

ADDITIVES AND LUBRICANT FORMULATIONS FOR IMPROVED CORROSION PROTECTION

TECHNICAL FIELD

- 5 The following disclosure is directed to lubricants, lubricant compositions and additives, lubricated parts and engines, and methods for lubricating moving parts to provide improved performance in harsh atmospheres.

BACKGROUND

- 10 Environmental concerns have led to continued efforts to reduce the CO, hydrocarbon and nitrogen oxide (NO_x) emissions of engines, particularly of compression ignition engines such as diesel engines. Several methods are currently used to reduce such emissions. One method used to reduce the emissions of diesel engines is known as exhaust gas recirculation or EGR. EGR reduces NO_x emissions
15 by introducing non-combustible components (exhaust gas) into the engine combustion chamber. The non-combustible components reduce the peak flame temperature and thus reduce NO_x formation. Additional reduction of NO_x emissions is achieved by cooling the exhaust gas before it is returned to the engine. A cooler combustion mixture leads to greater power generation and better fuel economy at a fixed NO_x
20 emission level.

While reducing NO_x emissions, EGR systems in engines increase the levels of NO_x and sulfur oxide (SO_x)-based acids and particulate matter in the lubricants circulated through such engines. The API CI-4 oil specification was established for lubricating oil compositions for use in cooled EGR equipped diesel engines.

- 25 Other methods for reducing emissions involve adjusting engine timing to provide an early close of the engine exhaust valve; use of a pilot fuel injector(s) upstream of the main fuel injectors to reduce NO_x generation; rate shaping of combustion to reduce the peak combustion temperature and reduce NO_x generation; forcing excess air into the combustion chamber using a turbocharger to boost power
30 output, and the use of catalytic after-treatment devices, such as devices containing oxidation catalysts to reduce levels of unburned hydrocarbons, carbon monoxide, nitrogen oxide and the soluble organic fraction of particulate matter in the engine exhaust gas.

- 35 However, diesel fuels contain sulfur. When a sulfur containing fuel is burned in an engine, the sulfur is converted to SO_x. Water vapor formed by the combustion

of the fuel mixes with the NO_x and SO_x to form corrosive acidic compounds such as nitric acid and sulfuric acid in the recirculated and cooled exhaust gases. Such acids attack metal components in the engines causing an increase in corrosion of such metal components. Improved protection of metal engine components is thus required for such applications.

Other harsh environments for lubricated parts and engines include, for example, marine applications where lubricated parts and engines are constantly exposed to a salt water atmosphere. Lubricants having improved corrosion protection characteristics are needed for such applications.

In view of the foregoing, lubricants are undergoing constant improvement to meet demanding needs and ever changing requirements. However, there continues to be a need for lubricant compositions and additives that can meet the demands of harsh environments as described above.

SUMMARY OF THE EMBODIMENTS

In one aspect, there is provided a lubricated surface comprising a thin film coating of a lubricant composition containing a base oil of lubricating viscosity and from about 9.5 to about 25 percent by weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of copolymer, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000 and wherein the amount of additive in the lubricant composition is based on a total weight of the lubricant composition.

In another aspect, there is provided a vehicle having moving parts and containing a lubricant for lubricating the moving parts, the lubricant comprising an oil of lubricating viscosity and from about 9.5 to about 25 percent by weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 10,000 to 100,000; and wherein the amount of additive in the lubricant composition is based on a total weight of the lubricant composition.

In yet another aspect, there is provided a fully formulated lubricant comprising a base oil component of lubricating viscosity and from about 9.5 to about 25 percent by weight of a lubricant additive comprising a nitrogen containing olefin copolymer derived from an

olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, and wherein the amount of additive in the lubricant composition is based on a total weight of the lubricant composition.

In a further aspect, there is provided a method for reducing corrosion of metal parts in an engine comprising contacting the engine parts with a lubricant composition comprising a base oil component of lubricating viscosity and from about 9.5 to about 25 percent by

weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, and wherein the amount of additive in the lubricant composition is based on a total weight of the lubricant composition.

In still another aspect, there is provided a lubricant additive concentrate comprising a diluent or carrier oil and from about 5 to about 90 percent by weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer dissolved in a suitable solvent, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, wherein the amount of additive in the concentrate is based on a total weight of the concentrate, and wherein a fully formulated lubricant composition containing the concentrate will contain from about 9.5 to about 25 percent by weight of the additive based on a total weight of the lubricant composition.

In yet another aspect, there is provided a method of lubricating moving parts of a vehicle, the method comprising using as a lubricating oil for one or more moving parts of the vehicle a lubricant composition containing a base oil and a lubricant additive, the lubricant additive comprising a diluent or carrier oil and a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0

carboxylic groups per 1000 number average molecular weight units of the copolymer dissolved in a suitable solvent, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, wherein the lubricant composition contains from about 9.5 to about 25 percent by weight of the additive based on a total weight of the lubricant composition.

