n is an aliphatic group or alkyl substituted phenyl group of 8 to 30 carbon atoms; and Z is a number from 12 to 30. In yet another embodiment, the poly-(oxyalkylene)amine of the present invention can be represented by the formula above wherein R^n is CH_{14}CH(CH)_{14}CH(=CH), CH_{14}CH(CH), CH_{14}CH, and Z is a number from 16 to 28. Poly(oxyalkylene)amines of the present invention can have a molecular weight in the range from 300 to 5,000.

The polyetheramines of the present invention can be prepared by using the polyesters described above as intermediates and converting them to polyetheramines. The polyether intermediates can be converted to polyetheramines by several methods. The polyether intermediate can be converted to a polyetheramine by a reductive amination with ammonia, a primary amine or a polyamine as described in U.S. Pat. Nos. 5,112,364 and 5,752,991. In one embodiment, the polyether intermediate can be converted to a polyetheramine via an addition reaction of the polyether to acrylonitrile to form a nitrile which is then hydrogenated to form the polyetheramine. U.S. Pat. No. 5,264,006 provides reaction conditions for the cyanohydration of the polyether with acrylonitrile and the
subsequent hydrogenation to form the polyetheramine. In yet another embodiment, the polyether intermediate or poly(oxyalkylene) alcohol is converted to the corresponding poly(oxyalkylene) chloride via a suitable chlorinating agent followed by displacement of chlorine with ammonia, a primary or secondary amine, or a polyanime as described in U.S. Pat. No. 4,247,301.

The mixed alkoxylates of the present invention may also include an alkoxylated fatty amine, which can include amines represented by the formula:

\[ \text{R}^{11} \text{N}(\text{A}^{0})_{\text{x}} \text{H} \]

\[ (\text{A}^{0})_{\text{y}} \text{H} \]

wherein \( R^{11} \) is a hydrocarbyl group having 4 to 30 carbon atoms, \( A^1 \) and \( A^2 \) are vicinal alkylene groups, and the sum of \( x \) and \( y \) is an integer that is at least 1. The hydrocarbyl group is a univalent radical of carbon atoms that is predominantly hydrocarbon in nature, but can have nonhydrocarbonaceous substituent groups and can have heteroatoms. The hydrocarbon group \( R^{11} \) can be an alkyl or alkyne group of 4 to 30 carbon atoms, or 10 to 22 carbon atoms. The vicinal alkylene groups \( A^1 \) and \( A^2 \) can be the same or different and include: ethylene (--\( \text{CH}_2=\text{CH}_2 \)), propylene (--\( \text{CH}_2=\text{CH}-(\text{CH}_3) \)) and butylene (--\( \text{CH}_2=\text{CH}-(\text{CH}_2) \)) having the carbon to nitrogen and carbon to oxygen bonds on adjacent or neighboring carbon atoms. Examples of alkoxylated fatty amines can include: diethoxytallowamine, diethoxytallow oleylamine, diethoxytallow stearlamine, and the diethoxytallow anine from soybean oil fatty acids. Alkoxylated fatty amines are commercially available from Akzo under the Ethoomen® series.

The nitrogen-containing compound may be present at 0.01 percent by weight to 5 percent by weight, or 0.1 percent by weight to 3 percent by weight, or 0.2 percent by weight to 1.5 percent by weight, or 0.25 percent by weight to 1 percent by weight, or 0.5 percent by weight to 1 percent by weight of the described composition.

Additional Additives

[0113] Optionally, the lubricating compositions of the invention include one or more additional additives, which may be selected from the group including: a foam inhibitor, a demulsifier, a pour point depressant, an antioxidant, a dispersant other than those described above, a metal deactivator (such as a copper deactivator), an antiknock additive other than those described above, extreme pressure agent, viscosity modifiers, or mixtures thereof. The optional additives may each be present in the range from 50, 75, 100 or even 150 ppm up to 5, 4, 3, 2 or even 1.5 percent by weight, or from 75 ppm to 0.5 percent by weight, from 100 ppm to 0.4 percent by weight, or from 150 ppm to 0.3 percent by weight, where the percent by weight values are with regards to the overall lubricating oil composition. However, it is noted that some optional additives, including viscosity modifying polymers, which may alternatively be considered as part of the base fluid, may be present in higher amounts including up to 30, 40, or even 50% by weight when considered separate from the base fluid. The optional additives may be used alone or mixtures thereof.

