

TITLE: STABLE DISPERSIONS OF OIL-INSOLUBLE COMPOUNDS IN
HYDROCARBONS FOR USE IN LUBRICANTS

Field of Invention

The use of hydrocarbons as lubricants is known along with the use of functional additives to enhance the lubricating properties of the hydrocarbons. Oil-insoluble (or relatively insoluble) additives are disclosed for use in lubricants. These oil-insoluble functional additives can be incorporated by dissolving or dispersing the functional additives in an oil-insoluble solvent forming a dispersion or blend, dispersing that dispersion or blend into a hydrocarbon lubricating fluid, and then removing part of all of said oil-insoluble solvent. Dispersing the dispersion or blend is facilitated using an emulsifier capable of forming a water-in-oil emulsion. Oil-insoluble functional additives include but are not limited to KOH, NaOH, guanidine carbonate, ammonium and amine carbonates, CaCO_3 , di-sodium salt of dimercapto-thiadiazole, and others.

Background of Invention

GB 789,920 describes stable dispersions of inorganic metal compounds in lubricating oil and methods of making the same. Such compositions possessing increased detergency and increase reserve basicity find utility as additives in lubricating oils and possibly as corrosion inhibitors. The oil soluble surface active agents are typically sulfonates and the compositions include an aliphatic alcohol having less than six carbon atoms, which is removed. It appears that a mutual solvent for the alcohol and the lubricating oil, such as benzene, is used to form a homogeneous mass that later separate into phases when the benzene and alcohol are removed.

Emulsions of water in oil have been described for use in hydraulic applications such as in US Patents 3,269,946; 3,281,356; 3,311,561; and 3,378,494 where fire resistance was provided by the high water content of the fluid and the use temperature was low enough that the water of the water in oil emulsion was not readily evaporated. Water in oil emulsions were generally not desired in engine oils as discussed in column 1 of US Patent 3,509,052, lines 41-55, where a mayonnaise-like sludge was observed in the

rocker arm covers and oil fill caps of smaller car engines when moisture condensed from the air and was emulsified into the engine oil.

Water in oil emulsions are also used as liquid fuels in some patent applications such as US 4,002,435. A water in oil emulsion is described therein comprising a hydrocarbon, water, a water-soluble alcohol, and a novel combination of surface-active agents to provide a clear fuel, which is stable against phase separation.

Summary of Invention

Two different embodiments of dispersed oil-insoluble additives in hydrocarbons are described. One embodiment is a concentrate of at least one oil-insoluble additive dispersed in a hydrocarbon to be used as part or all of an additive package for manufacturing lubricating fluids. This additive package may further contain a variety of conventional lubricating fluid additives (e.g. oil soluble ones) for their known intended purpose. Additive packages are used by lubricant formulators to facilitate measuring and dosing the correct amount of additives to formulated lubricating fluids.

A second embodiment is a formulated or partially formulated lubricant that comprises as one component an oil-insoluble additive dispersed in the lubricant. This embodiment will also generally contain a variety of other conventional oil-soluble or dispersed additives.

The functional oil-insoluble additive in this application is not the commercially known material known as neutral or overbased metal detergents which are generally characterized as the reaction product of an equivalent of an oil-soluble acid with an equivalent or more of alkali or alkaline earth metal such as Ca, Mg, Na, K, or Li along with an acidic gas such as CO₂, SO₂, or SO₃. The functional oil-insoluble additives of this application are also not the borate compounds such as those known to be made into dispersion in oil for fuel and lubricant applications.

The additive package/lubricant can also comprise various conventional lubricating additives to assist in the performance of the lubricant such as dispersants, detergents (including neutral and overbased detergents), extreme pressure agents, antioxidants, viscosity index modifiers, etc. The lubricating oil can be selected from a wide variety of oils of American Petroleum Institute (API) Groups I through V including mineral oils or combinations of grades or synthetic oil or combinations with synthetic oils.

Detailed Description of the Invention

Additive packages for lubricating fluids and lubricating oils having at least one oil-insoluble functional additives dispersed therein are described. The oil-insoluble functional additive is typically added as dissolved or dispersed compound in water or other oil-insoluble solvent forming a dispersion or blend. The dispersion or blend is then dispersed as a water or solvent in oil emulsion using the lubricating oil as the continuous phase. The water or oil-insoluble solvent can remain or can be partially or fully removed. An emulsifier(s) is used to colloidally stabilize the dispersed phase. These resulting oil-insoluble functional additives in a lubricating fluid can be used over a variety of temperature ranges including use in the combustion chamber of an internal combustion engine, gear boxes, pumps, automatic transmissions, hydraulic cylinders, differentials etc. The use of oil-insoluble functional additives within oil has been limited in the past due to the limited solubility of these compounds in hydrocarbon based fluids. The use of water or other oil insoluble solvent(s) emulsified in oil has been discouraged except for the use of water in oil emulsions for flame resistant hydraulic fluids and related lower temperature applications. Elimination of part or all of the water or oil-insoluble solvent can alleviate many of the concerns about the use of water and oil-insoluble solvents in a lubricating fluid. Some oil insoluble solvents like lower alcohols and ethers have been avoided in lubricants for volatility reasons.

The use of bases such as oxides, hydroxides, carbonates and bicarbonates of alkali and alkaline earth metals primarily or solely for neutralizing acidic materials is described in a separate application and will not generally be claimed herein.

A major component to the lubricating oil is base oil, hydrocarbon in most situations although some synthetic oils that would not be strictly defined as hydrocarbon could be used (e.g. esters and polyol esters). The word major is used because the amount of hydrocarbon based oil is often more than 50 weight, often about 50 to about 99 weight percent of the lubricating fluid but it need only be the continuous phase and can be as little as 20 or 30 weight percent of the final lubricating fluid, depending on the application. In additive packages the base oil(s) is often used in much smaller percentages and is primarily present to function as a diluent to keep the additives

dissolved, to keep them from negatively interacting, and to keep the additive package in an easy to handle moderate viscosity fluid.

Emulsifiers help emulsify the oil insoluble solvent e.g. water in the hydrocarbon oil along with any dissolved or dispersed oil-insoluble functional additive. The emulsifier(s) can be any known emulsifier useful to disperse oil insoluble solvents e.g. water in oil. Preferably the emulsifiers include one high HLB (hydrophilic/lipophilic balance) emulsifier and/or one low HLB emulsifier. The low HLB emulsifier can be an ester/salt made by reacting polyisobutenyl succinic anhydride with ethylene glycol and dimethyl ethanol amine in an equivalent ratio of about 2:1:2. This emulsifier can have a high molecular weight polyisobutylene chain (~1500MW). The high HLB emulsifier can be an ester/salt made by reacting hexadecyl succinic anhydride with dimethylethanolamine in an equivalent ratio of about 1:1 (low molecular weight) or a salixarene emulsifier. The emulsifier(s) can be present in any amount to effectively emulsify the water and water soluble or water dispersible base in the hydrocarbon oil phase. Preferred amounts of emulsifier include from about 0.02 or 0.5 to about 15 weight percent based on the weight of the formulated lubricant. In additive packages or components thereof the emulsifier can be from about 0.05 to about 30 weight percent of the additive package.

Oil Insoluble Solvent

Water or another oil insoluble solvent or a blend(s) thereof is a necessary component to the system. Water soluble organic materials or salts can be added to depress the freezing point of the water/solvent and/or blend to make the water/solvent more effective in dissolving or dispersing the base. While very pure water was used in some to the examples and is preferred since it would eliminate contaminants that might interfere with other additives or function, it is anticipated that water with various impurities could be used in various applications without any significant disadvantages. Therefore water will include deionized water, tap water, recycled water, etc. Water or oil-insoluble solvent or blends can be up to 50 weight percent of the initially formulated lubricant as long as it remains a dispersed phase rather than the continuous phase. In most embodiments this water/ oil-insoluble solvent or blends thereof is partially or fully removed before the material is formulated into an additive package or lubricating fluid.

