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(54) **Overbased lithium salt lubricant additives and production thereof**

(57) A lubricant additive concentrate which comprises a base oil of lubricating viscosity and:

(a) at least one non-lithium oil-soluble overbased al-

kali or alkaline earth metal-containing overbased detergent; and

(b) at least one oil-soluble overbased lithium salt detergent.

EP 0 731 159 A2

DescriptionTechnical Field

5 The present invention is in the field of lubricant additives, and the lubricants and lubricant concentrates containing them. A method for producing highly basic lithium sulfonate products suitable for use in lubricant and fuel applications is disclosed. The invention also includes a product produced by the inventive method, and a method of its use.

Background

10 Applications- of lubricants often require the lubricant to possess a high basicity. This basicity is usually acquired through the addition of highly basic surface active or "detergent" additives. These detergents, especially in engine crankcase applications, aid lubrication by neutralizing oxidized species which are produced as a result of combustion processes, by acting as surface active agents to "clean" particulates which accumulate on engine parts, and/or by
15 aiding in the dispersion of suspended solids which accumulate in the lubricant. This invention deals with highly basic or "overbased" lithium sulfonate detergents which possess a significant amount of colloiddally suspended basic carbonates.

In the field of lubricant additives, there are many patents which teach processes for making overbased additives containing alkali metal or alkaline earth metals. The following may be considered examples of preparations to over-based additives: GB Nos. 1388021; 1551820; 2055885; 2055886 and U.S. Pat. Nos. 3,346,493; 3,428,561; 3,437,465; 3,471,403; 3,488,284; 3,489,682; 4,137,186; and 4,326,972. More specifically, U.S. Patent No. 4,797,217 to Cleverley teaches how to make a lithium sulfonate overbased detergent via the use of lithium hydroxide monohydrate and an alkoxyalkanol promoter. Such earlier methods described in the literature for preparing overbased lithium sulfonate required the use of 2-ethoxyethanol, which is both toxic and expensive.

25 Prior art processes, such as those typified by that disclosed in U.S. Patent No. 4,797,217, require the azeotropic removal of water during the initial stages of the alkoxyalkanol process. Alkoxyalkanols must also be removed by heating in order to purify and recycle the promoter. U.S. Patent No. 4,797,217 teaches that the azeotropic removal of water must be done before the carbonization step to avoid turbidity in the final product.

30 With respect to the importance of ash levels in lubricants, A. A. Schetelich, SAE Technical paper Series, Paper No. 831722 (1983) reports on the effect of lubricating oil parameters on PC-1 type heavy duty diesel lubricating oil performance. It is noted that over the past 30 years, the trend in heavy duty diesel oil industry has been to decrease the sulfated ash levels from 2.5 wt. % sulfated ash (SASH) in 1960 to the typical North American SASH level of 0.8 to 1 wt. %, and to correspondingly decrease the HD oils total base number (TBN) (by ASTM method D-2896) values from over 20 to the present typical North American TBN values of from 7 to 10. Such reductions in SASH and TBN levels
35 are attributed by the author to be due to improvement in performance of ashless components, including ashless diesel detergents and ashless dispersants. In diesel engine tests, no significant correlation was seen between the level of either piston deposits or oil consumption and the SASH and TBN levels, for about 1% to 2% SASH levels and about 8 to 17 TBN levels. In contrast, a significant correlation was seen between the level of ashless component treat and the amount of piston deposits (at the 92% confidence level) and oil consumption (at the 98% confidence level). It is noted by the authors that this correlation is drawn with respect to diesel fuels having average sulfur levels of less than about 0.5%. It is indicated that the level of buildup of ash is accelerated in the hotter engine areas. The author concludes that at the 97% confidence level there should be a correlation between oil consumption and piston deposits, especially top land deposits, which are believed to contribute to increased oil consumption due to two phenomena: (1) these deposits decrease the amount of blow-by flowing downwardly past the top land, which results in a decreased gas
40 loading behind the top ring of the piston, which in turn leads to higher oil consumption; and (2) increased bore polishing of the piston cylinder liner by the top land deposits which in turn contributes to higher oil consumption by migration of the oil into the firing chamber of the cylinder along the polished bore paths. Therefore, the Paper concluded that reduced ash in the oil should be sought to reduce top land deposits, and hence oil consumption.

45 One of the standing problems in the lubrication in high-soot combustion engines, particularly diesel engines, is to inhibit viscosity increase while being able to disperse soot. This is especially problematic in older diesel engines that use wholly mechanical fuel delivery systems. Such systems are subject to ignition retard which results in greater amounts of combustion products being deposited on the combustion chamber walls.

50 Another problem encountered in internal combustion engines using fluoropolymer seals, such as Viton seals, is that many overbased additives can degrade these seals over time. Also, those additives containing sodium may mask internal engine coolant leakage tests which rely on the detection of sodium. Also, additives containing sodium may corrode Inconel valves, such as those used in diesel engines.

55 Accordingly, it is an object to provide highly basic lithium additives by a process which uses less costly and toxic reactants, and one that inhibits viscosity increase as soot content increases, as measured, for instance, by the Mack

T-8 soot dispersancy test.

Another object of the present invention is to provide highly basic lithium additives by a process that can proceed at a lower temperature during the carbonation step.

It is also an object of the present invention to produce highly basic lithium additives by a process which requires fewer steps and is able to provide a more easily regenerated promoter.

Still another object of the present invention is to provide highly basic lubricant additives which are relatively less corrosive on fluoropolymer engine seals, and to provide a lubricant which will not mask engine leakage tests.

Other advantages of the present invention may become apparent to one of ordinary skill in light of the disclosure of the invention or its practice.

Summary of the Invention

Advantageous lubricant additives are developed through the use of a combination of at least one overbased lithium salt and at least one non-lithium overbased salt. Also included are lubricant concentrates and lubricants containing additives in accordance with the invention; and a method of lubricating using such lubricants.

The invention also includes a method of making these additives using a non-alkoxyalcohol/water promoter system. Also included are lubricant concentrates and lubricants containing additives made in accordance with the invention; and a method of lubricating using such lubricants.

The overbased lithium salt detergent additives of the present invention typically have a total base number ("TBN") in the range of 240 to 400.

The lubricant composition of the present invention, in broadest terms comprises: (a) at least one non-lithium oil-soluble overbased alkali or alkaline earth metal-containing overbased detergent; (b) at least one oil-soluble overbased lithium salt detergent; and (c) at least one oil of lubricating viscosity. It is also preferred that the oil-soluble overbased lithium salt detergent(s) be present in an amount no greater than about 0.5 times the total amount of the non-lithium oil-soluble overbased alkali or alkaline earth metal-containing overbased detergent(s).

The oil-soluble overbased lithium salt detergent(s) may be selected from the group consisting of lithium sulfonates, lithium phenates, lithium carboxylates and lithium salicylates, preferably lithium sulfonate. The oil-soluble overbased lithium salt detergent(s) are present in a preferred amount of at least about 0.08 percent of the lubricant.

The non-lithium oil-soluble overbased alkali or alkaline earth metal-containing overbased detergent(s) may be selected from the group consisting of phenates, sulfonates and salicylates of calcium, magnesium, potassium and sodium, their sulfurized and aromatic derivatives, and mixtures thereof.

The present invention also includes a lubricant additive concentrate containing a lubricant additive in accordance with the present invention. The overbased lithium salt detergent is preferably present in an amount of at least about 0.6 percent by weight of the concentrate. Such a concentrate may contain any one or more of the additional components typically included in lubricant additive concentrates, such as antioxidants, corrosion inhibitors, antifoam agents, anti-wear agents, anti-rust agents, extreme pressure additives, dispersants, ashless dispersants, pour point depressants, viscosity improvers, friction modifiers, seal swell agents and base oils. Examples of these additional additive components are described below.