In still another aspect, there is provided a method of lubricating moving parts comprising contacting the moving parts with a lubricant composition containing a lubricant additive, the lubricant additive comprising a diluent or carrier oil and a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer dissolved in a suitable solvent, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, wherein the lubricant composition contains from about 9.5 to about 25 percent by weight of the additive based on a total weight of the lubricant composition.

In yet another aspect, there is provided a metal surface comprising a corrosion inhibiting amount of an oleaginous coating composition containing from about 9.5 to about 25 percent by weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, and wherein the amount of additive in the composition is based on a total weight of the oleaginous coating composition.

Without desiring to be bound by theoretical considerations, it is believed that an additive including the nitrogen containing olefin component, when present in a lubricant composition in an amount of about 9.5 weight percent or more, forms an effective corrosion barrier film on a metal surface. The corrosion barrier film can effectively reduce or prevent contact between the surface and corrosive agents such as acids. The additive may be mixed with an oleaginous fluid and applied to a surface as a protective coating material. In other applications, the additive is provided in a fully formulated lubricant composition. Despite the presence of detergents and dispersants in the fully formulated lubricant composition, the nitrogen containing olefin component remains tightly adhered to a metal surface thereby prolonging its protective effects on the surface of the metal.

The compositions and methods described herein are particularly suitable for harsh environments such as present in marine applications and heavy duty diesel engines equipped with exhaust gas recirculation (EGR). Other features and advantages of the of the compositions and methods described herein will be evident by reference to the following detailed description which is intended to exemplify

aspects of the preferred embodiments without intending to limit the embodiments described herein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 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 a predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

10 (1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical);

15 (2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of the description herein, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

(3) hetero-substituents, that is, substituents which, while having a
20 predominantly hydrocarbon character, in the context of this description, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Hetero-atoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the
25 hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

In all of the embodiments of the disclosure, a particular lubricant component or additive is provided. The additive is referred to generally as a multi-functional viscosity index modifier. However, when used in fully formulated lubricant
30 compositions in amounts of 9.5 percent by weight or more, the lubricant additive provides an effective corrosion inhibiting film that is compatible with detergents and dispersants in the lubricant composition. Specifically, the lubricant additive includes a nitrogen containing olefin copolymer derived from a highly grafted, multi-functional olefin copolymer and a polyamine compound, generally as described in

U.S. Patent No. 6,107,257 to Valcho et al. The nitrogen containing olefin copolymer is dissolved in a suitable solvent such as Solvent Neutral 100 to provide the additive component.

5 One particularly useful nitrogen containing olefin copolymer is derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer. The carboxylic groups are subsequently reacted with amines to provide the nitrogen containing olefin copolymers. The olefin copolymer may have a number average molecular weight ranging from about 10,000 to about 100,000.

10 Another nitrogen containing olefin copolymer for use in lubricant compositions according to the disclosure is an olefin copolymer derived from a copolymer having grafted thereon from about 0.3 to about 0.75 carboxylic groups per 1000 number average molecular weight units of the copolymer. In this case, the copolymer may have a number average molecular weight ranging from about 30,000 to about 60,000.

15 Other nitrogen containing olefin copolymers which may be used according to the disclosure are described, for example, in U.S. Patent Nos. 4,089,794 to Engel et al., 4,137,185 to Gardiner et al., 4,146,489 to Stambaugh et al., 4,320,019 to Hayashi, 4,357,250 to Hayashi, 4,382,007 to Chafetz et al., 4,144,181 to Elliott et al., 20 4,863,623 to Nalesnik, 5,075,383 to Migdal et al., 5,556,923 to Caines et al., 5,932,525 to Ney et al., 5,162,086 to Migdal et al., and 5,744,429 to Chung et al. A particularly useful nitrogen containing olefin copolymer is described in U.S. Patent No. 6,107,257 to Valcho et al.

25 The terms polymer and copolymer are used generically to encompass ethylene copolymers, terpolymers or interpolymers. Such materials may contain minor amounts of other olefinic monomers so long as the basic characteristics of the ethylene copolymers are not materially changed.

30 The polymer or copolymer backbone of the lubricant component is a highly grafted, multi-functional olefin copolymer prepared from ethylene and propylene or it may be prepared from ethylene and at least one higher olefin within the range of C₃ to C₂₃ alpha-olefins. Copolymers of ethylene and propylene are most preferred. Other alpha-olefins suitable in place of propylene to form the copolymer or to be used in combination with ethylene and propylene to form a terpolymer include 1-butene, 1-pentene, 1-hexene, 1-octene and styrene; α,ω -diolefins such as 1,5-hexadiene, 1,6-

heptadiene, 1,7-octadiene; branched chain alpha-olefins such as 4-methylbutene-1, 5-methylpentene-1 and 6-methylheptene-1; and mixtures thereof.