For most embodiments it is preferred that less than 20 weight percent of the additive package or lubricant is water or other oil-insoluble solvent. In most embodiments, more preferred amounts of oil-insoluble solvents (e.g. water) is from about 0 to about 20 weight percent and more preferred from about 0 to about 5 or 10 weight percent based on the weight of the oil-insoluble functional additive. Oil insoluble solvents include C1-C5 monohydric and polyhydric alcohols, C2-C5 ethers including polyethers such as hydroxyl terminated, ester terminated and/or ether terminated, and various other solvents that are not soluble in SAE 30 paraffinic oils to an extent of 1g/100 ml of oil at 25°C. Ammonia and other hydrocarbyl amines may be added to the water/solvent/blend to enhance one or more properties necessary of the solvent or of the final dispersion of base.

Oil Insoluble Functional Additives

The oil-insoluble functional additives may have partial solubility in oil as specified by the definition of oil-insoluble given in the definitions below. The oil-insoluble functional additives may be defined by function. Their functions are desirably selected from the group consisting of antioxidant, antiwear agent, extreme pressure additive, friction modifier, corrosion inhibitor, and metal protectorant. Preferred functions are antioxidant, and antiwear agent.

The oil-insoluble functional additive can be compounds like NaOH, KOH, CaCO_3 (although bases are claimed in a separate application), guanidine carbonate, ammonium and amine carbonates, di-sodium salt of dimethylthiuram disulfide, and other similar compounds having good solubility in polar solvents but poor or no solubility in hydrocarbon solvents.

The oil-insoluble functional additives can function in a lubricating fluid in several different ways. In one embodiment the dispersed phase containing the functional additive serves as a reservoir of the oil-insoluble functional additive that constantly replenishes the small portion of oil-insoluble functional additive in the oil phase. The functional additive in the oil phase may be being consumed or de-activated by reaction with other components in the lubricating system or by impurities introduced into the lubricant. In another embodiment the dispersed functional additive can remove undesirable components from the oil phase and de-activate or bind the undesirables in the dispersed phase where they present lesser possibility of a deleterious effect to the

lubricant. In yet another embodiment, the dispersed functional additive is available to react with or coat mechanical surfaces in contact with the oil phase to impart, for example, antiwear or anticorrosive properties.

The amount of oil-insoluble functional additive in a lubricating fluid can range from about 0.01 to about 40 weight percent, based on the weight of the formulated lubricating fluid, more desirably from about 0.2 to about 20 weight percent and preferably from about 0.5 to about 10 weight percent. In an additive package to be later diluted with base oil, the amount of oil-insoluble function additive would typically be higher such as from about 0.2 to about 80 weight percent, more desirably from about 1 or 2 to about 40 weight percent.

Further the oil-insoluble functional additive according to this invention will not be part of those overbased metal compounds described in patents such as US 2,626,904; 3,626,905; 3,695,910 or 2,739,125 where a first base is added to the oil along with an oil soluble acid or surfactant and then said base is chemically reacted with another chemical, typically a gas such as CO_2 or SO_2 , to form another second different base in situ in the oil phase, said second base having different solubility or dispersibility in the oil phase due to the method of preparation and the presence of oil soluble acid or surfactant. These overbased components formed by in situ chemical reactions may be present as other functional additives in the lubricant and may be formed in trace amounts due to exposure of bases to trace CO_2 in the air.

As expressed above the oil-insoluble functional additive added with the oil insoluble solvents, e.g. water, generally have low oil solubility and thus are present in the dispersed phase, i.e. in the dispersed oil insoluble solvents, or if the oil insoluble solvent has been partially or fully remove, the base can become the major or only component in the dispersed phase, stabilized as a colloidal dispersion by the emulsifier. Dispersed phases above 100 microns in any dimension are less preferred in colloidal dispersions because they are harder to stabilize than smaller sized phases and can contribute to haziness. Dispersed phases above 20 microns in size tend to get caught in conventional engine oil filters. Dispersed phases below 5 nanometers in size typically require significantly larger amounts of emulsifier than dispersed phases of 50 or 500 nanometers. Therefore, the dispersed phases of base and optional oil insoluble solvent, e.g. water,

desirably has a intensity average particle size by light scattering of 1 or 5 nanometers to 100 microns, more desirably from 1 or 5 nanometers to 20 microns, and preferably from about 10 nanometers to about 10 microns.

Further the base in this application is not an alkali or alkaline metal borate or hydrated alkali or alkaline metal borate as described in US 3,853,772 and related patent documents on the use of borate compounds in lubricants.

Definitions

The term lower when used in conjunction with terms such as alkyl, alkenyl, and alkoxy is intended to describe such groups that contain a total of up to 7 carbon atoms.

The term water-soluble refers to materials that are soluble in water to the extent of at least one gram per 100 milliliters of water at 25°C.

The term lubricant or hydrocarbon lubricant soluble refers to materials that are soluble in a SAE 30 paraffinic base oil lubricant to the extent of at least one gram per 100 milliliters of lubricant at 25°C.

A material which is less soluble in SAE 30 paraffin oil than 1g/100mL of oil at 25°C will be classified as oil-insoluble.

Hydrocarbyl groups or substituents refers to a group having one or more carbon atoms directly attached to the remainder of the molecule having a hydrocarbon nature or predominantly so and includes 1) pure hydrocarbon groups (e.g. alkyl, alkenyl, alkylene, and cyclic materials), 2) substituted hydrocarbon groups, which are still predominantly hydrocarbon in nature (e.g. halo, hydroxyl, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy), and 3) heterosubstituted hydrocarbon groups such as described in 2) with no more than 1 or 2 halogen, oxygen, sulfur, or nitrogen atoms or combinations per 10 carbon atoms.

The Emulsifier(s)

In one embodiment, the emulsifier used in accordance with the invention is an emulsifier composition which comprises: (i) a hydrocarbon lubricant-soluble product made by reacting a hydrocarbyl substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl substituent of said acylating agent having about 50 to about 500 carbon atoms; (ii) an ionic or a nonionic compound having a hydrophilic lipophilic balance (HLB) of about 1 to about 30; a mixture of (i) and (ii); or a mixture of (i) and (ii)

in combination with (iii) a water-soluble salt distinct from (i) and (ii). Mixtures of (i), (ii) are preferred. These emulsifiers are described as fuel soluble emulsifiers in US 6,383,237, hereby incorporated by reference (hereinafter US '237). This emulsifier composition is present in the lubricating oil compositions of the invention at a concentration of about 0.02 or 0.05 to about 15 or 20% by weight, and in one embodiment about 0.05 to about 10% by weight, and in one embodiment about 0.1 to about 5% by weight, and in one embodiment about 0.1 to about 3% by weight, and in one embodiment about 0.1 to about 2.5% by weight. Emulsifiers have been defined to distinguish them from overbased detergents and similar materials even though overbased detergents may have an effect on emulsion stability. It is also noted that dispersants, which are commonly used in lubricants, have some similarity to low HLB surfactants.

In additive packages the amount of emulsifier is typically from about 0.05 to about 30 weight percent, more desirably from about 0.2 to about 20 weight percent and preferably from about 0.3 to about 15 weight percent.

The hydrocarbyl-substituted carboxylic acid acylating agent for the hydrocarbon lubricant-soluble product (i) may be a carboxylic acid or a reactive equivalent of such acid. The reactive equivalent may be an acid halide, anhydride, or ester, including partial esters and the like. The hydrocarbyl substituent for the carboxylic acid acylating agent may contain from about 50 to about 300 or 500 carbon atoms, and in one embodiment about 60 to about 200 carbon atoms. In one embodiment, the hydrocarbyl substituent of the acylating agent has a number average molecular weight of about 500 or 750 to about 3000, and in one embodiment about 900 to about 2000 or 2300.

In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent for the hydrocarbon lubricant-soluble product (i) may be made by reacting one or more alpha-beta olefinically unsaturated carboxylic acid reagents containing 2 to about 20 carbon atoms, exclusive of the carboxyl groups, with one or more olefin polymers as described more fully hereinafter.