[0114] Anti-foams, also known as foam inhibitors, are known in the art and include but are not limited to organic silicones and non-silicon foam inhibitors. Examples of organic silicones include dimethyl silicone and polysiloxanes. Examples of non-silicon foam inhibitors include but are not limited to polyethers, polyacrylates and mixtures thereof as well as copolymers of ethyl acrylate, 2-ethylhexyl acrylate, and optionally vinyl acetate. In some embodiments, the anti-foam is a polyacrylate. Anti-foams may be present in the composition from 0.001 to 0.012 or 0.004 pbw or even 0.001 to 0.003.

[0115] Demulsifiers are known in the art and include but are not limited to derivatives of propylene oxide, ethylene oxide, polyoxyalkylene alcohols, alkyl amines, amino alcohols, diamines or polyamines reacted sequentially with ethylene oxide or substituted ethylene oxides or mixtures thereof. Examples of demulsifiers include polyethylene glycols, polyethylene oxides, polypropylene oxides, (ethylene oxide-propylene oxide) polymers and mixtures thereof. In some embodiments, the demulsifiers is a polyether. Demulsifiers may be present in the composition from 0.002 to 0.012 pbw.

[0116] Pour point depressants are known in the art and include but are not limited to esters of maleic anhydride-styrene copolymers, polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkyl furanates, vinyl esters of fatty acids, ethylene-vinyl acetate copolymers, alkyl phenol formaldehyde condensation resins, alkyl vinyl ethers and mixtures thereof.

[0117] The compositions of the invention may also include a rust inhibitor, other than some of the additive described above. Suitable rust inhibitors include hydrocarbonyl amine salts of dialkylthiophosphoric acid, hydrocarbonyl amine salts of hydrocarbonyl arsensaliphonic acid, fatty carboxylic acids or esters thereof, an ester of a nitrogen-containing carboxylic acid, an ammonium sulfonate, an imidazoline, mono-thio phosphate salts or esters, or any combination thereof; or mixtures thereof.

[0118] Examples of hydrocarbonyl amine salts of dialkylthiophosphoric acid of the invention include but are not limited to those described above, as well as the reaction product(s) of dihexyl or diocetyl or dinonyl diothiophosphoric
acids with ethylenediamine, morpholine or Primene 81R or mixtures thereof. Suitable hydrocarbyl amine salts of hydrocarbyl arenesulphonic acids used in the rust inhibitor package of the invention are represented by the formula:

$$\text{(V)}$$

wherein Cy is a benzene or naphthalene ring. R$^{23}$ is a hydrocarbyl group with about 4 to about 30, preferably about 6 to about 25, more preferably about 8 to about 20 carbon atoms. Z is independently 1, 2, 3, or 4 and most preferably z is 1 or 2. R$^{23}$, R$^{24}$ and R$^{25}$ are as described above.

[0119] Examples of hydrocarbyl amine salts of hydrocarbyl arenesulphonic acid of the invention include but are not limited to the ethylenediamine salt of dinonylnaphthalene sulfonic acid.

[0120] Examples of suitable fatty carboxylic acids or esters thereof include glycerol monooleate and oleic acid. An example of a suitable ester of a nitrogen-containing carboxylic acid includes oleyl sarcosine.

[0121] The rust inhibitors may be present in the range from 0.02 to 0.2, from 0.03 to 0.15, from 0.04 to 0.12, or from 0.05 to 0.1 pbw of the lubricating oil composition. The rust inhibitors used in the invention may be used alone or in mixtures thereof.

[0122] The lubricating compositions of the invention may also include a metal deactivator. Metal deactivators are used to neutralize the catalytic effect of metal for promoting oxidation in lubricating oil. Suitable metal deactivators include but are not limited to triazoles, tolytriazoles, a thiadiazole, or combinations thereof, as well as derivatives thereof. Examples include derivatives of benzotriazoles other than those described above, benzimidazoles, 2-alkylthiobenzimidazoles, 2-alkylthiobenzothiazoles, 2-(N,N'-dialkylthiocarbamoyl)benzothiazoles, 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles, 2,5-bis(N,N'-dialkylthiocarbamoyl)-1,3,4-thiadiazoles, 2-alkylthiao-5-mercapto thiadiazoles or mixtures thereof. These additives may be used from 0.01 to 0.25 percent by weight in the overall composition.

[0123] In some embodiments, the metal deactivator is a hydrocarbyl substituted benzotriazole compound. The benzotriazole compounds with hydrocarbyl substitutions include at least one of the following ring positions 1- or 2- or 4- or 5- or 6- or 7-benzotriazoles. The hydrocarbyl groups contain about 1 to about 30, preferably about 1 to about 15, more preferably about 1 to about 7 carbon atoms, and most preferably the metal deactivator is 5-methylbenzotriazole used alone or mixtures thereof.