The present invention also includes a lubricant containing an additive in accordance with the present invention. As referred to herein, the term "lubricant" will be understood as including at least one base oil and any additional component(s) not otherwise contained in the lubricant additive or lubricant additive concentrate. For instance, the lubricant may be made up of one or more base oils, the multi-component lubricant additive concentrate, and additional components such as viscosity increase improvers and pour point depressants which may be added separately.

Base Oils

The additive combinations of this invention can be incorporated in a wide variety of lubricants and functional fluids in effective amounts to provide suitable active ingredient concentrations. The base oils useful herein can be hydrocarbon oils of suitable viscosities; synthetic oils such as hydrogenated polyolefin oils; poly- α -olefin oligomers (such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol; alkyl esters of carbonic or phosphoric acids; polysilicones; fluorohydrocarbon oils; and mixtures of mineral, natural and/or synthetic oils in any proportion, etc. The term "base oil" for this disclosure includes all the foregoing.

The additive combinations of this invention can thus be used in lubricating oil and functional fluid compositions, such as automotive crankcase lubricating oils, automatic transmission fluids, gear oils, hydraulic oils, cutting oils, etc., in which the base oil of lubricating viscosity is a mineral oil, a synthetic oil, a natural oil such as a vegetable oil, or a mixture thereof, e.g. a mixture of a mineral oil and a synthetic oil.

It is also possible in accordance with this invention to utilize blends of one or more liquid hydrogenated 1-alkene oligomers in combination with other oleaginous materials having suitable viscosities, provided that the resultant blend

has suitable compatibility and possesses the physical properties desired.

Typical natural oils that may be used as base oils or as components of the base oils include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and the like. Such oils may be partially or fully hydrogenated, if desired.

The fact that the base oils used in the compositions of this invention may be composed of (i) one or more mineral oils, (ii) one or more synthetic oils, (iii) one or more natural oils, or (iv) a blend of (i) and (ii), or (i) and (iii), or (ii) and (iii), or (i), (ii) and (iii) does not mean that these various types of oils are necessarily equivalents of each other. Certain types of base oils may be used in certain compositions for the specific properties they possess such as high temperature stability, non-flammability or lack of corrosivity towards specific metals (e.g. silver or cadmium). In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the various types of base oils discussed above may be used in the compositions of this invention, they are not necessarily functional equivalents of each other in every instance.

Proportions and Concentrations

In general, the components of the additive compositions of this invention are employed in the oleaginous liquids (e.g., lubricating oils and functional fluids) in minor amounts sufficient to improve the performance characteristics and properties of the base oil or fluid employed, the viscosity characteristics desired in the finished product, the service conditions for which the finished product is intended, and the performance characteristics desired in the finished product. However, generally speaking, it is preferred that the overbased lithium salt detergent be present in an amount of at least about 0.08 percent by weight of the total lubricant blend.

The concentrations (weight percentage of active ingredient) of typical optional ingredients in the oleaginous liquid compositions of this invention are generally as follows :

	Typical Range	Preferred Range
Antioxidant	0 - 4	0.05 - 2
Corrosion Inhibitor	0 - 3	0.02 - 1
Foam inhibitor	0 - 0.3	0.0002 - 0.1
Neutral Metal Detergent	0 - 3	0 - 2.5
Supplemental Antiwear EP Agent	0 - 5	0 - 2
Supplemental Ashless Dispersant	0 - 10	0 - 5
Pour Point Depressant	0 - 5	0 - 2
Viscosity Index Improver	0 - 20	0 - 12
Friction Modifier	0 - 3	0 - 1
Seal Swell Agent	0 - 20	0 - 10
Dye	0 - 0.1	0 - 0.05

It will be appreciated that the additive of the present invention, and any and all auxiliary components employed, can be separately blended into the base oil or fluid or can be blended therein in various subcombinations, if desired. Moreover, such components can be blended in the form of separate solutions in a diluent. Except for viscosity index improvers and/or pour point depressants (which are usually blended apart from other components), it is preferable to blend the components used in the form of an additive concentrate of this invention, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate.

When forming the lubricant compositions of the present invention, it is usually desirable to introduce the additive ingredients into the base oil with stirring and application of mildly elevated temperatures, as this facilitates the dissolution of the components in the oil and achieves product uniformity.

Lubricants of the present invention include those adapted for use in diesel engines. Such lubricants typically have a sulfated ash content in the range of from about 0.5 to about 2.2 percent by weight, preferably in the range of from about 0.7 to about 1.8 percent by weight, and most preferably in the range of from about 0.8 to about 1.5 percent by weight.

The present invention further includes a method for improving the performance of a lubricant oil adapted for use in an engine, such method involving including in the engine's oil an effective amount of a lubricant additive of the present invention. The method of the present invention may be performed on any internally lubricated engine, such as gasoline or diesel engines.

Also disclosed is a method for preparing an overbased lubricant additive.

The process is novel in part because a non-alkoxy-alcohol, preferably hydrocarbon-based (mono-functional) alcohol (i.e. an alcohol having no other functional group other than the alcohol OH group) is used to promote carbonation. The lithium sulfonate useful herein has been shown to inhibit viscosity increase in the Mack T-8 soot dispersancy test.

The process of the present invention enables one to produce highly basic lithium sulfonate detergents having relatively high total base numbers (TBN) of 240 mg KOH/g or more. TBN is a measure of the basicity of a product and is measured by the method ASTM D-2896.

The process of the present invention produces an overbased lithium detergent, and, in broadest terms comprises

(a) combining the following: (i) a lithium source, said lithium source selected from the group consisting of anhydrous lithium hydroxide and monohydrated lithium hydroxide and mixtures thereof; (ii) at least one source of sulfonic acid or salt thereof; and (iii) at least one non-alkoxy alcohol selected from the group consisting of primary, secondary and tertiary alcohols; so as to produce a mixture comprising lithium hydroxide and at least one sulfonate; and (b) combining said mixture resulting from step (a) with a source of carbon dioxide so as to convert at least a portion of said lithium hydroxide to lithium carbonate.

Typically the mixture resulting from step (b) will contain an aqueous portion (usually brought about through the use of the monohydrated lithium hydroxide). This aqueous portion is normally removed from the reaction mixture resulting from step (b). This may be done by any method appropriate to the production of overbased materials, such as by application of heat, application of vacuum, or a combination thereof.

The mixture resulting from step (b) may also contain unreacted lithium salts depending, for instance on reaction conditions and stoichiometry of the reactants. The method of the present invention also preferably may involve the step of removing any such unreacted lithium salts the mixture resulting from step (b). This may be done by any method appropriate to the production of overbased materials, such as by filtration.

The method of the present invention has been found to benefit from the presence of at least a small amount of water during the reaction process. This water may be supplied in the form of water of crystallization, such in the form of the monohydrate lithium salt, or may be supplied as liquid water, ice or steam. In this regard, where only anhydrous lithium hydroxide is used, a small amount of water should be included in the reaction mixture in order to be able to produce a lithium additive of the present invention with an effective TBN level.

It is also preferred that the mixture combined in step (a) additionally comprises at least one organic diluent, which assists in the interaction of the reactants. Such organic diluents may include hexane, heptane, octane, decane, dodecane, benzene, toluene, xylene, toluene, white spirit, naphtha, isoparaffins, raffinate, and mixtures thereof. Typically, the solvent is a hydrocarbon, but it may be a halogenated hydrocarbon, for example chlorobenzene. The most preferred solvents are hydrocarbons. Commercial raffinate, a mixture of low boiling hydrocarbons, is used in most of the Examples given below. The diluent(s) is/are preferably removed by any method appropriate to the production of overbased materials, such as by application of heat, application of vacuum, or a combination thereof. The diluent(s) may be removed prior to or subsequent to step (b); preferably subsequent to step (b).