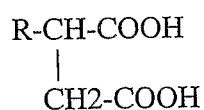
The alpha-beta olefinically unsaturated carboxylic acid reagents may be either monobasic or polybasic in nature. They are described in US '237 column 13.

The olefin monomers from which the olefin polymers may be derived are polymerizable olefin monomers characterized by having one or more ethylenic

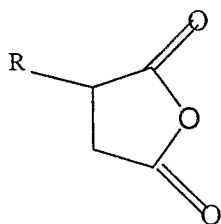
unsaturated groups and they (monomers and polymers) are described in US '237 column 14.

In one embodiment, the olefin polymer is a polyisobutene group (or polyisobutylene group) having a number average molecular weight of about 750 to about 3000, and in one embodiment about 900 to about 2000.

In one embodiment, the acylating agent for the hydrocarbon lubricant-soluble product (i) is a hydrocarbyl-substituted succinic acid or anhydride represented correspondingly by the formulae



or



wherein R is hydrocarbyl group of about 50 to about 500 carbon atoms, and in one embodiment from about 50 to about 300, and in one embodiment from about 60 to about 200 carbon atoms. The production of these hydrocarbyl-substituted succinic acids or anhydrides via alkylation of maleic acid or anhydride or its derivatives with a halohydrocarbon or via reaction of maleic acid or anhydride with an olefin polymer having a terminal double bond is well known to those of skill in the art and need not be discussed in detail herein.

In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent for the product hydrocarbon lubricant-soluble product (i) is a hydrocarbyl-substituted succinic acylating agent consisting of hydrocarbyl substituent groups and succinic groups. The hydrocarbyl substituent groups are derived from an olefin polymer as discussed above. The hydrocarbyl-substituted carboxylic acid acylating agent is characterized by the presence within its structure of an average of at least 1.3 succinic

groups, and in one embodiment from about 1.5 to about 2.5, and in one embodiment from about 1.7 to about 2.1 succinic groups for each equivalent weight of the hydrocarbyl substituent. In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent is characterized by the presence within its structure of about 1.0 to about 1.3, and in one embodiment from about 1.0 to about 1.2, and in one embodiment from about 1.0 to about 1.1 succinic groups for each equivalent weight of the hydrocarbyl substituent.

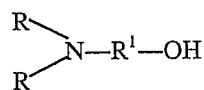
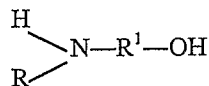
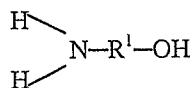
In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent is a polyisobutene-substituted succinic anhydride, the polyisobutene substituent having a number average molecular weight of about 1500 to about 3000, and in one embodiment about 1800 to about 2300, said first polyisobutene-substituted succinic anhydride being characterized by about 1.3 to about 2.5, and in one embodiment about 1.7 to about 2.1 succinic groups per equivalent weight of the polyisobutene substituent.

In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent is a polyisobutene-substituted succinic anhydride, the polyisobutene substituent having a number average molecular weight of about 700 to about 1300, and in one embodiment about 800 to about 1000, said polyisobutene-substituted succinic anhydride being characterized by about 1.0 to about 1.3, and in one embodiment about 1.0 to about 1.2 succinic groups per equivalent weight of the polyisobutene substituent. They are further described in US '237 columns 15 and 16.

The hydrocarbon lubricant-soluble product (i) may be formed using ammonia and/or an amine. The amines useful for reacting with the acylating agent to form the product (i) include monoamines, polyamines, and mixtures thereof.

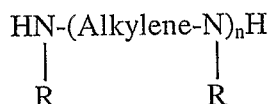
The monoamines have only one amine functionality whereas the polyamines have two or more. The amines may be primary, secondary or tertiary amines. The primary amines are characterized by the presence of at least one -NH_2 group; the secondary by the presence of at least one H-N< group. The tertiary amines are analogous to the primary and secondary amines with the exception that the hydrogen atoms in the -NH_2 or H-N< groups are replaced by hydrocarbyl groups. Examples of primary and secondary monoamines are described in US '237 column 16. .

The amines may be hydroxyamines. The hydroxyamines may be primary, secondary or tertiary amines. Typically, the hydroxamines are primary, secondary or tertiary alkanolamines. The alkanol amines may be represented by the formulae:



Further described in US '237 columns 16 and 17.

The amine may be an alkylene polyamine. Especially useful are the linear or branched alkylene polyamines represented by the formula



wherein n has an average value between 1 and about 10, and in one embodiment about 2 to about 7, the "Alkylene" group has from 1 to about 10 carbon atoms, and in one embodiment about 2 to about 6 carbon atoms, and each R is independently hydrogen, an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms. These alkylene polyamines are described in US '237 column 18.

Ethylene polyamines are useful. In one embodiment, the amine is a polyamine bottoms or a heavy polyamine. The term "polyamine bottoms" refers to those polyamines resulting from the stripping of a polyamine mixture to remove lower molecular weight polyamines and volatile components to leave, as residue, the polyamine bottoms. In one embodiment, the polyamine bottoms are characterized as having less than about 2% by weight total diethylene triamine or triethylene tetramine. These are described in US '237 in column 18.

The hydrocarbon lubricant-soluble product (i) may be a salt, an ester, an amide, an imide, or a combination thereof. The salt may be an internal salt involving residues of a molecule of the acylating agent and the ammonia or amine wherein one of the carboxyl

groups becomes ionically bound to a nitrogen atom within the same group; or it may be an external salt wherein the ionic salt group is formed with a nitrogen atom that is not part of the same molecule. In one embodiment, the amine is a hydroxyamine, the hydrocarbyl-substituted carboxylic acid acylating agent is a hydrocarbyl-substituted succinic anhydride, and the resulting hydrocarbon lubricant-soluble product (i) is a half ester and half salt, i.e., an ester/salt.

Component (i)(b) is a hydrocarbon lubricant-soluble product made by reacting an acylating agent with at least one ethylene polyamine such as TEPA (tetraethylenepentamine), PEHA (pentaethylenehexamine), TETA (triethylenetetramine), polyamine bottoms, or at least one heavy polyamine. The ethylene polyamine can be condensed to form a succinimide. The equivalent ratio of the reaction for CO:N is from 1:1.5 to 1:0.5, more preferably from 1:1.3 to 1:0.70, and most preferably from 1:1 to 1:0.70, wherein CO:N is the carbonyl to amine nitrogen ratio. Also, component (i)(b) is preferably made from a polyisobutylene group having a number average molecular weight of from about 700 to about 1300 and that is succinated in the range from 1.0 up to 1.3.

The reaction between the hydrocarbyl-substituted carboxylic acid acylating agent and the ammonia or amine is carried out under conditions that provide for the formation of the desired product, which are set forth in US '237 column 17. In one embodiment, the lubricant soluble product (i) comprises: (i)(a) a first lubricant-soluble product made by reacting a first hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl substituent of said first acylating agent having about 50 to about 500 carbon atoms; and (i)(b) a second lubricant-soluble product made by reacting a second hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl substituent of said second acylating agent having about 50 to about 500 carbon atoms. In this embodiment, the products (i)(a) and (i)(b) are different. For example, the molecular weight of the hydrocarbyl substituent for the first acylating agent may be different than the molecular weight of the hydrocarbyl substituent for the second acylating agent. In one embodiment, the number average molecular weight for the hydrocarbyl substituent for the first acylating agent may be in the range of about 1500 to about 3000, and in one embodiment about 1800 to about 2300, and the number average