More complex polymer backbones, often designated as interpolymers, may be prepared using a third component. The third component generally used to prepare an
5 interpolymers backbone is a polyene monomer selected from non-conjugated dienes and trienes. The non-conjugated diene component is one having from 5 to 14 carbon atoms in the chain. Preferably, the diene monomer is characterized by the presence of a vinyl group in its structure and can include cyclic and bicyclo compounds. Representative dienes include 1,4-hexadiene, 1,4-cyclohexadiene, dicyclopentadiene,
10 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 1,5-heptadiene, and 1,6-octadiene. A mixture of more than one diene can be used in the preparation of the interpolymers. A preferred non-conjugated diene for preparing a terpolymer or interpolymers substrate is 1,4-hexadiene.

The triene component will have at least two non-conjugated double bonds, and
15 up to about 30 carbon atoms in the chain. Typical trienes useful in preparing the interpolymers backbone are 1-isopropylidene-3 α ,4,7 α -tetrahydroindene, 1-isopropylidenedicyclopentadiene, dihydro-isodicyclopentadiene, and 2-(2-methylene-4-methyl-3-pentenyl)[2.2.1] bicyclo-5-heptene.

Ethylene-propylene or higher alpha-olefin copolymers may consist of from
20 about 15 to 80 mole percent ethylene and from about 85 to 20 mole percent C₃ to C₂₃ alpha-olefin with the preferred mole ratios being from about 35 to 75 mole percent ethylene and from about 65 to 25 mole percent of a C₃ to C₂₃ alpha-olefin, with the more preferred proportions being from 50 to 70 mole percent ethylene and 50 to 30 mole percent C₃ to C₂₃ alpha-olefin, and the most preferred proportions being from 55
25 to 65 mole percent ethylene and 45 to 35 mole percent C₃ to C₂₃ alpha-olefin.

Terpolymer variations of the foregoing polymers may contain from about 0.1 to 10 mole percent of a non-conjugated diene or triene.

The polymer backbone, that is the ethylene copolymer or terpolymer, is an oil-soluble, linear or branched polymer having a number average molecular weight from
30 about 20,000 to 100,000 as determined by gel permeation chromatography and universal calibration standardization, with a preferred number average molecular weight range of 30,000 to 60,000.

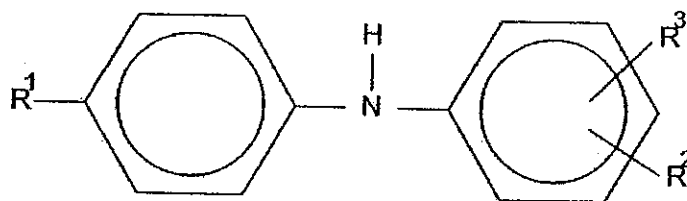
An ethylenically unsaturated carboxylic acid material is grafted onto the prescribed polymer backbone to form an acylated ethylene copolymer. These carboxylic reactants which are suitable for grafting onto the copolymer backbone contain at least one ethylenic bond and at least one, preferably two, carboxylic acid or its anhydride groups or a polar group which is convertible into said carboxyl groups by oxidation or hydrolysis. Preferably, the carboxylic reactants are selected from the group consisting of acrylic, methacrylic, cinnamic, crotonic, maleic, fumaric and itaconic reactants. More preferably, the carboxylic reactants are selected from the group consisting of maleic acid, fumaric acid, maleic anhydride, or a mixture of two or more of these. Maleic anhydride or a derivative thereof is generally most preferred due to its commercial availability and ease of reaction. In the case of unsaturated ethylene copolymers or terpolymers, itaconic acid or its anhydride is preferred due to its reduced tendency to form a cross-linked structure during the free-radical grafting process.

The ethylenically unsaturated carboxylic acid materials typically can provide one or two carboxylic groups per mole of reactant to the grafted polymer. That is, methyl methacrylate can provide one carboxylic group per molecule to the grafted polymer while maleic anhydride can provide two carboxylic groups per molecule to the grafted polymer.

The carboxylic reactant is grafted onto the prescribed polymer backbone in an amount to provide 0.15 to 1.0 carboxylic groups per 1000 number average molecular weight units of the polymer backbone, preferably 0.3 to 0.75 carboxylic groups per 1000 number average molecular weight. For example, a copolymer substrate with a number average molecular weight of 20,000 may be grafted with 3 to 20 carboxylic groups per polymer. A copolymer with a number average molecular weight of 100,000 may be grafted with 15 to 100 carboxylic groups per polymer chain.