When both monohydrated lithium hydroxide and anhydrous hydroxide are present, it is preferred that the molar ratio of said monohydrated lithium hydroxide to said anhydrous lithium hydroxide is in the range of from about 1:10 to about 10:1, and more preferably in the range of from about 1:1 to about 4:1.

It is also preferred that the molar ratio of the total alcohol to the total amount of lithium hydroxide combined or produced in step (a) is in the range of from about 0.5:1 to about 5:1.

The preferred non-alkoxy alcohols are those from 1 to 10 carbons; most preferably from 1 to 4 carbons. Examples include 2-methyl hexanol and methanol. The most preferred alcohol is methanol.

With respect to the source(s) of sulfonic acid, it is preferred that the molar ratio of the total source of sulfonic acid to the total amount of lithium hydroxide combined in step (a) is in the range of from about 1:5 to about 1:35; more preferably in the range of from about 1:10 to about 1:30; and most preferably in the range of from about 1:10 to about 1:20.

The source of carbon dioxide may be any source appropriate to the production of overbased materials, such as, for example, gaseous carbon dioxide, liquid carbon dioxide and solid carbon dioxide.

It is also preferred that the mixture combined in step (a) additionally comprises at least one surfactant of a molecular weight in the range of from about 240 to about 1400, more preferably in the range of from about 900 to about 1100.

The preferred method of combining the mixture combined in step (a) is under reflux conditions.

The lubricant additives of the present invention typically and preferably will have a TBN in the range of from about 240 to about 400.

The invention includes lubricant additives made by the method of the invention, and lubricant concentrates and lubricants containing them. Such lubricant concentrates and lubricants may be made using the components described above, and in accordance with methods known in the art.

The Lithium Source

Anhydrous and/or monohydrated lithium hydroxide may be used as the source(s) of lithium. These materials are readily available commercial products and are often used in the manufacture of lithium greases. The ratio of monohydrated to anhydrous lithium hydroxide may vary, but usually is between 1:10 and 10:1, and preferably more specifically between 1:1 to 4:1. The amount of lithium hydroxide added being enough to neutralize all the organic acid or anhydride species and create at least 240 mg KOH equivalence per gram of final product.

The Non-Lithium Overbased Metal Detergent(s)

Examples of suitable non-lithium overbased metal-containing detergents include, but are not limited to, overbased salts of such substances as sodium phenates, potassium phenates, calcium phenates, magnesium phenates, sulfurized sodium phenates, sulfurized potassium phenates, sulfurized calcium phenates, and sulfurized magnesium phenates wherein each aromatic group has one or more aliphatic sulfonates, and magnesium sulfonates wherein each sulfonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility; sodium salicylates, potassium salicylates, calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic substituents to impart hydrocarbon solubility; the sodium, potassium, calcium and magnesium salts of hydrolyzed phosphosulfurized olefins having 10 to 2,000 carbon atoms or of hydrolyzed phosphosulfurized alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2,000 carbon atoms; sodium, potassium, calcium and magnesium salts of aliphatic carboxylic acids and aliphatic substituted cycloaliphatic carboxylic acids; and many other similar alkali and alkaline earth metal salts of oil-soluble organic acids. Mixtures of overbased salts of two or more different non-lithium alkali and/or alkaline earth metals can be used. Likewise, overbased salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more overbased calcium phenates with one or more overbased calcium sulfonates) can also be used.

As is well known, overbased metal detergents are generally regarded as containing overbasing quantities of inorganic bases, probably in the form of micro dispersions or colloidal suspensions. Thus the term "oil-soluble" as applied to component materials herein is intended to include metal detergents wherein inorganic bases are present that are not necessarily completely or truly oil-soluble in the strict sense of the term, inasmuch as such detergents when mixed into base oils behave in much the same way as if they were fully and totally dissolved in the oil.

Collectively, the various overbased detergents referred to hereinabove, have sometimes been called, quite simply, basic or overbased alkali metal or alkaline earth metal-containing organic acid salts.

Methods for the production of oil-soluble overbased alkali and alkaline earth metal-containing detergents are well known to those skilled in the art and are extensively reported in the patent literature. See for example, the disclosures of U.S. Pat. Nos. 2,451,345; 2,451,346; 2,485,861; 2,501,731; 2,501,732; 2,585,520; 2,671,758; 2,616,904; 2,616,905; 2,616,906; 2,616,911; 2,616,924; 2,616,925; 2,617,049; 2,695,910; 3,178,368; 3,367,867; 3,496,105; 3,629,109; 3,865,737; 3,907,691; 4,100,085; 4,129,589; 4,137,184; 4,148,740; 4,212,752; 4,617,135; 4,647,387; 4,880,550; GB Published Patent Application 2,082,619 A, and European Patent Application Publication Nos. 121,024 B1 and 259,974 A2.

The Organic Solvent

The solvent for this process can be, for example, any aliphatic, naphthenic or aromatic solvent which can azeotrope with water and/or methanol. Examples of such solvents include, but are not restricted to: hexane, heptane, octane, decane, dodecane, benzene, toluene, xylene, toluene, white spirit, naphtha, isoparaffins, and raffinate. Typically, the solvent is a hydrocarbon, but it may be a halogenated hydrocarbon, for example chlorobenzene. The most preferred solvents are hydrocarbons. Commercial raffinate, a mixture of low boiling hydrocarbons, is used in most of the Examples given below.

The Promoter Alcohol

The promoter alcohol for the carbonation of the lithium hydroxide should be a non-alkoxy alcohol. The alcohol may be tertiary, secondary, or primary, but most specifically a primary alcohol. The alcohol can have between 1 to 10 carbons, but most desirable are alcohols with 1 to 4 carbons, with the most preferred being methyl alcohol (methanol).

The amount of alcohol added in the beginning of the procedure may vary, but usually the amount is approximately 0.5 to 5 times the amount of lithium hydroxide used or created, and more specifically approximately 3 times the amount of the total lithium hydroxide.

The Organic Sulfonic Acid Compounds

As used herein, the term "organic sulfonic acid compound" includes sulfonic acids and their sulfonate-generating derivatives.

The organic sulfonic acid compounds are usually obtained from the sulfonation of natural hydrocarbons or synthetic hydrocarbons; e.g. a mahogany or petroleum alkyl sulfonic acid; an alkyl sulfonic acid or an alkylaryl sulfonic acid. Such sulfonic acids are obtained by treating lubricating oil base stocks with concentrated or fuming sulfuric acid (oleum) to produce oil-soluble "mahogany" acids or by sulfonating alkylated aromatic hydrocarbons. Sulfonates derived from synthetic hydrocarbons include those prepared by the alkylation of aromatic hydrocarbons with olefins or olefin polymers; e.g. C₁₅-C₃₀ polypropylenes or polybutenes. Also suitable are the sulfonic acids of alkyl benzenes, alkyl toluenes or alkyl xylenes, which may have one or more alkyl groups, wherein each group, may be straight or branched chain, preferably contains at least 12 carbon atoms. The preferred sulfonic acids have molecular weights from 300 to 1000, for example, between 400 and 800, e.g. about 550. Most preferred are sulfonic acids with the aforementioned properties and have been mostly or completely neutralized by ammonia to create an ammonium alkyl aryl sulfonate species. Mixtures of any of these sulfonic acids may be used.