molecular weight for the hydrocarbyl substituent for the second acylating agent may be in the range of about 700 to about 1300, and in one embodiment about 800 to about 1000. The first hydrocarbyl-substituted carboxylic acid acylating agent may be a polyisobutene-substituted succinic anhydride, the polyisobutene substituent having a number average molecular weight of about 1500 to about 3000, and in one embodiment about 1800 to about 2300. This first polyisobutene-substituted succinic anhydride may be characterized by at least about 1.3, and in one embodiment about 1.3 to about 2.5, and in one embodiment about 1.7 to about 2.1 succinic groups per equivalent weight of the polyisobutene substituent. The amine used in this first lubricant-soluble product (i)(a) may be an alkanol amine and the product may be in the form of an ester/salt. The second hydrocarbyl-substituted carboxylic acid acylating agent may be a polyisobutene-substituted succinic anhydride, the polyisobutene substituent of said second polyisobutene-substituted succinic anhydride having a number average molecular weight of about 700 to about 1300, and in one embodiment about 800 to about 1000. This second polyisobutene-substituted succinic anhydride may be characterized by about 1.0 to about 1.3, and in one embodiment about 1.0 to about 1.2 succinic groups per equivalent weight of the polyisobutene substituent. The amine used in this second lubricant-soluble product (i)(b) may be an alkanol amine and the product may be in the form of an ester/salt, or the amine may be an alkylene polyamine and the product may be in the form of a succinimide. The lubricant-soluble product (i) may be comprised of: about 1% to about 99% by weight, and in one embodiment about 30% to about 70% by weight of the product (i)(a); and about 99% to about 1% by weight, and in one embodiment about 70% to about 30% by weight of the product (i)(b).

In one embodiment, the lubricant soluble product (i) comprises: (i)(a) a first hydrocarbyl-substituted carboxylic acid acylating agent, the hydrocarbyl substituent of said first acylating agent having about 50 to about 500 carbon atoms; and (i)(b) a second hydrocarbyl-substituted carboxylic acid acylating agent, the hydrocarbyl substituent of said second acylating agent having about 50 to about 500 carbon atoms, said first acylating agent and said second acylating agent being the same or different; said first acylating agent and said second acylating agent being coupled together by a linking group derived from a compound having two or more primary amino groups, two or more

secondary amino groups, at least one primary amino group and at least one secondary amino group, at least two hydroxyl groups, or at least one primary or secondary amino group and at least one hydroxyl group; said coupled acylating agents being reacted with ammonia or an amine. The molecular weight of the hydrocarbyl substituent for the first acylating agent may be the same as or it may be different than the molecular weight of the hydrocarbyl substituent for the second acylating agent.

In one embodiment, the number average molecular weight for the hydrocarbyl substituent for the first and/or second acylating agent is in the range of about 1500 to about 3000, and in one embodiment about 1800 to about 2300. In one embodiment, the number average molecular weight for the hydrocarbyl substituent for the first and/or second acylating agent is in the range of about 700 to about 1300, and in one embodiment about 800 to about 1000. The first and/or second hydrocarbyl-substituted carboxylic acid acylating agent may be a polyisobutene-substituted succinic anhydride, the polyisobutene substituent having a number average molecular weight of about 1500 to about 3000, and in one embodiment about 1800 to about 2300. This first and/or second polyisobutene-substituted succinic anhydride may be characterized by at least about 1.3, and in one embodiment about 1.3 to about 2.5, and in one embodiment about 1.7 to about 2.1 succinic groups per equivalent weight of the polyisobutene substituent. The first and/or second hydrocarbyl-substituted carboxylic acid acylating agent may be a polyisobutene-substituted succinic anhydride, the polyisobutene substituent having a number average molecular weight of about 700 to about 1300, and in one embodiment about 800 to about 1000. This first and/or second polyisobutene-substituted succinic anhydride may be characterized by about 1.0 to about 1.3, and in one embodiment about 1.0 to about 1.2 succinic groups per equivalent weight of the polyisobutene substituent. The linking group may be derived from any of the amines or hydroxamines discussed above having two or more primary amino groups, two or more secondary amino groups, at least one primary amino group and at least one secondary amino group, or at least one primary or secondary amino group and at least one hydroxyl group. The linking group may also be derived from a polyol. The polyol may be a compound represented in US '237 column 20.

The ratio of reactants utilized in the preparation of these linked products may be varied over a wide range. Generally, for each equivalent of each of the first and second acylating agents, at least about one equivalent of the linking compound is used. The upper limit of linking compound is about two equivalents of linking compound for each equivalent of the first and second acylating agents. Generally the ratio of equivalents of the first acylating agent to the second acylating agent is about 4:1 to about 1:4, and in one embodiment about 1.5:1.

The first and second acylating agents may be reacted with the linking compound according to conventional ester and/or amide-forming techniques. This normally involves heating acylating agents with the linking compound, optionally in the presence of a normally liquid, substantially inert, organic liquid solvent/diluent.

The reaction between the linked acylating agents and the ammonia or amine may be carried out under salt, ester/salt, amide or imide forming conditions using conventional techniques.

The hydrocarbon lubricant soluble product (i) may be present in the aqueous hydrocarbon lubricant compositions of the invention at a concentration of about 0.1 to about 15% by weight, and in one embodiment about 0.1 to about 10% by weight, and in one embodiment about 0.1 to about 5% by weight, and in one embodiment about 0.1 to about 2% by weight, and in one embodiment about 0.1 to about 1% by weight, and in one embodiment about 0.1 to about 0.7% by weight.

The ionic or nonionic compound (ii) has a hydrophilic lipophilic balance (HLB) in the range of about 1 to about 20 or 30, and in one embodiment about 4 to about 15 or 20. Examples of these compounds are disclosed in McCutcheon's Emulsifiers and Detergents, 1998, North American & International Edition. Pages 1-235 of the North American Edition and pages 1-199 of the International Edition are incorporated herein by reference for their disclosure of such ionic and nonionic compounds having an HLB in the range of about 1 to about 10 or 30. These are set forth in US '237 column 27. In one embodiment, the ionic or nonionic compound (ii) is a poly(oxyalkene) compound. These include copolymers of ethylene oxide and propylene oxide. In one embodiment, the ionic or nonionic compound (ii) is a hydrocarbon lubricant-soluble product made by reacting an acylating agent having about 12 to about 30 carbon atoms with ammonia or an amine.

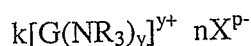
The acylating agent may contain about 12 to about 24 carbon atoms, and in one embodiment about 12 to about 18 carbon atoms. These are set forth in US '237 column 27. The amine may be any of the amines described above as being useful in making the hydrocarbon lubricant-soluble product (i). The product of the reaction between the acylating agent and the ammonia or amine may be a salt, an ester, an amide, an imide, or a combination thereof.

In one embodiment, the ionic or nonionic compound (ii) is an ester/salt made by reacting hexadecyl succinic anhydride with dimethylethanolamine in an equivalent ratio (i.e., carbonyl to amine ratio) of about 1:1 to about 1:1.5, and in one embodiment about 1:1.35.

In one embodiment, the ionic or nonionic compound can be the reaction product of a copolymer of an alpha olefin of 3 to 25 carbon atoms with maleic anhydride reacted with an amine (as previously described). One such reaction product would be a copolymer of octadecene with maleic anhydride that is reacted with triethylene-tetramine. It may be desirable to control crosslinking with these multifunctional reactants by having large amounts of carboxylic acids of lower functionality and/or amines of lower functionality present to avoid forming an insoluble product.

The ionic or nonionic compound (ii) may be present in the aqueous hydrocarbon fuel compositions of the invention at a concentration of about 0.01 to about 15% by weight, and in one embodiment about 0.01 to about 10% by weight, and one embodiment about 0.01 to about 5% by weight, and in one embodiment about 0.01 to about 3% by weight, and in one embodiment about 0.1 to about 1% by weight.