[0124] The metal deactivators are in the range from 0.01 to 0.1, from 0.01 to 0.04 or from 0.015 to 0.03 pbw of the lubricating oil composition. Metal deactivators may also be present in the composition from 0.002 to 0.004 to 0.02 pbw. The metal deactivator may be used alone or mixtures thereof.

[0125] Antioxidants may also be present including (i) an alkylated diphenylamine, and (ii) a substituted hydrocarbyl mono-sulphide. In some embodiments, the alkylated diphenylamines of the invention are bis- or octylated diphenylamine and bis-octylated diphenylamine. In some embodiments, the substituted hydrocarbyl mono-sulphides include n-dodecyl-2-hydroxyethyl sulphide, 1-(tert-dodecylthio)-2-propanol, or combinations thereof. In some embodiments, the substituted hydrocarbyl mono-sulphide is 1-(tert-dodecylthio)-2-propanol.

[0126] The antioxidant package may also include sterically hindered phenols. Examples of suitable hydrocarbyl groups include but are not limited to 2-ethylhexyl or n-butyl ester, dodecyl or mixtures thereof. Examples of methylene-bridged sterically hindered phenols include but are not limited to 4,4'-methylene-bis(6-tert-butyl o-cresol), 4,4'-methylene-bis(2-tert-amyl-o-cresol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-methylene-bis(2,6-di-tert-butylphenol) or mixtures thereof.

[0127] In some embodiments, the compositions of the invention are essentially free of, or even completely free of alkylated phenols, alkaryl amines, or both, or contain them at not more than 2.0 percent by weight, 1.0 percent by weight, or even 0.5 percent by weight where the percent by weight values refer to the total amount of alkylated phenols and/or alkaryl amines present in the overall lubricant.

EXEMPLARY EXAMPLES

[0128] The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the examples are provided to illustrate the invention, they are not intended to limit it.

Example Set 1

[0129] A set of examples of coal pulverizer lubricant compositions is prepared. The formulations of the examples are summarized in the table below in percent by weight, with the phosphorus-containing compound and nitrogen containing dispersant listed on an activs basis:

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Ex 1 COMP</th>
<th>Ex 2 COMP</th>
<th>Ex 3 COMP</th>
<th>Ex 4</th>
<th>Ex 5</th>
<th>Ex 6</th>
<th>Ex 7</th>
<th>Ex 8 COMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>99.26</td>
<td>97.80</td>
<td>98.6</td>
<td>95.55</td>
<td>96.87</td>
<td>96.45</td>
<td>97.81</td>
<td>96.66 NA</td>
</tr>
<tr>
<td>Medium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphorus-containing compound</td>
<td>0.74</td>
<td>0.74</td>
<td>0.74</td>
<td>0.74</td>
<td>0.74</td>
<td>0.74</td>
<td>0.74</td>
<td>0.74</td>
</tr>
<tr>
<td>Nitrogen Containing Dispersant</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

- Ex 1 COMP
- Ex 2 COMP
- Ex 3 COMP
- Ex 4
- Ex 5
- Ex 6
- Ex 7
- Ex 8 COMP
- Base
- Medium
- Phosphorus-containing compound
- Nitrogen Containing Dispersant
<table>
<thead>
<tr>
<th>TABLE 1-continued</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>COMP</td>
</tr>
<tr>
<td>Additional O.74</td>
</tr>
</tbody>
</table>

³The base medium is a mixture of polychloro-olefin (Group IV) base oil and polyethylene base oil. The same base medium is used in each example unless otherwise noted, and on a P8W basis is present in the same amount in each example. Differences in the percent by weight listed for each example is solely due to the different amounts of the phosphorus-containing compound and nitrogen containing dispersant that are in each example.

³The phosphorus-containing compound in the examples is an alkenyl phosphate.

³The nitrogen containing dispersant in the examples is a succinimide dispersant.

³The same additional additive package is used for each example, and on a P8W basis is present in the same amount in each example. Differences in the percent by weight listed for each example is solely due to the different amounts of the phosphorus-containing compound and nitrogen containing dispersant that are in each example.

³Example 9 is a commercially available lubricant marketed for this application. The formulation of the lubricant is not known and so the material is included only as an example of the conventional lubricants commercially available for this application.