The ratio of sulfonic acid compound to lithium hydroxide is usually between 1:5 to 1:35, for example 1:10 to 1:20, and most preferred 1:10 to 1:30. In the case of 375 TBN the mole ratio of 1 mole of sulfonic per 14 to 18 moles of lithium hydroxide is especially preferred.

The sulfonic acid, e.g. an alkyl benzene sulfonic acid, acts as a surfactant for the colloidal carbonate, and may be sufficient if it has a relatively high molecular weight aliphatic chain of approximately 400 or more. However, it can be desirable to include a surfactant with a higher weight long aliphatic chain with an approximate molecular weight of 240 to 1400, or more specifically 900 to 1100, in the reaction mixture.

This additional surfactant may be a mono- or dihydrocarbyl substituted acid or anhydride, or an ester, amide, imide, amine salt or ammonium salt of a dicarboxylic acid, wherein the (or each) hydrocarbyl group which may be substituted contains at least 16 carbon atoms. The use of such a second surfactant is described in U.S. 4,601,837, incorporated herein by reference.

The most preferred dicarboxylic compounds are those where the optionally substituted hydrocarbyl groups contains 40 to 200 carbon atoms and has no atoms other than carbon, hydrogen and halogen, and especially unsubstituted hydrocarbyl groups. Preferred hydrocarbyl groups are aliphatic groups.

The acid, anhydride, ester, amide, imide, amine salt or ammonium salt is preferably substantially saturated, but the hydrocarbyl group(s) may be unsaturated. In practice, it is preferred that the hydrocarbyl group(s) be a polymer of a mono-olefin, for example, a C₂ to C₅ mono-olefin, such as polyethylene, polypropylene, or polyisobutylene. Such polymers will usually have only one double bond so that they could be regarded as predominantly saturated, especially since they must have at least 16 carbons.

Mono-(hydrocarbyl)-substituted dicarboxylic acids and their derivatives where the carboxylic groups are separated by 2 to 4 carbon atoms are preferred. In general, acids or anhydrides are the preferred surfactant. However, if an ester, monoamide or ammonium salt is used, it is preferred that the N-substituents or O-substituents are alkyl groups, especially C₁ to C₅ alkyl groups, for example, methyl, ethyl or propyl. If desired, however, the ester could be derived from a glycol, for example, ethylene glycol or propylene glycol.

The most preferred additional surfactants are monosubstituted succinic acids and anhydrides, especially polyisobutenyl succinic acids or anhydrides, preferably where the polyisobutenyl group has 16 to 200 carbon atoms, especially 40 to 65 carbon atoms. Such anhydrides derived from isobutylene are known as polyisobutenyl succinic anhydrides ("PIBSA"); taught in U.S. Patent No. 4,601,837. Those derived from ethylene oligomers are known as α -olefin succinic anhydrides.

When such an acid, anhydride or ester is used, the molar ratio of organic sulfonic acid to the acid, amide imide, amine salt, or ammonium salt, anhydride or ester can vary, but is usually between 10:1 to 2:1, e.g. between 8:1 and 4:1.

The first step of the method of the present invention is the mixing (and preferably heating at reflux) of the lithium hydroxides (monohydrate and/or anhydrous), the source of organic sulfonic acids/ammonium organic sulfonic salts, the non-alkoxy alcohol(s) (sometimes referred to as the "promoter alcohol(s)"), the diluent hydrocarbon solvents, the "PIBSA" and the process oil (as desired). During this stage of the process, the acid/anhydrides present are neutralized by a portion of the basic lithium hydroxide. As a result of this neutralization, water is formed as a by-product as well as ammonium hydroxide for those ammonium organic sulfonic salts which are reacted. The additional water and ammonium hydroxide produced by the reaction aids in the hydration and subsequent carbonation of the lithium hydroxide species which remain after neutralization. It should be noted that, preferably, appropriate ratios of monohydrated and anhydrous lithium hydroxide (described above) may be added initially to the reaction mixture to avoid the step of azeotropically removing all of the water as required in the procedure described in U.S. Pat. No. 4,797,217.

Once the reaction mixture has refluxed (typically at approximately 60° C), normally for at least one hour (reaction times may vary for different scale syntheses), carbon dioxide, preferably gaseous CO₂ is introduced to the refluxing,

stirring reaction mixture. The addition of carbon dioxide converts the residual lithium hydroxide to lithium carbonate. In addition to the production of basic metal carbonate species, water is formed. The carbon dioxide can be fed into the system at any rate, but usually the rate is fast enough to complete the carbonation reaction within a reasonable time, for instance 1 to 6 hours, and more specifically 2 to 4 hours. This reaction time and feed rate may vary according to the scale of the synthesis (i.e. large scale reactions may take longer to completely carbonate).

The carbon dioxide gas used is mostly free of water and other gases, and most preferably Coleman Grade. It should be noted that the U.S. Pat. No. 4,797,217 teaches the removal of all the hydration of the lithium hydroxide monohydrate before carbonation, whereas the monohydrate and waters of neutralization remain with the reaction mixture during the carbonation stage of the preferred embodiment of the method of the present invention.

The carbonation continues until no more carbon dioxide is absorbed by the mixture.

At this point the carbon dioxide feed is stopped and the reaction mixture is heated to azeotropically remove the alcohol/water promoter system. A gas purge, for example nitrogen, can be pushed through the reaction vessel to aid in removing the aqueous layer. Once all the aqueous species are removed, the product can be readily filtered (preferably while still warm) through filtering aid to remove unreacted lithium hydroxide species. Material losses, however, are minimal as most of the lithium hydroxide (90+ weight percent) is converted to colloidal lithium carbonate.

The filtrate may then be heated, most typically to 100-110°C, under reduced pressure, typically 15 to 30 inches Hg vacuum, and most preferably 20 to 25 inches Hg, so as to remove the organic hydrocarbon solvent remaining with the reaction product. The remaining product may be diluted with any appropriate processing oil, such as but not limited to 4 to 8 cSt mid-continent base stocks, in order to meet desired viscometric properties. The processing oil can be added in earlier stages of the process if desired for economic or practicality purposes.

The process of the present invention creates a high quality, high TBN lithium sulfonate in good yields (e.g. 80+ percent of theoretical) with little product lost in sludge and/or sediment.

The process creates overbased additives with properties suitable for use in fuels or lubricant oils, both synthetic and animal, vegetable, and/or mineral oils. For example, petroleum oil fractions ranging from naphthas or spindle oil to SAE 30, 40, or 50 lubricating oil grades, castor oil, fish oils, or oxidized mineral oils. Suitable synthetic oils include, but are not limited to, diesters, polyesters, and tri and tetra esters.

The amount of overbased lithium salt detergent added to the lubricating oil may vary as necessary to the function for which it performs. Typical loading levels can range from 0.01 to 15 percent by weight, but more preferably range between 0.05 and 7 percent, most preferably between 0.08 and 2 percent. Non-limiting examples of other additives that may be included in the oil containing the lithium sulfonate are outlined below. The amount of overbased lithium salt detergent added is preferably no greater than about 0.5 times the total amount of non-lithium overbased metal detergent present.

The final lubricating oil may contain other additives according to the particular use for the oil. For example, viscosity index improvers such as ethylene-polypropylene copolymers, graph polymers, and/or polymethacrylates; ashless polyol or polyamine dispersants based on substituted succinic acid or polyalkene phenol derivatives, other metal containing dispersant or detergent additives; antiwear/antioxidant additives such as zinc dialkyl-dithiophosphates; antioxidants, demulsifiers, corrosion inhibitors, extreme pressure additives and friction modifiers.

Other Additive Components

The lubricant and lubricant concentrates of this invention can and preferably will contain additional components in order to partake of the properties which can be conferred to the overall composition by such additional components. The nature of such components will, to a large extent, be governed by the particular use to which the ultimate oleaginous composition (lubrication or functional fluid) is to be subjected.