The water-soluble salt (iii) may be any material capable of forming positive and negative ions in an aqueous solution that does not interfere with the other additives. These include organic amine nitrates, nitrate esters, azides, nitramines, and nitro compounds. Also included are alkali and alkaline earth metal carbonates, sulfates, sulfides, sulfonates, and the like. Particularly useful are the amine or ammonium salts represented by the formula



wherein G is hydrogen or an organic group of 1 to about 8 carbon atoms, and in one embodiment 1 to about 2 carbon atoms, having a valence of y; each R independently is

hydrogen or a hydrocarbyl group of 1 to about 10 carbon atoms, and in one embodiment 1 to about 5 carbon atoms, and in one embodiment 1 to about 2 carbon atoms; X^{p-} is an anion having a valence of p ; and k , y , n and p are independently integers of at least 1. When G is H , y is 1. The sum of the positive charge ky^+ is equal to the sum of the negative charge nX^{p-} . In one embodiment, X is a nitrate ion; and in one embodiment it is an acetate ion. Examples include ammonium nitrate, ammonium acetate, methylammonium nitrate, methylammonium acetate, ethylene diamine diacetate, urea nitrate, urea, guanidinium nitrate, and urea dinitrate. Ammonium nitrate is particularly useful.

In one embodiment, the water-soluble salt (iii) functions as an emulsion stabilizer, i.e., it acts to stabilize the aqueous hydrocarbon lubricant compositions.

In one embodiment the water soluble salt may be present in the water-lubricant emulsion at a concentration of about 0.001 to about 1 % by weight, and in one embodiment from about 0.01 to about 1% by weight. In many embodiments the water soluble salt is absent or serves as a different component, such as the water soluble or water dispersible base.

Conventional Detergents

A detergent is an additive that reduces formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines; it normally has acid-neutralizing properties and is capable of keeping finely divided solids in suspension. Most detergents are based on metal "soaps" that is metal salts of acidic organic compounds, which are sometimes referred to as surfactants.

Detergents generally comprise a polar head with a long hydrophobic tail, the polar head comprising a metal salt of an acidic organic compound. The detergents in this invention can be low TBN (<200 mg KOH/g) in which the surfactants are neutralized with base to form metal soaps. Alternatively, they can be overbased detergents in which large amounts of a metal base are included by reacting an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide to give an overbased detergent which comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. The overbased detergents of this invention may have a TBN of at least 200, preferably at least 250, especially at least 300, such as up to 600.

Surfactants that may be used include sulfonates, phenates, sulfurized phenates, salicylates, calixarates, salicylic calixarenes, glyoxylates, saligenins, thiophosphonates, naphthenates, other oil-soluble carboxylates, or mixtures of any of these surfactants. Sulfurized phenates are preferred. The metal may be an alkali or alkaline earth metal, e.g., sodium, potassium, lithium, calcium, and magnesium. Calcium is preferred.

Surfactants for the surfactant system of the overbased metal compounds preferably contain at least one hydrocarbyl group, for example, as a substituent on an aromatic ring. The term "hydrocarbyl" as used herein means that the group concerned is primarily composed of hydrogen and carbon atoms and is bonded to the remainder of the molecule via a carbon atom, but does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the group. Advantageously, hydrocarbyl groups in surfactants for use in accordance with the invention are aliphatic groups, preferably alkyl or alkylene groups, especially alkyl groups, which may be linear or branched. The total number of carbon atoms in the surfactants should be at least sufficient to impart the desired oil-solubility.

These overbased salts can be of oil-soluble organic sulfur acids such as sulfonic, sulfamic, thiosulfonic, sulfinic, sulfonic, partial ester sulfuric, sulfurous and thiosulfuric acid. Generally they are salts of carbocyclic or aliphatic sulfonic acids.

The carbocyclic sulfonic acids include the mono- or poly-nuclear aromatic or cycloaliphatic compounds. The oil-soluble sulfonates can be represented for the most part by the following formulae:



In the above formulae, M is either a metal cation as described hereinabove or hydrogen; T is a cyclic nucleus such as, for example, benzene, naphthalene, anthracene, phenanthrene, diphenylene oxide, thianthrene, phenothioxine, diphenylene sulfide, phenothiazine, diphenyl oxide, diphenyl sulfide, diphenylamine, cyclohexane, petroleum naphthenes, decahydro-naphthalene, cyclopentane, etc.; R^{11} in Formula XIV is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, carboalkoxyalkyl, etc.; x is at

least 1, and $(R^{11})_x-T$ contains a total of at least about 15 carbon atoms, R^{12} in Formula XV is an aliphatic radical containing at least about 15 carbon atoms and M is either a metal cation or hydrogen. Examples of the type of the R^{12} radical are alkyl, alkenyl, alkoxyalkyl, carboalkoxyalkyl, etc. Specific examples of R^{12} are groups derived from petrolatum, saturated and unsaturated paraffin wax, and polyolefins, including polymerized C_2 , C_3 , C_4 , C_5 , C_6 , etc., olefins containing from about 15 to 7000 or more carbon atoms. The groups T, R^{11} and R^{12} in the above formulae can also contain other inorganic or organic substituents in addition to those enumerated above such as, for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfide, disulfide, etc. In Formula XIV, x, y, z and b are at least 1, and likewise in Formula XV, a, b and d are at least 1.

Specific examples of sulfonic acids useful in this invention are mahogany sulfonic acids; bright stock sulfonic acids; sulfonic acids derived from lubricating oil fractions having a Saybolt viscosity from about 100 seconds at 100°F. to about 200 seconds at 210°F.; petrolatum sulfonic acids; mono- and poly-wax substituted sulfonic and polysulfonic acids of, e.g., benzene, naphthalene, phenol, diphenyl ether, naphthalene disulfide, diphenylamine, thiophene, alpha-chloronaphthalene, etc.; other substituted sulfonic acids such as alkyl benzene sulfonic acids (where the alkyl group has at least 8 carbons), cetylphenol mono-sulfide sulfonic acids, dicetyl thianthrene disulfonic acids, dilauryl beta naphthyl sulfonic acid, dicapryl nitronaphthalene sulfonic acids, and alkaryl sulfonic acids such as dodecyl benzene "bottoms" sulfonic acids.

The latter acids derived from benzene which as been alkylated with propylene tetramers or isobutene trimers to introduce 1, 2, 3 or more branched-chain C_{12} substituents on the benzene ring. Dodecyl benzene bottoms, principally mixtures of mono- and di-dodecyl benzenes, are available as by-products from the manufacture of household detergents. Similar products obtained from alkylation bottoms formed during manufacture of linear alkyl sulfonates (LAS) are also useful in making the sulfonates used in this invention.

The production of sulfonates from detergent manufacture-by-products by reaction with, e.g., SO_3 , is well known to those skilled in the art. See, for example, the article

"Sulfonates" in Kirk-Othmer "Encyclopedia of Chemical Technology," Second Edition, Vol. 19, pp. 291 at seq. published by John Wiley & Sons, N.Y. (1969).

Other descriptions of overbased sulfonate salts and techniques for making them can be found in the following U.S. Patent Nos.: 2,174,110; 2,174,506; 2,174,508; 2,193,824; 2,197,800; 2,202,781; 2,212,786; 2,213,360; 2,228,598; 2,223,676; 2,239,974; 2,263,312; 2,276,090; 2,276,297; 2,315,514; 2,319,121; 2,321,022; 2,333,568; 2,333,788; 2,335,259; 2,337,552; 2,346,568; 2,366,027; 2,374,193; 2,383,319; 3,312,618; 3,471,403; 3,488,284; 3,595,790 and 3,798,012. These are hereby incorporated by reference for their disclosures in this regard.

Also included are aliphatic sulfonic acids such as paraffin wax sulfonic acids, unsaturated paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic acids, hexapropylene sulfonic acids, tetra-amylenesulfonic acids, polyisobutene sulfonic acids wherein the polyisobutene contains from 20 to 7000 or more carbon atoms, chloro-substituted paraffin wax sulfonic acids, nitroparaffin wax sulfonic acids, etc.; cycloaliphatic sulfonic acids such as petroleum naphthene sulfonic acids, cetyl cyclopentyl sulfonic acids, lauryl cyclohexyl sulfonic acids, bis-(di-isobutyl) cyclohexyl sulfonic acids, etc.