The polymer intermediate possessing carboxylic acid acylating functions is reacted with a polyamine compound to provide the nitrogen containing olefin copolymer. The polyamine compound may be selected from the group consisting of:

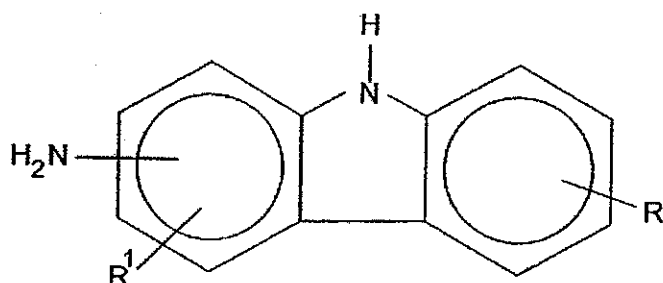
(a) an N-arylphenylenediamine represented by the formula:



- in which R^1 is hydrogen, $-NH$ -aryl, $-NH$ -arylalkyl, $-NH$ -alkyl, or a branched or straight chain radical having from 4 to 24 carbon atoms that can be alkyl, alkenyl, alkoxy, aralkyl, alkaryl, hydroxyalkyl or aminoalkyl; R^2 is $-NH_2$, $CH_2-(CH_2)_n-NH_2$, CH_2 -aryl- NH_2 , in which n has a value from 1 to 10; and R^3 is hydrogen, alkyl, alkenyl, alkoxy, aralkyl, alkaryl having from 4 to 24 carbon atoms;

(b) an aminothiazole from the group consisting of aminothiazole, aminobenzothiazole, aminobenzothiadiazole and aminoalkylthiazole;

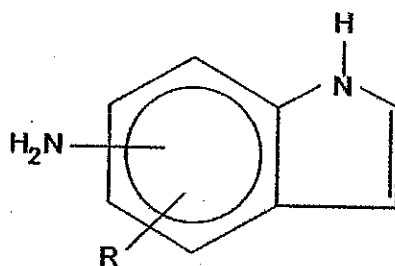
(c) an aminocarbazole represented by the formula:



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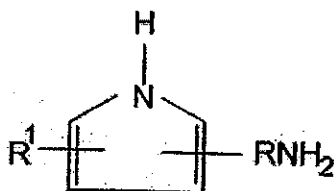
in which R and R^1 represent hydrogen or an alkyl, alkenyl, or alkoxy radical having from 1 to 14 carbon atoms;

(d) an aminoindole represented by the formula:



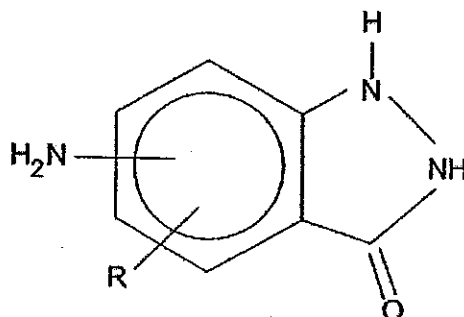
- 15 in which R represents hydrogen or an alkyl radical having from 1 to 14 carbon atoms;

(e) an aminopyrrole represented by the formula:



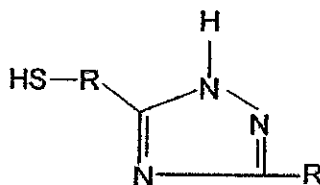
in which R is a divalent alkylene radical having from 2 to 6 carbon atoms and R¹ is hydrogen or an alkyl radical having from 1 to 14 carbon atoms;

(f) an amino-indazolinone represented by the formula:



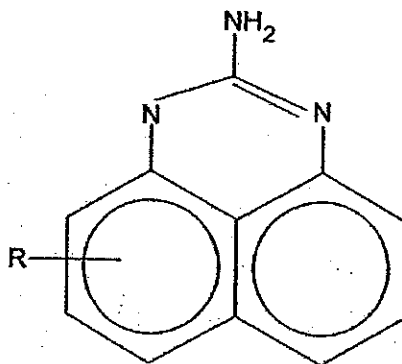
5 in which R is hydrogen or an alkyl radical having from 1 to 14 carbon atoms;

(g) an aminomercaptotriazole represented by the formula:



in which R can be absent or is a C₁-C₁₀ linear or branched hydrocarbon selected from the group consisting of alkyl, alkenyl, arylalkyl, or aryl;

10 (h) an aminoperimidine represented by the formula:



in which R represents hydrogen or an alkyl or alkoxy radical having from 1 to 14 carbon atoms;

(i) aminoalkyl imidazoles, such as 1-(2-aminoethyl) imidazole, 1-(3-aminopropyl) imidazole; and

(j) aminoalkyl morpholines, such as 4-(3-aminopropyl) morpholine.