Antioxidants

Most oleaginous compositions will contain a conventional quantity of one or more antioxidants in order to protect the composition from premature degradation in the presence of air, especially at elevated temperatures. Typical antioxidants include hindered phenolic antioxidants, secondary aromatic amine antioxidants, sulfurized phenolic antioxidants, oil-soluble copper compounds, phosphorus-containing antioxidants, and the like.

Mixtures of different antioxidants can also be used. One suitable mixture is comprised of a combination of (i) an oil-soluble mixture of at least three different sterically-hindered tertiary butylate monohydric phenols which is in the liquid state at 25°C, (ii) an oil-soluble mixture of at least three different sterically-hindered tertiary butylate methylene-bridged polyphenols, and (iii) at least one bis(4-alkyl-phenyl) amine wherein the alkyl group is a branched alkyl group having 8 to 12 carbon atoms, the proportions of (i), (ii) and (iii) on a weight basis falling in the range of 3.5 to 5.0 parts of component (i) and 0.9 to 1.2 parts of component (ii) per part by weight of component (iii).

The lubricating compositions of this invention preferably contain 0.01 to 1.0% by weight, more preferably 0.05 to

07% by weight, of one or more sterically-hindered phenolic antioxidants of the types described above.

Alternatively or additionally the lubricants of this invention may contain 0.01 to 1.0% by weight, more preferably 0.05 to 0.7% by weight of one or more aromatic amine antioxidants of the types described above.

5 Corrosion Inhibitors

It is also useful to this invention to employ in the lubricant compositions and additive concentrates a suitable quantity of a corrosion inhibitor. This may be a single compound or a mixture of compounds having the property of inhibiting corrosion of metallic surfaces.

10 One type of such additives are inhibitors of copper corrosion. Such compounds include thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercaptobenzothiazole, 2, 5-dimercapto-1, 3, 4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1, 3, 4-thiadiazoles, 2, 5-bis(hydrocarbylthio)-1, 3, 4-thiadiazoles, and 2, 5-(bis)hydrocarbyldithio, 1, 3, 4-thiadiazoles. The preferred compounds are the 1, 3, 4-thiadiazoles, a number of which are available
15 as articles of commerce. Such compounds are generally synthesized from hydrazine and carbon disulfide by known procedures. See for example 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.

Other types of corrosion inhibitors are known and suitable for use in the compositions of this invention. Suitable corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated
20 amines, ethoxylated and/or propoxylated phenols, and ethoxylated alcohols; imidazolines; and the like. Materials of these types are well known to those skilled in the art and a number of such materials are available as articles of commerce.

The lubricant compositions of this invention most preferably contain from 0.005 to 0.5% by weight, and especially from 0.01 to 0.2% by weight, of one or more corrosion inhibitors and/or metal including but not limited to the type
25 described above.

Antifoam Agents

Suitable antifoam agents include silicones and organic polymers such as acrylate polymers. Various antifoam
30 agents are described in Foam Control Agents by H. T. Kerner (Noyes Data Corporation, 1976, pages 125-176), the disclosure of which is incorporated herein by reference. Mixtures of silicone-type antifoam agents such as the liquid di-alkyl silicone polymers with various other substances are also effective. Typical of such mixtures are silicones mixed with an acrylate polymer, silicones mixed with one or more amines, and silicones mixed with one or more amine carboxylates. Neutral and Low Basicity Metal-Containing Detergents

35 For some applications such as crankcase lubricants for diesel engines, it is desirable to include an oil-soluble neutral metal-containing detergent in which the metal is an alkali metal or an alkaline earth metal. Combinations of such detergents can also be employed. The neutral detergents of this type are those which contain an essentially stoichiometric equivalent quantity of metal in relation to the amount of acidic moieties present in the detergent. Thus in general, the neutral detergents will have a TBN of up to about 50. If desired, metal-containing detergents having a
40 low basicity, i.e., alkali or alkaline earth metal-containing detergents having a TBN below 200 can be used as optional components.

The acidic materials utilized in forming such detergents include carboxylic acids, salicylic acids, alkyphenols, sulfonic acids, sulfurized alkyphenols, and the like. Typical detergents of this type and/or methods for their preparation are known and reported in the literature. See for example U.S. Pat. Nos. 2,001,108; 2,081,075; 2,095,538; 2,144,078;
45 2,163,622; 2,180,697; 2,180,698; 2,180,699; 2,211,972; 2,223,127; 2,228,654; 2,228,661; 2,249,626; 2,252,793; 2,270,183; 2,281,824; 2,289,795; 2,292,205; 2,294,145; 2,321,463; 2,322,307; 2,335,017; 2,336,074; 2,339,692; 2,356,043; 2,360,302; 2,362,291; 2,399,877; 2,399,878; 2,409,687; and 2,416,281. A number of such compounds are available as articles of commerce, such as for example, HiTEC®-614 additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.); Chevron OLOA 246A additive, Chevron OLOA 246B additive, Chevron OLOA 246C additive,
50 Chevron OLOA 246P additive (Chevron Chemical Company); and Witco Calcinat T., Calcinat T-2, and Petronate 25-H (Witco Corporation).

Care should be exercised in selecting these supplemental neutral or low basicity metal detergents as at least some of them (e.g., neutral metal sulfonates) can substantially increase wear of metal parts when included in a composition of this invention.

55 Supplemental Antiwear and/or Extreme Pressure Additives

For certain applications such as use as gear oils, the compositions of this invention will preferably contain one or

more oil-soluble supplemental antiwear and/or extreme pressure additives. These comprise a number of well known classes of materials including, for example, sulfur-containing additives, esters of boron acids, esters of phosphorus acids, amine salts of phosphorous acids and acid esters, higher carboxylic acids and derivatives thereof, chlorine-containing additives, and the like.

Typical sulfur-containing antiwear and/or extreme pressure additives include dihydrocarbyl polysulfides; sulfurized olefins, sulfurized fatty acid esters of both natural (e.g. sperm oil) and synthetic origins; trithiones; thienyl derivatives; sulfurized terpenes; sulfurized oligomers of C₂-C₈ monoolefins; xanthates of alkanols and other organo-hydroxy compounds such as phenols; thiocarbamates made from alkyl amines and other organo amines; and sulfurized Diels-Alder adducts such as those disclosed in U.S. reissue patent Re 27,331. Specific examples include sulfurized polyisobutene of Mn 1,110, sulfurized isobutylene, sulfurized triisobutene, dicyclohexyl disulfide, diphenyl and dibenzyl disulfide, di-tert-butyl trisulfide, and dinonyl trisulfide, among others.

Supplemental Ashless Dispersants

If desired, the compositions of this invention can include one or more supplemental ashless dispersants in order to supplement the dispersancy contributed by the additives of the present. The supplemental ashless dispersant(s) can be a phosphorylated or boronated ashless dispersant formed by using procedures of the types conventionally employed for producing conventional technology ashless dispersants containing phosphorus or boron. For example, the supplemental ashless dispersant can be a basic nitrogen-containing or hydroxyl-containing ashless dispersant which has been heated with either one or more inorganic or one or more organic phosphorus compounds, or a combination of one or more inorganic and one or more organic phosphorus compounds.

Thus, the supplemental ashless dispersant(s) which may be used in the compositions of this invention can be any of the basic nitrogen-containing or hydroxyl group-containing ashless dispersants. Use can therefore be made of any of the carboxylic dispersants and/or any of the hydrocarbyl polyamine dispersants and/or any of the Mannich polyamine dispersants and/or any of the polymeric polyamine dispersants. Other ashless dispersants which can be included in the compositions of this invention are imidazoline containing dispersants. Such long-chain alkyl (or long-chain alkenyl) imidazoline compounds may be made by reaction of a corresponding long-chain fatty acid (or formula R₁COOH), for example oleic acid, with an appropriate polyamine.