With respect to the sulfonic acids or salts thereof described herein and in the appended claims, it is intended that the term "petroleum sulfonic acids" or "petroleum sulfonates" includes all sulfonic acids or the salts thereof derived from petroleum products. A particularly valuable group of petroleum sulfonic acids are the mahogany sulfonic acids (so called because of their reddish-brown color) obtained as a by-product from the manufacture of petroleum white oils by a sulfuric acid process.

The terminology "metal ratio" is used to designate the ratio of the total chemical equivalents of the metal in the overbased salt to the chemical equivalents of the metal in the salt which would be expected to result in the reaction between the organic acid to be overbased and the basic reacting metal compound according to the known chemical reactivity and stoichiometry of the two reactants. Thus, in a normal or neutral salt the metal ratio is one and, in an overbased salt, the metal ratio is greater than one. The overbased salts usually have metal ratios of at least 1.1:1. Typically they have ratios of 2:1 or 3:1 to 40:1. Salts having ratios of 12:1 to 20:1 are often used.

The basically reacting metal compounds used to make the overbased salts are usually an alkali or alkaline earth metal compound (i.e., the Group IA, IIA, and IIB metals, but normally excluding francium and radium and typically also excluding rubidium, cesium and beryllium), although other basically reacting metal compounds can be used. Compounds of Ca, Ba, Mg, Na and Li, such as their hydroxides and alkoxides of lower alkanols are usually used as basic metal compounds in preparing these overbased salts but others can be used as shown by the prior art referred to herein. Overbased salts containing a mixture of ions of two or more of these metals can be used in the present invention.

Overbased materials are generally prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, such as carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (mineral oil, naphtha, toluene, xylene, etc.) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter.

The acidic material used in preparing the overbased material can be a liquid such as formic acid, acetic acid, nitric acid, or sulfuric acid. Acetic acid is particularly useful. Inorganic acidic materials can also be used, such as HCl, SO₂, SO₃, CO₂, or H₂S, and in one embodiment, CO₂ or mixtures thereof, e.g., mixtures of CO₂ and acetic acid.

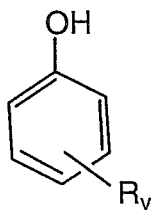
A promoter is a chemical employed to facilitate the incorporation of metal into the basic metal compositions. The promoters are diverse and are well known in the art and include lower alcohols. A discussion of suitable promoters is found in U.S. Patents 2,777,874, 2,695,910, and 2,616,904.

Patents specifically describing techniques for making basic salts of acidic organic compounds generally include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109.

Phenate surfactants for use in this invention, may be non-sulfurized or sulfurized. Further, phenate includes those containing more than one hydroxyl group (for example, from alkyl catechols) or fused aromatic rings (for example, alkyl naphthols) and those which have been modified by chemical reaction, for example, alkylene-bridged and

Mannich base-condensed and saligenin-type (produced by the reaction of a phenol and an aldehyde under basic conditions).

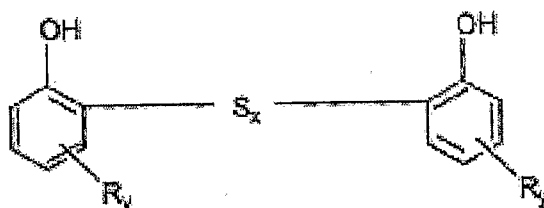
Preferred, phenols on which the phenate surfactants are based may be derived from the formula I below:



Formula I

where R represents a hydrocarbyl group and y represents 1 to 4. Where y is greater than 1, the hydrocarbyl groups may be the same or different.

The phenols are frequently used in sulfurized form. Sulfurized hydrocarbyl phenols may typically be represented by the formula II below:



Formula II

where x is generally from 1 to 4. In some cases, more than two phenol molecules may be linked by S_x bridges.

In the above formulae, hydrocarbyl groups represented by R are advantageously alkyl groups, which advantageously contain 5 to 100, preferably 5 to 40, especially 9 to 12, carbon atoms, the average number of carbon atoms in all of the R groups being at least about 9 in order to ensure adequate solubility in oil. Preferred alkyl groups are dodecyl (tetrapropylene) groups.

In the following discussion, hydrocarbyl-substituted phenols will for convenience be referred to as alkyl phenols.

A sulfurizing agent for use in preparing a sulfurized phenol or phenate may be any compound or element which introduces $-(S)_x-$ bridging groups between the alkyl

phenol monomer groups, wherein x is generally from 1 to about 4. Thus, the reaction may be conducted with elemental sulfur or a halide thereof, for example sulfur dichloride. If elemental sulfur is used, the sulfurization reaction may be effected by heating the alkyl phenol compound at from 50 to 250, preferably at least 100°C. If a sulfur halide is used, the sulfurization reaction may be effected by treating the alkyl phenol at from -10 to 120, preferably at least 60°C. The reaction may be conducted in the presence of a suitable diluent. The diluent advantageously comprises a substantially inert organic diluent, for example mineral oil or an alkane. In any event, the reaction is conducted for a period of time sufficient to effect substantial reaction. It is generally preferred to employ from 0.1 to 5 moles of the alkyl phenol material per equivalent of sulphurizing agent.

Where elemental sulfur is used as the sulfurizing agent, it may be desirable to use a basic catalyst, for example, sodium hydroxide or an organic amine, preferably a heterocyclic amine (e.g., morpholine).

Details of sulfurization processes are well known to those skilled in the art.

Regardless of the manner in which they are prepared, sulfurized alkyl phenols useful in preparing overbased metal compounds generally comprise diluent and unreacted alkyl phenols and generally contain from 2 to 20, preferably 4 to 14, most preferably 6 to 12, mass % of sulfur, based on the mass of the sulfurized alkyl phenol.

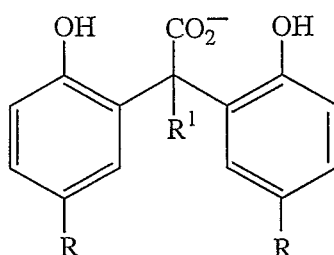
As indicated above, the term "phenol" as used herein includes phenols which have been modified by chemical reaction with, for example, an aldehyde, and Mannich base-condensed phenols.

Aldehydes with which phenols may be modified include, for example, formaldehyde, propionaldehyde and butyraldehyde. The preferred aldehyde is formaldehyde. Aldehyde-modified phenols suitable for use are described in, for example, US-A-5 259 967.

Mannich base-condensed phenols are prepared by the reaction of a phenol, an aldehyde and an amine. Examples of suitable Mannich base-condensed phenols are described in GB-A-2 121 432.

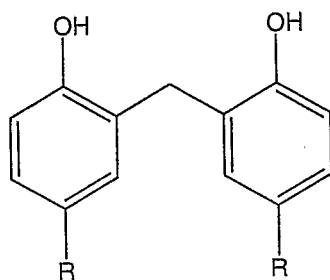
In general, the phenols may include substituents other than those mentioned above provided that such substituents do not detract significantly from the surfactant properties of the phenols. Examples of such substituents are methoxy groups and halogen atoms.

The functionalization of the alkyl phenol can comprise the addition of any functional group to the phenolic compound, other than an additional hydroxy group or an additional hydrocarbyl group, at least one such alkyl or hydrocarbyl group already being present in sufficient amount to provide oil solubility to the detergent. Typical functional groups include t-butyl groups, methylene coupling groups, ester-substituted alkyl groups, and aldehyde groups. In one embodiment the functionalization is by addition of carboxy functionality, in which case the detergent can be an alkyl salicylate or a derivative thereof. Salicylate detergents are well known; see, for instance, U.S. Patent 5,688,751 or 4,627,928. In another embodiment, the substituent can be based on a glyoxylic acid condensation. Glyoxylic acid itself is $\text{HC}(=\text{O})\text{--CO}_2\text{H}$; related ketones of the structure $\text{R}^1\text{C}(=\text{O})\text{--CO}_2\text{H}$ are also contemplated; thus R^1 can be hydrogen or a hydrocarbyl group of, for instance, 1 to 20 carbon atoms. A typical glyoxylate condensation product is shown here as an anionic species, which will typically be neutralized with a metal salt.