Particularly preferred polyamines for reaction with the olefin copolymer are the N-arylphenylenediamines, more specifically the N-phenylphenylenediamines, for

example, N-phenyl-1,4-phenylenediamine, N-phenyl-1,3-phenylenediamine, and N-phenyl-1,2-phenylenediamine.

It is preferred that the polyamines contain only one primary amine group so as to avoid coupling and/or gelling of the olefin copolymers.

5 The highly grafted, multi-functional olefin copolymers may be post-treated so as to impart additional properties necessary or desired for a specific lubricant application. Post-treatment techniques are well known in the art and include boronation, phosphorylation, maleination, and reaction with an aldehyde, ketone, acid or acid anhydride.

10 Methods for stabilizing the color of nitrogen containing olefin copolymers using an aldehyde, ketone, acid or acid anhydride are known and are set forth, for example, in U.S. Patent No. 5,207,938.

15 The highly grafted, multi-functional olefin copolymers may be incorporated into a base oil in any convenient way. Thus, the highly grafted, multi-functional olefin copolymers may be added directly to the base oil by dispersing or dissolving the same in the lubricating oil at the desired level of concentration. Such blending into the base oil can occur at room temperature or elevated temperatures. Alternatively, the highly grafted, multi-functional olefin copolymers may be dissolved in a suitable solvent in an amount ranging from about 10 to about 20% by weight to
20 form a solution. The solution may be blended with a suitable oil-soluble solvent/diluent (such as benzene, xylene, toluene, lubricating base oils and petroleum distillates) to form a concentrate, and the concentrate then blended with a lubricating oil to obtain the final formulation. Such additive concentrates will typically contain (on an active ingredient (A.I.) basis, i.e., excluding the weight of impurities, diluents
25 and solvents typically associated therewith) from about 5 to about 90 wt. %, and preferably from about 40 to about 60 wt. %, highly grafted, multi-functional olefin copolymer solution, and typically from about 10 to 90 wt %, preferably from about 40 to 60 wt %, base oil based on the concentrate weight.

30 In the preparation of lubricating oil formulations it is common practice to introduce the additives in the form of 5 to 30 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent. Usually these concentrates may be diluted with 3 to 100, e.g., 5 to 40, parts by weight of lubricating oil per part by weight of the additive package in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling

of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend. Thus, the highly grafted, multi-functional olefin copolymer solution would usually be employed in the form of a 40 to about 60 wt. % concentrate, for example, in a lubricating oil fraction.

5 Lubricant compositions made with the additive containing the nitrogen containing olefin copolymer described above are used in a wide variety of applications. For compression ignition engines and spark ignition engines, it is preferred that the lubricant compositions meet or exceed published GF-4 or API-CI-4 standards. Lubricant compositions according to the foregoing GF-4 or API-CI-4
10 standards include a base oil and an oil additive package to provide a fully formulated lubricant. The base oil for lubricants according to the disclosure is an oil of lubricating viscosity selected from natural lubricating oils, synthetic lubricating oils and mixtures thereof. Such base oils include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal
15 combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil), liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types.
20 Oils of lubricating viscosity derived from coal or shale are also useful base oils. The synthetic lubricating oils used in this invention include one of any number of commonly used synthetic hydrocarbon oils, which include, but are not limited to, poly-alpha-olefins, alkylated aromatics, alkylene oxide polymers, interpolymers, copolymers and derivatives thereof here the terminal hydroxyl groups have been
25 modified by esterification, etherification etc, esters of dicarboxylic acids and silicon-based oils.

Fully formulated lubricants conventionally contain an additive package that will supply the characteristics that are required in the formulations. Among the types of additives included in the additive package are detergents/dispersants, friction
30 modifiers, seal swell agents, antiwear agents, extreme pressure agents, antioxidants, foam inhibitors, lubricity agents, rust inhibitors, corrosion inhibitors, demulsifiers, viscosity index improvers, dyes, and the like. Various of these components are well known to those skilled in the art and are preferably used in conventional amounts with the additives and compositions described herein.

For example, suitable detergents/dispersants are selected from the group consisting of, but not limited to, oil-soluble ashless dispersants having a basic nitrogen and/or at least one hydroxyl group in the molecule. Suitable detergents/dispersants include alkenyl succinimides, alkenyl succinic acid esters, alkenyl succinic ester-amides, Mannich bases, hydrocarbyl polyamines, polymeric polyamines, or olefin copolymers.

The alkenyl succinimides in which the succinic group contains a hydrocarbyl substituent containing at least 30 carbon atoms are described, for example, in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; and 4,234,435.

Alkenyl succinic acid esters and diesters of polyhydric alcohols containing 2-20 carbon atoms and 2-6 hydroxyl groups can be used in forming phosphorus-containing ashless dispersants. Representative examples are described in U.S. Pat. Nos. 3,331,776; 3,381,022; and 3,522,179.