0130] Each of the example lubricants is tested in a procedure that simulates the harsh conditions seen in the bearings of pulverizers, and specifically coal pulverizers. Coal dust is added to the example lubricant to simulate the contamination that occurs in the field and the impact on lubricant performance is measured to demonstrate the examples ability to provide acceptable performance under those conditions. The test uses a high load KRL type tester and a SNR 32008 C test bearing. The test procedure involves the following steps:

0131] (1) Clean a new test bearing in an ultrasonic bath with toluene for 15 minutes. Rinse with textile spirits and allow the bearing to dry.

0132] (2) Obtain the start of test bearing weight to the tenth of a milligram.

0133] (3) Place bearing in the test head of the KRL type tester.

0134] (4) Add 0.9 percent by weight coal dust to the example lubricant. Mix the lubricant and coal dust well using a high speed shaker and then fill the test head with 30 ml of the coal dust contaminated example lubricant.

0135] (5) Install test head into the KRL type tester.

0136] (6) Run the test conditions outlined in Table 2, which are designed to simulate the harsh conditions and manner of operation experienced in the bearings of pulverizers:

<table>
<thead>
<tr>
<th>TABLE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
</tr>
<tr>
<td>Break In</td>
</tr>
<tr>
<td>Break In</td>
</tr>
<tr>
<td>Break In</td>
</tr>
<tr>
<td>Break In</td>
</tr>
<tr>
<td>Break In</td>
</tr>
<tr>
<td>Break In</td>
</tr>
<tr>
<td>Break In</td>
</tr>
<tr>
<td>Break In</td>
</tr>
<tr>
<td>Test</td>
</tr>
</tbody>
</table>

0137] (7) At the end of test remove, save, and label the example lubricant.

0138] (8) Clean the test bearing by rinsing with textile spirits and then clean the bearing in ultrasonic bath with toluene for 15 minutes. Rinse again with textile spirits and allow the bearing to dry.

0139] (9) Obtain the end of test bearing weight to the tenth of a milligram.

0140] (10) Determine weight loss from the start and end of test weights and analyze the end of test example lubricant for the amount of wear metals.

0141] The results from the testing of the example lubricants are summarized in the table below:

<table>
<thead>
<tr>
<th>TABLE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex 1</td>
</tr>
<tr>
<td>COMP</td>
</tr>
<tr>
<td>Total Weight</td>
</tr>
<tr>
<td>Loss (mg)³</td>
</tr>
<tr>
<td>Iron in</td>
</tr>
</tbody>
</table>

³For the total weight loss, the lower the value the better the performance of the lubricant. Total weight loss is the more important result presented above in regard to evaluating lubricant performance.

³The results shown for Example 7 are the average of two test results.

³The results shown for Example 8 are the average of three test results.

³The results shown for Example 9 are the average of four test results.
The results show that the pulverizer bearing lubricants of the present invention, and the methods of using the same, can provide significant performance under the harsh conditions seen by pulverizer bearings. The described lubricants and methods are particularly advantageous compared to the current commercially available options for these applications.

Example Set 2

A second set of examples of coal pulverizer lubricant compositions is prepared without adding any additional additives. The formulations of the examples are summarized in the table below in percent by weight, with the phosphorus-containing compound and nitrogen containing dispersant listed on an actives basis:

| TABLE 4 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Ex 10³ | Ex 12³ | Ex 13³ | Ex 14³ | Ex 15³ | Ex 16³ | Ex 17³ | Ex 18³ |
| Base Medium    | NA     | NA     | 100    | 99.26  | 94.44  | 98.53  | 99.01  | 99.50  | 99.63  |
| Phosphorus-containing compound | NA | 0.50 | 0.00 | 0.50 | 3.70 | 0.98 | 0.99 | 0.00 | 0.25 |
| Nitrogen Containing Dispersant  | NA | 0.25 | 0.00 | 0.25 | 1.85 | 0.49 | 0.50 | 0.12 |
| Additional Additive³ | NA | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

The base medium is a mixture of polyisobutylene (Group IV) and polyisobutylene base oil. The same base medium is used in each example unless otherwise noted. See footnote 1 in Table 1 above.

The phosphorus-containing compound in the examples is an alkenyl phosphate.

The nitrogen containing dispersant in the examples is a succinimide dispersant.

Additional additives are added to these examples.

Example 10 is a commercially available lubricant marketed for this application. The formulation of the lubricant is not known and so the material is included only as an example of the conventional lubricants commercially available for this application.

Table 4 shows the results for the additive combination of the present invention.