The above and many other types of ashless dispersants can be utilized either singly or in combination in the compositions of this invention, provided of course that they are compatible with the other additive components being employed and are suitably soluble in the base oil selected for use.

Pour Point Depressants

Another useful type of additive included in compositions of this invention is one or more pour point depressants. The use of pour point depressants in oil-base compositions to improve the low temperature properties of the compositions is well known to the art. See, for example, the books Lubricant Additives by C.V. Smalher and R. Kennedy Smith (Lezius-Hiles Co. Publishers, Cleveland, Ohio, 1967); Gear and Transmission Lubricants by C.T. Boner (Reinhold Publishing Corp., New York, 1964); and Lubricant Additives by M.W. Ranney (Noyes Data Corporation, New Jersey, 1973). Among the types of compounds which function satisfactorily as pour point depressants in the compositions of this invention are polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds, and vinyl carboxylate polymers. Also useful as pour point depressants are terpolymers made by polymerizing a dialkyl fumarate, a vinyl ester of a fatty acid and a vinyl alkyl ether. Techniques for preparing such polymers and their uses are disclosed in U.S. Pat. No. 3,250,715. Generally, when they are present in the compositions of this invention, the pour point depressants are present in the amount of 0.01 to 5, and preferably 0.01 to 1, weight percent of the total composition.

Viscosity Index Improvers

Depending upon the viscosity grade required, the lubricant compositions can contain up to 15 weight percent of one or more viscosity index improvers (excluding the weight of solvent or carrier fluid with which viscosity index improvers are often associated as supplied). Among the numerous types of materials known for such use are hydrocarbon polymers grafted with, for example, nitrogen-containing polymers, olefin polymers such as polybutene, ethylene-propylene copolymers, hydrogenated polymers and copolymers and terpolymers of styrene with isoprene and/or butadiene, polymers of alkyl acrylates or alkyl methacrylates, copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate; post-grafted polymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine; styrene/maleic anhydride polymers post-treated with alcohols and/or amines, and the like.

Dispersant viscosity index improvers, which combine the activity of dispersants and viscosity index improvers, suitable for use in the compositions of this invention are described, for example, in U.S. Pat. Nos. 3,702,300; 4,068,056; 4,068,058; 4,089,794; 4,137,185; 4,146,489; 4,149,984; 4,160,739; and 4,519,929.

5 Friction Modifiers

These materials, sometimes known as fuel economy additives, includes such substances as the alkyl phosphonates as disclosed in U.S. Pat. No. 4,356,097, aliphatic hydrocarbyl-substituted succinimides derived from ammonia or alkyl monoamines as disclosed in European Patent Publication No. 20037, dimer acid esters as disclosed in U.S. Patent No. 4,105,571, oleamide, and the like. Such additives, when used are generally present in amounts of 0.1 to 5 weight percent. Glycerol oleates are another example of fuel economy additives and these are usually present in very small amounts, such as 0.05 to 0.5 weight percent based on the weight of the formulated oil.

Other suitable friction modifiers include aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble.

A desirable friction modifier additive combination which may be used in the practice of this invention is described in European Patent Publication No. 389,237. This combination involves use of a long chain succinimide derivative and a long chain amide.

20 Seal Swell Agents

Additives may be introduced into the compositions of this invention in order to improve the seal performance (elastomer compatibility) of the compositions. Known materials of this type include, but are not limited to, dialkyl diesters such as dioctyl sebacate, aromatic hydrocarbons of suitable viscosity such as Panasol AN-3N, products such as Lu-25 brizol 730, polyol esters such as Emery 2935, 2936, and 2939 esters from the Emery Group of Henkel Corporation and Hatcol 2352, 2962, 2925, 2938, 2939, 2970, 3178, and 4322 polyol esters from Hatco Corporation. Generally speaking the most suitable diesters include the adipates, azelates, and sebacates of C₈-C₁₃ alkanols (or mixtures thereof), and the phthalates of C₄-C₁₃ alkanols (or mixtures thereof). Mixtures of two or more different types of diesters (e.g., dialkyl adipates and dialkyl azelates, etc.) can also be used. Examples of such materials include the n-octyl, 30 2-ethylhexyl, isodecyl, and tridecyl di-esters of adipic acid, azelaic acid, and sebacic acid, and the n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and tridecyl diesters of phthalic acid.

35 The Process

An illustrative example of a general process to produce overbased lithium sulfonate detergents may be described as follows:

I. The following are combined in a suitable reaction vessel in no particular order:

(a) a suitable amount of lithium hydroxide monohydrate and anhydrous lithium hydroxide so that the lithium/water molar ratio is approximately 1:1 to 10:1, more specifically 4:1 to 2:1. The quantity of lithium hydroxide used is enough to neutralize all organic sulfonic acids and anhydride present with sufficient lithium hydroxide equivalent to at least 240mg KOH per gram of total product.

(b) a suitable amount of an organic sulfonic acid which is mostly, or completely reacted with ammonia.

(c) a suitable amount of an alcohol promoter, e.g. methyl alcohol.

(d) a suitable amount of process oil as needed for viscometric purposes.

(e) a suitable amount of an organic anhydride species. More specifically, but not limited to, organic mono- or di-(hydrocarbyl) substituted acid or anhydride, or ester, amide, imide, amine salt or ammonium salt of a dicarboxylic acid species, or more specifically a "PIBSA" or α -olefin succinic anhydride.

(f) a suitable amount of an organic solvent as a diluent for the process. The organic solvent should readily azeotrope with water at reasonable temperatures (including, but not limited to, 80 to 120°C) and should have a reasonably low boiling point such as, but not limited to, 90 to 140°C.

II. The initial reactants are allowed to mix at a temperature which water/methanol reflux such that a portion of the lithium hydroxide species neutralizes the organic sulfonic acid and organic succinic anhydride species.

III. Carbon dioxide gas is introduced to the stirring reaction mixture at a suitable rate during methanol/water reflux until the residual basic species (mostly unreacted lithium hydroxide) is converted to carbonate, thereby producing

a highly basic, colloiddally suspended species.

IV. Azeotropic removal of the alcohol/water or "aqueous" species with the organic diluent solvent until all aqueous species are removed.

V. Filtration of the alcohol/water free product while it is still warm (temperature approximately 75 to 120°C) through a filtering aid (including, but not limited to Dicalite, diatomaceous earth, and Celite).

VI. Addition of process oil as necessary to establish proper viscometrics. This may be done in steps (Id), (II), or (VI), if desired.

The present invention also includes a method for improving the performance of a lubricant adapted for use in an engine using a lubricant in accordance with the present invention. The method in broadest terms comprises including in said lubricant an effective amount of a lubricant additive comprising: (a) at least one non-lithium oil-soluble overbased alkali or alkaline earth metal-containing overbased detergent; and (b) at least one oil-soluble overbased lithium salt detergent. Typically, most lubricants where the method of the present invention will be advantageously applied will be those having ash content in the range of from about 0.5 to about 2.2 percent by weight, for instance 0.5 to 2.0 preferably in the range of from about 0.7 to about 1.8 percent by weight, and most preferably in the range of from about 0.8 to about 1.5 percent by weight, for instance 0.8 to 1.3.

The present invention specifically also includes a method for improving the performance of a diesel lubricant adapted for use in a diesel engine using a lubricant in accordance with the present invention.

The present invention also includes such a method applied to engines containing fluoropolymer engine seals.