Suitable alkenyl succinic ester-amides for forming phosphorylated ashless dispersant are described, for example, in U.S. Pat. Nos. 3,184,474; 3,576,743; 3,632,511; 3,804,763; 3,836,471; 3,862,981; 3,936,480; 3,948,800; 3,950,341; 3,957,854; 3,957,855; 3,991,098; 4,071,548; and 4,173,540.

Hydrocarbyl polyamines are described in U.S. Pat. Nos. 3,275,554; 3,394,576; 3,438,757; 3,454,555; 3,565,804; 3,671,511; and 3,821,302.

The Mannich base dispersants are preferably a reaction product of an alkyl phenol, typically having a long chain alkyl substituent on the ring, with one or more aliphatic aldehydes containing from 1 to about 7 carbon atoms (especially formaldehyde and derivatives thereof), and polyamines (especially polyalkylene polyamines). Examples of Mannich condensation products, and methods for their production are described in U.S. Pat. Nos. 2,459,112; 2,962,442; 2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,454,497; 3,459,661; 3,493,520; 3,539,633; 3,558,743; 3,586,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229; 3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,872,019; 3,904,595; 3,957,746; 3,980,569; 3,985,802; 4,006,089; 4,011,380; 4,025,451; 4,058,468; 4,083,699; 4,090,854; 4,354,950; and 4,485,023.

Polymeric polyamine dispersants suitable as the ashless dispersants of the present invention are polymers containing basic amine groups and oil solubilizing groups (for example, pendant alkyl groups having at least about 8 carbon atoms). Such materials are illustrated by interpolymers formed from various monomers such as decyl methacrylate, vinyl decyl ether or relatively high molecular weight olefins, with aminoalkyl acrylates and aminoalkyl acrylamides. Examples of polymeric polyamine dispersants are set forth in U.S. Pat. Nos. 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; and 3,702,300.

Olefin copolymer dispersants are described in US Patent Nos. 5,075,383 6,117,825; 6,107,258; 5,266,223; 5,350,532; 5,435,926; 4,952,637, 5,356,999, 5,374,364, and 5,424,366.

The various types of ashless dispersants described above may be phosphorylated by procedures described in U.S. Pat. Nos. 3,184,411; 3,342,735; 3,403,102; 3,502,607; 3,511,780; 3,513,093; 3,513,093; 4,615,826; 4,648,980; 4,857,214 and 5,198,133.

The dispersants of the present invention may be boronated. Methods for boronating (borating) the various types of ashless dispersants described above are described in U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 2,284,409; 2,284,410; 3,338,832; 3,344,069; 3,533,945; 3,658,836; 3,703,536; 3,718,663; 4,455,243; and 4,652,387.

Preferred procedures for phosphorylating and boronating ashless dispersants such as those referred to above are set forth in U.S. Pat. Nos. 4,857,214 and 5,198,133.

In the alternative, the dispersants described above may be glycolated and Mannich base coupled as described in U.S. Patent Nos. 4,633,322; and 5,122,161.

The amount of ashless dispersant on an active ingredient basis is generally within the range of about 0.5 to about 7.5 weight percent (wt %), typically within the range of about 0.5 to 5.0 wt %, preferably within the range of about 0.5 to about 3.0 wt %, and most preferably within the range of about 2.0 to about 3.0 wt %, based on the finished oil.

Suitable friction modifiers are described in U.S. Pat. Nos. 5,344,579; 5,372,735; and 5,441,656. Seal swell agents are described, for example, in U.S. Patent Nos. 3,794,081 and 4,029,587. Antiwear and/or extreme pressure agents are disclosed in U.S. Patent Nos. 4,857,214; 5,242,613; and 6,096,691. Suitable

antioxidants are described in U.S. Patent Nos. 5,559,265; 6,001,786; 6,096,695; and 6,599,865. Foam inhibitors suitable for compositions and additives described herein are set forth in U.S. Patent Nos. 3,235,498; 3,235,499; and 3,235,502. Rust or corrosion inhibitors are described in U. S. Pat. Nos. 2,765,289; 2,749,311; 2,760,933; 2,850,453; 2,910,439; 3,663,561; 3,862,798; and 3,840,549. Viscosity index improvers and processes for making them are taught in, for example, U.S. Pat. Nos. 4,732,942; 4,863,623; 5,075,383; 5,112,508; 5,238,588; and 6,107,257. Multi-functional viscosity index improvers are taught in U.S. Pat. Nos. 4,092,255; 4,170,561; 4,146,489; 4,715,975; 4,769,043; 4,810,754; 5,294,354; 5,523,008; 5,663,126; and 5,814,586; and 6,187,721. Demulsifiers are described in U.S. Patent Nos. 4,444,654 and 4,614,593.