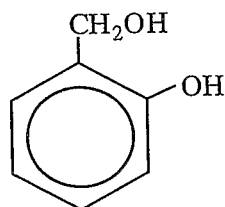
In this structure, the R groups are alkyl groups. The material shown would be the condensation of 2 moles of alkyl phenol with 1 mole of glyoxylic acid or derivative thereof. Other molar ratios are also possible; when a 1:1 ratio is approached, the condensation product becomes oligomeric or polymeric. These materials and methods for their preparation are disclosed in greater detail in U.S. Patent 5,356,546.

In other embodiments the functionalized alkyl phenol can be a condensation product of the alkyl phenol with formaldehyde or other lower aldehydes. The acidic substituent, in this case, would be considered to be the one or more additional phenolic groups. The simplest such condensation product would be

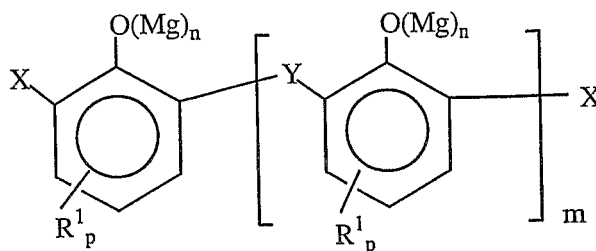


shown here as the 2:1 molar condensate of phenol:formaldehyde. Also, depending on the conditions of reaction, the formaldehyde unit may appear in other oxidation states. As in the case of glyoxylates, oligomeric structures can be formed when the molar ratio of formaldehyde:phenol increases. Examples of such type of oligomeric species are the calixarates, which are cyclic materials containing 4 to 8 phenol-formaldehyde repeat units. Calixarates and methods of their preparation are disclosed in greater detail in U.S. Patent 5,114,601. As will be apparent, mixtures of formaldehyde, other aldehydes, and glyoxylic acid can also be employed in such condensation reactions.

One category of functionalized derivatives of alkyl phenols, however, is certain saligenin derivatives. Saligenin itself, also known as salicyl alcohol and o-hydroxybenzyl alcohol, is represented by the structure



Useful saligenin derivatives include certain metal saligenin derivative which function as detergents. When the metal is magnesium, these compounds can be represented by the formula



This represents generally a metal salt, such as a magnesium salt, of a compound containing one aromatic ring or a multiplicity of aromatic rings linked by "Y" groups, and also containing "X" groups. (Mg) represents a valence of a magnesium ion, and n, in each instance, is 0 or 1. (When n is zero the Mg is typically replaced by H to form an -OH group.) The value for "m" is typically 0 to 10, so number of such rings will be 1 to 11, although it is to be understood that the upper limit of "m" is not a critical variable. In one embodiment m is 2 to 9, such as 3 to 8 or 4 to 6. Other metals include alkali metals such as lithium, sodium, or potassium; alkaline earth metals such as calcium or barium; and other metals such as copper, zinc, and tin. Saligenins useful in this invention include those described in U.S. Patent 6,310,009 hereby incorporated by reference for its teachings.

Most of the rings contain at least one R^1 substituent, which is the aforementioned hydrocarbyl group, such as alkyl group. R^1 can contain 1 to 60 carbon atoms, such as 7 to 28 carbon atoms or 9 to 18 carbon atoms. Of course it is understood that R^1 will normally comprise a mixture of various chain lengths, so that the foregoing numbers will normally represent an average number of carbon atoms in the R^1 groups (number average). Each ring in the structure will be substituted with 0, 1, 2, or 3 such R^1 groups (that is, p is 0, 1, 2, or 3), most typically 1, and of course different rings in a given molecule may contain different numbers of such substituents. At least one aromatic ring in the molecule must contain at least one R^1 group, and the total number of carbon atoms in all the R^1 groups in the molecule should be at least 7, such as at least 12.

In the above structure the X and Y groups may be seen as groups derived from formaldehyde or a formaldehyde source, by condensative reaction with the aromatic molecule. The relative amount of the various X and Y groups depends to a certain extent on the conditions of synthesis of the molecules. While various species of X and Y may be present in the molecules in question, the commonest species comprising X are -CHO (aldehyde functionality) and -CH₂OH (hydroxymethyl functionality); similarly the commonest species comprising Y are -CH₂- (methylene bridge) and -CH₂OCH₂- (ether bridge). The relative molar amounts of these species in a sample of the above material can be determined by ¹H/¹³C NMR as each carbon and hydrogen nucleus has a distinctive environment and produces a distinctive signal. (The signal for the ether linkage, -

CH₂OCH₂- must be corrected for the presence of two carbon atoms, in order to arrive at a correct calculation of the molar amount of this material. Such a correction is well within the abilities of the person skilled in the art.)

In one embodiment, X is at least in part -CHO and such -CHO groups comprise at least 10, 12, or 15 mole percent of the X and Y groups. In another embodiment the -CHO groups comprise 20 to 60 mole percent of the X and Y groups, such as 25 to 40 mole percent of the X and Y groups.

In another embodiment, X is at least in part -CH₂OH and such -CH₂OH groups comprise 10 to 50 mole percent of the X and Y groups, such as 15 to 30 mole percent of the X and Y groups.

In an embodiment in which m is non-zero, Y is at least in part -CH₂- and such -CH₂- groups comprise 10 to 55 mole percent of the X and Y groups, such as 25 to 45 or 32 to 45 mole percent of the X and Y groups.

In another embodiment Y is at least in part -CH₂OCH₂- and such -CH₂OCH₂- groups comprise 5 to 20 mole percent of the X and Y groups, such as 10 to 16 mole percent of the X and Y groups.

The above-described compound is, as mentioned, typically a magnesium salt and, indeed, the presence of magnesium during the preparation of the condensed product is believed to be useful in achieving the desired ratios of X and Y components described above. The number of Mg ions in the compound is characterized by an average value of "n" of 0.1 to 1 throughout the composition, such as 0.2 or 0.3 to 0.4 or 0.5, or 0.35 to 0.45. Since Mg is normally a divalent ion, when all of the phenolic structures shown are entirely neutralized by Mg⁺² ions, the average value of n in the composition will be 0.5, that is, each Mg ion neutralizes 2 phenolic hydroxy groups. Those two hydroxy groups may be on the same or on different molecules. If the value of n is less than 0.5, this indicates that the hydroxy groups are less than completely neutralized by Mg ions. If the value of n is greater than 0.5, this indicates that a portion of the valence of the Mg ions is satisfied by an anion other than the phenolic structure shown. For example each Mg ion could be associated with one phenolic anion and one hydroxy (OH⁻) ion, to provide an n value of 1.0. The specification that n is 0.1 to 1.0 is not directly applicable to overbased

versions of this material (described below and also a part of the present invention) in which an excess of Mg or another metal can be present.

It is understood that in a sample of a large number of molecules, some individual molecules may exist which deviate from these parameters, for instance, there may be some molecules containing no R^1 groups whatsoever. These molecules could be considered as impurities, and their presence will not negate the present invention so long as the majority (and generally the substantial majority) of the molecules of the composition are as described.

The above-described component can be prepared by combining a phenol substituted by the above-described R^1 group with formaldehyde or a source of formaldehyde and magnesium oxide or magnesium hydroxide under reactive conditions, in the presence of a catalytic amount of a strong base. Common reactive equivalents of formaldehyde include paraformaldehyde, trioxane, and formalin. For convenience, paraformaldehyde is can be used.