Detailed Description of the Preferred Embodiment

In accordance with the foregoing embodiment of the present invention, the following Examples, with the exception of Examples 5 and 6, provide a detailed description of the preferred embodiments of the invention.

Example 1

A reaction mixture of 102 g ammonia neutralized sulfonic acid, 150 ml methanol, 200 ml raffinate, a two mole ratio of lithium hydroxide to water (29.4 g (0.7 moles) lithium hydroxide monohydrate and 16.8 g (0.7) moles anhydrous lithium hydroxide), 57 g process oil and 20 g PIBSA (1300 molecular weight) were charged to reaction flask. The mixture was heated to the reflux temperature of methanol and was allowed to reflux for one hour.

The temperature was adjusted to 60°C and gaseous carbon dioxide was injected into the mixture for 2.5 hours at a rate of 102 ml/min. This is equivalent to 30.1 g of CO₂. The methanol and water were removed by distillation to 110°C. All of the methanol was recovered, as well as an azeotrope of water and raffinate. The product was then filtered through Dicalite SpeedPlus filter aid under vacuum. The theoretical yield before filtration of the product was over 99%. The remaining raffinate was stripped by heating to 110°C under 24 inches Hg vacuum. The material was dark and clear. It contained 25% lithium sulfonate and had a TBN of 330 mg KOH/g product.

Example 2

This preparation was as given in Example 1 with the exception that a three mole ratio of lithium hydroxide to water (22.4 g (0.93 moles) anhydrous lithium hydroxide and 19.7 g (0.47 moles) lithium hydroxide monohydrate) was used in place of the two mole ratio. Filtration and stripping gave a clear and dark product with 25% lithium sulfonate and a TBN of 360 mg KOH/g product.

Example 3

This preparation was as given in Example 1 with the exception that 20 g alkenylsuccinnic anhydride with a carbon chain length of 16-18, was used in place of the PIBSA. The product filtered quickly and stripped to a clear, dark product. The product contained 25% lithium sulfonate and had a TBN of 372 mg of KOH/g product.

Example 4

This preparation was as given in Example 1 with the exception that a three mole ratio of lithium hydroxide to water (22.4 g (0.93 moles) anhydrous lithium hydroxide and 19.7 g (0.47 moles) lithium hydroxide monohydrate) was used in place of the two mole ratio. Filtration and stripping gave a clear and dark product with 25% lithium sulfonate and a TBN of 390 mg KOH/g product.

Example 5

A reaction mixture of 90 g ammonia neutralized sulfonic acid and 37.8 g (0.9 moles) lithium hydroxide monohydrate dissolved in 200 g water, and 20 g process oil were charged to reaction flask. The mixture was heated and refluxed for one hour. The temperature was adjusted to 90°C and carbon dioxide was injected into the mixture for 2.5 hours at a rate of 102 ml/min. The water was allowed to reflux into a Dean Stark trap during the carbonation process. On completion of the carbonation process, the apparatus was changed from reflux to distillation. The water and some raffinate were removed by distillation to 155°C. The product was centrifuged for 20 minutes at 1700 rpm. About 3% solids were collected in the bottom of the centrifuge tubes. The remaining raffinate was stripped from the decantant of the centrifuge tubes. The solution was light in color and cloudy. The product yielded a TBN of only about 50 mg KOH/g product using a Dexsil Titra-Lube TBN kit. This process shows that little overbased product is made with water alone, and that some promoter alcohol is required.

Example 6

A reaction mixture of 90 g ammonia neutralized sulfonic acid, 100 ml methanol, 300 ml xylene, 21.6 g (0.9 moles) anhydrous lithium hydroxide and 20g process oil were charged to a reaction flask. The mixture was heated to allow methanol to reflux for an hour.

The temperature was raised to distill the methanol and water. Some xylene formed an azeotrope with water. Carbonation was started when the temperature reached 140°C and continued for a little over 2.5 hours at 102 ml/min. The remaining xylene was removed by distillation. The product was light and cloudy with solids on the bottom of the reaction flask. Solvent was added back to the product to help centrifuge. This solvent was removed with a vacuum after centrifuging. The resulting product was dark and cloudy with no TBN from the Titra-Lube test kit. This procedure showed that no overbased additive is attained using methanol alone, and that it is therefore preferred to have the lithium source be comprised of at least some monohydrated lithium hydroxide.

Example 7

This preparation was similar in process to Example 1 but on a smaller scale. The reaction flask was charged with 90 g ammonia neutralized sulfonic acid, 100ml methanol, 300 ml raffinate, 20.9g process oil, and a lithium hydroxide to water ratio of 2:1 (achieved by 11.9 g (0.5 moles) anhydrous lithium hydroxide and 20.88 g (0.5 moles) lithium hydroxide monohydrate). The reaction was heated to reflux methanol for one hour. Carbon dioxide was introduced at a rate of 102 ml/min after the mixture cooled 50°C. The mixture was carbonated at 50°C (instead of 60°C) for 2.5 hours. The methanol and water were distilled off by raising the temperature to 120°C. The remaining solution was centrifuged and then stripped. The resulting product was slightly cloudy and dark with a TBN of 368 mg KOH/g product.

Example 8

This preparation was a repeat of Example 7 except methanol 50 ml, and raffinate 200 ml, and a mole ratio of 4.0 lithium hydroxide to water (10.43 g, 0.25 moles lithium hydroxide monohydrate and 17.85 g, 0.75 moles anhydrous lithium hydroxide) was used. The product was cloudy and yielded a TBN of 367 mg KOH/g copolymer.

Example 9

This preparation was a repeat of Example 7 except a 3.0 mole ratio of lithium hydroxide to water (13.86 g, 0.33 moles lithium hydroxide monohydrate and 16.81 g, 0.67 moles anhydrous lithium hydroxide) was used. Carbonation was run at 60°C. The product was very cloudy and would not flow. It had a TBN of 393 mg KOH/g product.

Example 10

This preparation was a repeat of Example 1 except that to a solution of 165 g of 44.3% C-20 ammonium sulfonate, 72 g of process oil, 300 ml of xylene, and 36 g (1.5 mol) of lithium hydroxide was added a solution of 5 g of water in 29 ml methanol. The mixture was carbonated at 49°C for 2 hours. The product was stripped, centrifuged, and stripped again to give 156 g of product having a TBN of 207 by ASTM D-2896.

A summary of the preceding Examples is given below in Table 1.

Table 1

Example	Li/H ₂ O	MeOH/Li	Add'n	Temp	%	TBN
#	Ratio	Ratio	Soap/Li	(C)	Solid	
			Ratio		s	
1	2.0	2.56	0.011	60	1.7	335
2	3.0	2.64	0.011	60	0.10	370
3	2.0	2.64	0.044	60	0.25	372
4	3.0	2.64	0.044	60	0.40	390
5	1.0	0.00		90	3.0	50*
6	0.0	2.74		140		0*
7	2.0	2.49		50	<1.0	368
8	4.0	1.24		50	<1.0	367
9	3.0	2.47		60	<1.0	393
10	5.4	0.48		49	3.0	207

* TBN by test kit; all others by ASTM Method D-2896

ⁿ C16-18 ASA¹ H-053 PIBSA

A diesel lubricating oil composition was prepared using a blend of an Exxon 150N Low Pour Point Base oil with an Exxon 600N Base Oil combined with a bis-succinimide ashless dispersant, a borated succinate ester amide ashless dispersant, commercially available zinc dialkyl dithiophosphate, overbased calcium sulfonate, and additional components including neutral and low basicity metal-containing detergents, amine antioxidant, sulfurized dodecyl phenol, a demulsifier, an antifoam, a viscosity index improver, and a pour point depressant. This composition is designated Formulation A. Formulation B was prepared by incorporating 0.1 weight percent overbased lithium sulfonate with a TBN of 400 into Formulation A. Thus, Formulation A is identical to Formulation B with the exception that Formulation B contains an overbased lithium sulfonate detergent additive.