Base oils suitable for use in formulating the compositions, additives and concentrates described herein may be selected from any of the synthetic or natural oils or mixtures thereof. The synthetic base oils include alkyl esters of dicarboxylic acids, polyglycols and alcohols, poly-alpha-olefins, including polybutenes, alkyl benzenes, organic esters of phosphoric acids, and polysilicone oils. Natural base oils include mineral lubrication oils which may vary widely as to their crude source, e.g., as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. The base oil typically has a viscosity of about 2.5 to about 15 cSt and preferably about 2.5 to about 11 cSt at 100° C.

Accordingly, the base oil used which may be used may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. Such base oil groups are as follows:

Base Oil Group ¹	Sulfur (wt.%)		Saturates (wt.%)	Viscosity Index
Group I	> 0.03	and/or	< 90	80 to 120
Group II	≤ 0.03	And	≥ 90	80 to 120
Group III	≤ 0.03	And	≥ 90	≥ 120
Group IV	all polyalphaolefins (PAOs)			
Group V	all others not included in Groups I-IV			

¹Groups I-III are mineral oil base stocks.

The additives used in formulating the compositions described herein can be blended into the base oil individually or in various sub-combinations. However, it is preferable to blend all of the components concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent). The use of an additive

concentrate takes advantage of the mutual compatibility afforded by the combination of ingredients when in the form of an additive concentrate. Also, the use of a concentrate reduces blending time and lessens the possibility of blending errors.

The following example is given for the purpose of exemplifying aspects of the
5 embodiments and is not intended to limit the embodiments in any way.

Example

A heavy duty diesel lubricant formulation (SAE 15W-40) was prepared in a CITGO/Yubase base stock and included 10 % by weight solution of HiTEC® 5777D (nitrogen containing olefin copolymer solution in solvent neutral 100 diluent)
10 available from Ethyl Corporation of Richmond Virginia, 0.2 % by weight pour point depressant (HiTEC® 5789), 14.8 % by weight dispersant inhibitor package (HiTEC® 1229), and 0.2 % by weight amine antioxidant (HiTEC® 7190). ASTM D665 carbon steel rust pins were twice dipped in the lubricant formulation set forth above and in a lubricant formulation absent nitrogen containing olefin copolymer component. The
15 pins were then placed in 37 wt. % hydrochloric acid at room temperature in closed glass jars. The corrosion potential of the lubricants was assessed by monitoring the amount of gas bubbles generated by the reaction of hydrochloric acid on the metals. A ranking system ranging from 0-10 with 10 being the most bubbles was used to compare the results. The lubricant formulation containing the nitrogen containing
20 olefin copolymer had a ranking of 3 while the lubricant formulation having an absence of the nitrogen containing olefin copolymer had a ranking of 8. It was concluded that a lubricant formulation containing 10 wt.% or more of the nitrogen containing olefin copolymer solution provided superior corrosion protection in acid atmospheres.

25 At numerous places throughout this specification, reference has been made to a number of U.S. Patents. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

The foregoing embodiments are susceptible to considerable variation in its practice. Accordingly, the embodiments are not intended to be limited to the specific
30 exemplifications set forth hereinabove. Rather, the foregoing embodiments are within the spirit and scope of the appended claims, including the equivalents thereof available as a matter of law.

The patentees do not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally

fall within the scope of the claims, they are considered to be part hereof under the doctrine of equivalents.

What is claimed is:

1. A lubricated surface comprising a thin film coating of a lubricant composition containing a base oil of lubricating viscosity and from about 9.5 to about 25 percent by weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, and wherein the amount of additive in the lubricant composition is based on a total weight of the lubricant composition.
2. The lubricated surface of claim 1, wherein the lubricated surface comprises an engine drive train.
3. The lubricated surface of claim 1, wherein the lubricated surface comprises an internal surface or component of an internal combustion engine.
4. The lubricated surface of claim 1, wherein the lubricated surface comprises an internal surface or component of a compression ignition engine.
5. The lubricated surface of claim 1, wherein the copolymer has grafted thereon from about 0.3 to about 0.75 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 30,000 to about 60,000.
6. A motor vehicle comprising the lubricated surface of claim 1.
7. A vehicle having moving parts and containing a lubricant for lubricating the moving parts, the lubricant comprising an oil of lubricating viscosity and from about 9.5 to about 25 percent by weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, and wherein the amount of additive in the lubricant composition is based on a total weight of the lubricant composition.

8. The vehicle of claim 7, wherein the copolymer has grafted thereon from about 0.3 to about 0.75 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 30,000 to about 60,000.

9. The vehicle of claim 7, wherein the moving parts comprise a heavy duty diesel engine including exhaust gas recirculation and a lubricating system for the engine.

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10. A fully formulated lubricant composition comprising a base oil component of lubricating viscosity and from about 9.5 to about 25 percent by weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, and wherein the amount of additive in the lubricant composition is based on a total weight of the lubricant composition.