The examples of Table 4 are evaluated in the same test procedure described above. The results are summarized in the table below:

| TABLE 5 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Ex 10² | Ex 12³ | Ex 13³ | Ex 14³ | Ex 16³ | Ex 17³ | Ex 18³ |
| Total Weight Loss (mg)¹ | 22.6 | 21.5 | 8.7 | 8.7 | 11.4 | 11.3 | 4.7 | 13.3 | 4.2 |
| Iron in Lubricant (ppm)² | 770 | 177 | 172 | 124 | 258 | 156 | 440 | 222 | 123 |

The results shown for Example 10 are the average of three test results.

The results shown for Example 11 are the average of four test results.

The results show that the pulverizer bearing lubricants of the present invention, and the methods of using the same, can provide significant performance under the harsh conditions seen by pulverizer bearings. The described lubricants and methods are particularly advantageous compared to the current commercially available options for these applications.

In particular, it is noted that the inventive examples (Examples 13, 14, 15, and 18) all have better weight loss results than the conventional and un-additized lubricants (Examples 10 and 12). Example 16 has a good weight loss result but the amount of iron in the lubricant at end of test is far too high. Likewise, Example 17 has a reasonable, but still high, amount of iron, but has high weight loss. In contrast, the inventive examples give a good balance of results in both areas. Furthermore, the top treated commercial example (Example 12) showed significant improvement as well, when the present invention was applied to it.
permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

What is claimed is:

1. A method of lubricating the bearings of a solid fuel pulverizer comprising the steps of:
   1. supplying to said bearings a lubricant composition comprising:
      (a) an oil of lubricating viscosity;
      (b) a phosphorus-containing compound; and
      (c) a nitrogen-containing dispersant;
   and wherein the lubricant composition optionally further comprises:
      (d) a sulfur-containing compound.

2. The method of claim 1 wherein the oil of lubricating viscosity comprises a mineral base oil.

3. The method of claim 2 wherein the oil of lubricating viscosity comprises a synthetic base oil.

4. The method of claim 1 wherein the phosphorus-containing compound comprises an alkyl phosphate, a phosphoric acid ester, an amine salt of a phosphoric acid ester, or some combination thereof.

5. The method of claim 1 wherein the nitrogen-containing dispersant comprises: a polyetheramine; a borated succinimide dispersant; a non-borated succinimide dispersant; a Mannich dispersant comprising the reaction product of a dialkyamine, an aldehyde and a hydrocarbyl substituted phenol; or any combination thereof.

6. The method of claim 5 wherein the nitrogen-containing dispersant comprises a non-borated succinimide dispersant derived from an aromatic amine.

7. The method of claim 1 wherein the lubricant composition further comprises: (d) a sulfur-containing compound.

8. The method of claim 1 wherein the phosphorus-containing compound comprises an alkyl phosphate and the nitrogen-containing dispersant comprises a non-borated succinimide dispersant.

9. The method of claim 1 wherein the phosphorus-containing compound is present in the lubricant composition from 0.01 to 5.0 percent by weight; and wherein the nitrogen-containing dispersant is present in the lubricant composition from 0.01 to 4.0 percent by weight.

10. A bearing lubricant for a solid fuel pulverizer comprising:
    (a) an oil of lubricating viscosity;
    (b) a phosphorus-containing compound; and
    (c) a nitrogen-containing dispersant.

11. The bearing lubricant of claim 10 wherein the phosphorus-containing compound comprises an alkyl phosphate, a phosphoric acid ester, an amine salt of a phosphoric acid ester, or some combination thereof.

12. The bearing lubricant of claim 10 wherein the nitrogen-containing dispersant comprises: a polyetheramine; a borated succinimide dispersant; a non-borated succinimide dispersant; a Mannich dispersant comprising the reaction product of a dialkyamine, an aldehyde and a hydrocarbyl substituted phenol; or any combination thereof.

13. The bearing lubricant of claim 10 wherein the phosphorus-containing compound is present in the lubricant composition from 0.01 to 5.0 percent by weight; and wherein the nitrogen-containing dispersant is present in the lubricant composition from 0.01 to 4.0 percent by weight.

14. The bearing lubricant of claim 10 wherein the bearing lubricant further comprises: (d) a sulfur-containing compound.

15. The use of a lubricant composition to improve the service life or durability of bearings in solid fuel pulverizing equipment, said lubricant composition comprising:
    (a) an oil of lubricating viscosity;
    (b) a phosphorus-containing compound; and
    (c) a nitrogen-containing dispersant.

* * * * *