Table 2 shows that Formulation A, not of the invention, failed to come within the passing value of 11.5% increase in viscosity in accordance with the Mack T-8 test (i.e., giving an increase in viscosity of 18% at 3.8% soot). In contrast, Formulation B, of the invention, passed the Mack T-8 test by giving a viscosity increase of only 7.5% at 3.8% soot, well under the 11.5% passing value.

Table 2

Effect of Lithium Sulfonate on Mack T-8 Test		
	Formulation A Without Overbased Lithium Additive	Formulation B With Overbased Lithium Additive
Mack T8 Engine Test:		
Vis. Inc. @ 3.8% Soot ($\leq 11.5\%$ is passing)	18 (fail)	7.5 (pass)
Hour @ 3.8% Soot	238	160

In addition to serving as a source of oil alkalinity and traditional detergency, the lithium sulfonate surprisingly has been found to inhibit viscosity increase in the Mack T-8 soot dispersancy test; a test which a larger number of detergents fail.

The advantages of the lubricant additive of the present invention include the ability to provide a source of oil alkalinity and traditional detergency, while the overbased lithium, in combination with the overbased non-lithium salt, has been found to inhibit viscosity increase, as reflected in the T-8 soot dispersancy test, without having to provide an additive of substantially higher relative TBN value (as compared to an additive containing only overbased non-lithium salts). This result appears unexpected because the overbased lithium (even in relatively small amounts) allows the lubricant to pass the Mack T-8 soot dispersancy test without the need to substantially increase the total TBN of the

additive. Lubricants on the present invention were also found to have the advantage of being relatively well tolerated by fluoropolymer engine seals such as Viton seals, and to be advantageous by virtue of being substantially free of sodium which can be an interferant in internal engine coolant leak testing.

The advantages of the process of the present invention over prior art alkoxyalkanol process include: (i) the use of the disclosed ratios anhydrous lithium hydroxide to monohydrated lithium hydroxide avoids the azeotropic removal of water in the initial stages of the process; (ii) the use of a non-alkoxyalcohol, e.g. methyl alcohol, allows for the carbonation reaction to proceed at a lower temperature; (iii) the preferred alcohol, methanol, has a lower boiling temperature than the alkoxyalkanols and thereby is more readily removed from the product allowing easier product purification, and easier recyclability of the promoter alcohol; (iv) methanol is less toxic than alkoxyalkanols; and (v) methanol is less expensive than alkoxyalkanols.

In view of the foregoing disclosure, and through practice of the invention, it may become possible to make modifications to the processes or products of the present inventions, such as through the substitution of equivalent components, or the rearrangement or integration of process steps, without departing from the spirit of the invention as reflected in the appended claims.

Claims

1. A lubricant additive concentrate comprising a base oil of lubricating viscosity and:

- (a) at least one non-lithium oil-soluble overbased alkali or alkaline earth metal-containing overbased detergent; and
- (b) at least one oil-soluble overbased lithium salt detergent.

2. A lubricant additive concentrate according to claim 1 additionally comprising:

- (c) at least one additional substance selected from antioxidants, corrosion inhibitors, antifoam agents, anti-wear agents, extreme pressure additives, dispersants, ashless dispersants, pour point depressants, viscosity improvers, friction modifiers, and seal swell agents.

3. A lubricant additive concentrate according to claim 1 or claim 2 comprising at least 0.6 percent by weight of the lithium salt detergent.

4. A lubricant composition comprising:

- (a) at least one non-lithium oil-soluble overbased alkali or alkaline earth metal-containing overbased detergent;
- (b) at least one oil-soluble overbased lithium salt detergent; and
- (c) at least one base oil of lubricating viscosity.

5. A lubricant composition according to claim 4 with a sulfated ash content in the range of from 0.5 to 2.2 percent by weight.

6. A lubricant composition according to claim 4 or claim 5 comprising at least 0.08 percent by weight of the lithium salt detergent.

7. A lubricant or lubricant additive concentrate according to any one of claims 1 to 6 comprising lithium salt detergent in an amount no greater than 0.5 times the total weight of the non-lithium detergent.

8. A lubricant or lubricant additive concentrate according to any one of claims 1 to 7 wherein the lithium salt detergent is selected from lithium sulfonates, lithium carboxylates, lithium phenates and lithium salicylates; and wherein the non-lithium detergent is selected from phenates, sulfonates, carboxylates and salicylates of calcium, magnesium, potassium and sodium, their sulfurized and aromatic derivatives, and mixtures thereof.

9. A lubricant or lubricant additive concentrate according to any of claims 1 to 8 wherein the lithium salt detergent has a TBN from 240 to 400.

10. A process for producing an overbased lithium detergent suitable for use in a lubricant or lubricant additive concentrate, said process comprising:

(a) combining the following:

- (i) a lithium source selected from anhydrous lithium hydroxide, monohydrated lithium hydroxide and mixtures thereof;
- (ii) at least one source of sulfonic acid;
- (iii) at least one primary, secondary or tertiary non-alkoxy alcohol; and
- (iv) optionally, water; so as to produce a mixture comprising lithium hydroxide, water of neutralisation and at least one sulfonate;

(b) combining the mixture resulting from step (a) with a source of carbon dioxide under reaction conditions such that the lithium hydroxide is converted to lithium carbonate while retaining any water of neutralisation from step (a) and from the conversion of lithium hydroxide to lithium carbonate.

11. A process according to claim 10 comprising in step (a) heating under reflux the lithium source, at least one source of sulfonic acid, at least one alcohol and optionally, water; and (c) heating to remove the water and alcohol from the mixture resulting from step (b), thereby obtaining an overbased lithium detergent.

12. A process according to claim 10 or claim 11 wherein the mixture resulting from step (a) comprises up to one mole of water per mole of total lithium hydroxide.

13. A process according to any one of claims 10 to 12 wherein the mixture resulting from step (b) contains an aqueous portion and unreacted lithium salts and wherein the process additionally comprises a step of removing the aqueous portion and the unreacted lithium salts from the mixture resulting from step (b).

14. A process according to any one of claims 10 to 13 wherein the lithium source comprises anhydrous lithium hydroxide and monohydrated lithium hydroxide in a molar ratio of from 1:10 to 10:1.

15. A process according to claim 14 wherein the molar ratio of monohydrated lithium hydroxide to anhydrous lithium hydroxide is from 1:1 to 4:1.

16. A process according to any one of claims 10 to 15 wherein the molar ratio of the alcohol to the total amount of lithium hydroxide in step (a) is from 0.5:1 to 5:1.

17. A process according to any one of claims 10 to 16 wherein the alcohol is methanol or 2-ethylhexanol.

18. A process according to any one of claims 10 to 17 wherein the molar ratio of sulfonic acid to the total amount of lithium hydroxide in step (a) is in the range of from 1:5 to 1:35.

19. A process according to any one of claims 10 to 18 wherein the source of carbon dioxide is selected from gaseous carbon dioxide, liquid carbon dioxide and solid carbon dioxide.

20. A process according to any one of claims 10 to 19 wherein the mixture produced in step (a) additionally comprises at least one surfactant of a molecular weight in the range of from 240 to 1400.

21. A lubricant or lubricant additive concentrate comprising a lithium salt detergent obtainable by a process according to any one of claims 10 to 20.

22. Use of a lubricant or lubricant additive concentrate according to any one of claims 1 to 9 or 21 in an engine having fluoropolymer seals.