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11. The lubricant composition of claim 10 wherein the lubricant composition comprises a low ash, low sulfur lubricant compositions suitable for compression ignition engines.

12. The lubricant composition of claim 10, wherein the copolymer has grafted thereon from about 0.3 to about 0.75 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 30,000 to about 60,000.

13. A method for reducing corrosion of metal parts in an engine comprising contacting the engine parts with a lubricant composition comprising a base oil component of lubricating viscosity and from about 9.5 to about 25 percent by weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein

the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, and wherein the amount of additive in the lubricant composition is based on a total weight of the lubricant composition.

5 14. The method of claim 13 wherein the engine comprises a diesel engine provided with exhaust gas recirculation.

15 15. The method of claim 13 wherein the engine comprises an inboard or outboard marine engine.

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16. The method of claim 13 wherein the engine comprises an engine exposed to a salt water environment.

15 17. The method of claim 13, wherein the copolymer has grafted thereon from about 0.3 to about 0.75 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 30,000 to about 60,000.

20 18. A lubricant additive concentrate comprising a diluent or carrier oil and from about 5 to about 90 percent by weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer dissolved in a suitable solvent, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, 25 wherein the amount of additive in the concentrate is based on a total weight of the concentrate, and wherein a fully formulated lubricant composition containing the concentrate will contain from about 9.5 to about 25 percent by weight of the additive based on a total weight of the lubricant composition.

30 19. The additive concentrate of claim 18, wherein the copolymer has grafted thereon from about 0.3 to about 0.75 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 30,000 to about 60,000.

20. A lubricant composition comprising a base oil and the additive concentrate of claim 18.

21. A method of lubricating moving parts of a vehicle, the method comprising
5 using as a lubricating oil for one or more moving parts of the vehicle a lubricant composition containing a base oil and a lubricant additive, the lubricant additive comprising a diluent or carrier oil and a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0
10 carboxylic groups per 1000 number average molecular weight units of the copolymer dissolved in a suitable solvent, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, wherein the lubricant composition contains from about 9.5 to about 25 percent by weight of the additive based on a total weight of the lubricant composition.

15 22. The method of claim 21 wherein the vehicle includes a diesel engine provided with exhaust gas recirculation and wherein the moving parts include moving parts of the engine.

23. The method of claim 21 wherein the vehicle includes a marine vehicle
20 having an engine, and wherein the moving parts include moving parts of the engine.

24. The method of claim 21, wherein the copolymer has grafted thereon from about 0.3 to about 0.75 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular
25 weight ranging from about 30,000 to about 60,000.

25. The method of claim 21 wherein the vehicle includes an internal combustion engine having a crankcase and wherein the lubricant composition comprises a crankcase oil present in the crankcase of the vehicle.
30

26. The method of claim 21 wherein the lubricant composition comprises a drive train lubricant present in an automotive drive train of the vehicle.

27. A method of lubricating moving parts comprising contacting the moving parts with a lubricant composition containing a lubricant additive, the lubricant additive comprising a diluent or carrier oil and a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0
5 carboxylic groups per 1000 number average molecular weight units of the copolymer dissolved in a suitable solvent, wherein the copolymer has a number average molecular weight ranging from about 10,000 to about 100,000, wherein the lubricant composition contains from about 9.5 to about 25 percent by weight of the additive based on a total weight of the lubricant composition.

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28. The method of claim 27 wherein the moving parts comprise moving parts of a vehicle.

29. The method of claim 28 wherein the vehicle includes a marine vehicle
15 having an engine, and wherein the moving parts include moving parts of the engine.

30. The method of claim 27, wherein the copolymer has grafted thereon from about 0.3 to about 0.75 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular
20 weight ranging from about 30,000 to about 60,000.

31. The method of claim 27 wherein the moving parts include an internal combustion engine having a crankcase and wherein the lubricant composition comprises a crankcase oil present in the crankcase of the vehicle.

25

32. The method of claim 27 wherein the lubricant composition comprises a drive train lubricant present in an automotive drive train of the vehicle.

33. A metal surface comprising a corrosion inhibiting amount of an
30 oleaginous coating composition containing from about 9.5 to about 25 percent by weight of an additive comprising a nitrogen containing olefin copolymer derived from an olefin copolymer having grafted thereon from about 0.15 to about 1.0 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 10,000 to

about 100,000, and wherein the amount of additive in the composition is based on a total weight of the oleaginous coating composition.

34. The metal surface of claim 33, wherein the copolymer has grafted thereon
5 from about 0.3 to about 0.75 carboxylic groups per 1000 number average molecular weight units of the copolymer, wherein the copolymer has a number average molecular weight ranging from about 30,000 to about 60,000.