The relative molar amounts of the substituted phenol and the formaldehyde can be important in providing products with the desired structure and properties. In a typical embodiment, the substituted phenol and formaldehyde are reacted in equivalent ratios of 1:1 to 1:3 or 1:4, such as 1:1.1 to 1:2.9 or 1:1.4 to 1:2.6, or 1:1.7 to 1:2.3. Thus in one embodiment there will be about a 2:1 equivalent excess of formaldehyde. (One equivalent of formaldehyde is considered to correspond to one H_2CO unit; one equivalent of phenol is considered to be one mole of phenol.)

The strong base can be sodium hydroxide or potassium hydroxide, and can be supplied in an aqueous solution.

The process can be conducted by combining the above components with an appropriate amount of magnesium oxide or magnesium hydroxide with heating and stirring. A diluent such as mineral oil or other diluent oil can be included to provide for suitable mobility of the components. An additional solvent such as an alcohol can be included if desired, although it is believed that the reaction may proceed more efficiently in the absence of additional solvent. The reaction can be conducted at room temperature or at a slightly elevated temperature such as 35-120°C, 70-110°C, or 90-100°C, and of course the temperature can be increased in stages. When water is present in the reaction

mixture it is convenient to maintain the mixture at or below the normal boiling point of water. After reaction for a suitable time (e.g., 30 minutes to 5 hours or 1 to 3 hours) the mixture can be heated to a higher temperature, typically under reduced pressure, to strip off volatile materials. Favorable results are obtained when the final temperature of this stripping step is 100 to about 150°C, such as 120 to about 145°C.

Reaction under the conditions described above typically leads to a product which has a relatively high content of -CHO substituent groups, that is, 10%, 12%, and even 15% and greater. Such materials, when used as detergents in lubricating compositions, exhibit good upper piston cleanliness performance, low Cu/Pb corrosion, and good compatibility with seals. Use of metals other than magnesium in the synthesis typically leads to a reduction in the content of -CHO substituent groups.

Salicylate surfactants used in accordance with the invention may be non-sulfurized or sulfurized, and may be chemically modified and/or contain additional substituents, for example, as discussed above for phenates. Processes similar to those described above may also be used for sulfurizing a hydrocarbyl-substituted salicylic acid, and are well known to those skilled in the art. Salicylic acids are typically prepared by the carboxylation, by the Kolbe-Schmit process, of phenoxides, and in that case, will generally be obtained (normally in a diluent) in admixture with uncarboxylated phenol.

Calixarates such as salixarenes i.e. salicylic calixarenes are also useful compounds to add as surfactants to lubricating oils. Salicylic calixarenes useful in this invention include those described in US Patent 6,200,936B1 to the Lubrizol Corporation hereby incorporated by reference for its teachings.

Preferred substituents in oil-soluble salicylic acids from which salicylates in accordance with the invention may be derived are the substituents represented by R in the discussion above of phenols. In alkyl-substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 12 to 20, carbon atoms.

Oil of Lubricating Viscosity

The lubricating oil(s) (base oils or basestocks) used may vary significantly depending on the final intended use of the lubricating fluid. SAE 5 or 10 to about 70 are typical of the oils used in various internal combustion engines of various designs. Marine diesel applications typically call for the higher viscosity oils to provide a thicker

lubricating film. While multigrade oils are desirable where the oil needs to provide lubrication at higher use temperatures along with low energy consumption at cold starting temperatures, marine diesel applications tend to use a single grade oil because the engines are subject to minimal cycling on and off and run for extended periods of time when operational. If multigrade oil is used, desirably it has a viscosity index of at least 90, more desirably at least 100 and preferably at least 110. Desirably the lubricating oil basestock for marine diesel applications has a kinematic viscosity at 100 C (as measured by ASTM D445) of at least 14 centistokes, preferably at least 15 centistokes, more preferably in the range of from 16 to 30 centistokes, for example from 16 to 25 centistokes.

The lubricating oil can be any conventional oil or blends thereof used in internal combustion engines for a lubricant. Often for cost reasons the oil is a petroleum derived lubricating oil (e.g. distillation products), such as a naphthenic base, paraffinic base or a mixed base oil. The lubricant depending on the application may be a blend of petroleum derived oils and synthetic oils. Alternatively the lubricating oil may be synthetic lubricating oils such as synthetic ester lubricating oils. Other lubricating oils that can be used are hydrocracked oils where the refining process further breaks down the middle and heavy distillate fractions in the presence of hydrogen. Liquid alpha olefin polymers may also be part or all of the lubricant. Fischer-Tropsch oils can be used in the lubricant. Brightstock, typically characterized as solvent-extracted, de-asphalted products from vacuum residuum, typically having a kinematic viscosity at 100°C of from 28- 36 centistokes may also be used.

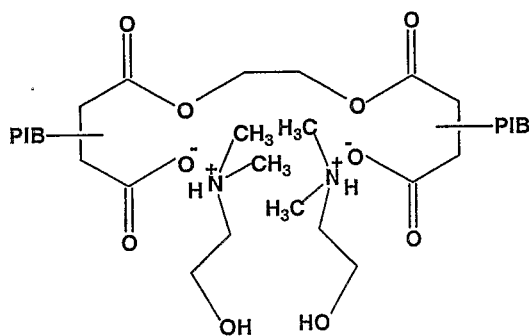
The lubricant of the invention also can include conventional additives like detergents, dispersants, viscosity modifiers, antioxidants, extreme pressure additives (antiwear additives), foam inhibitors, corrosion inhibitors, etc. that are well known to the lubricant art. These additives can be used in conventional amounts.

In one embodiment, the lubricant of the invention contains an antifreeze agent to prevent freezing of the water component. The antifreeze agent is typically an alcohol. Examples include but are not limited to ethylene glycol, propylene glycol, methanol, ethanol, glycerol and mixtures of two or more thereof. The antifreeze agent is typically used at a concentration sufficient to prevent freezing of the water used in the lubricant.

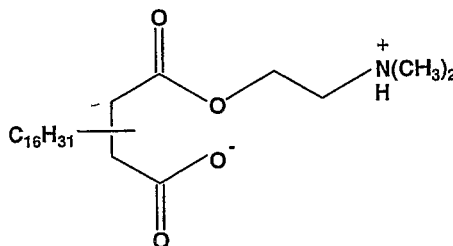
The concentration is therefore dependent upon the temperature at which the lubricant is stored or used. In one embodiment, the concentration is at a level of up to about 20% by weight based on the weight of the water-oil emulsion, and in one embodiment about 0.1 to about 20% by weight, and in one embodiment about 0.2 to about 10% by weight.

The emulsifiers play an important role in the emulsion preparation and storage stability. The first emulsifier of a blend of two emulsifiers used to prepare the examples was a PIBSA:EG:DMEA, polyisobutenyl succinic anhydride:ethylene glycol :dimethyl ethanol amine – 2:1:2 (eq). This emulsifier has a high molecular weight polyisobutylene chain (~1500MW) and a low HLB. Emulsifier two was a co-emulsifier. HDSA:DMEA, dodecahexylene succinic anhydride: dimethyl ethanolamine 1:1 (eq.). It has a low molecular weight and a high HLB. The structures of these two emulsifiers are presented below.

**Emulsifiers used in the laboratory manufacture of
water lubricating oil emulsion**



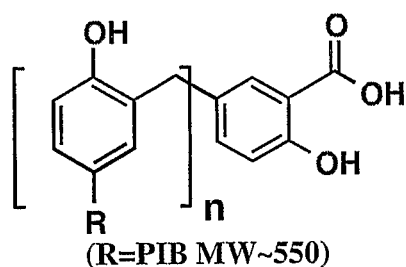
PIBSA:EG:DMEA
(≈2:1:2 (eq))



HDSA:DMEA
(≈1:1 (eq))

The emulsifiers can be either dosed through an emulsifying concentrate or could be directly dissolved in the SAE-50 oil. Other emulsifiers could be used for the preparation of water/marine lubricating oil emulsions. The emulsion may also contain a dispersant, like PIBSA:TEPA, a polyisobutenyl succinic anhydride:tetraethylene pentaamine —3:1 eq and an antioxidant, like calcium dodecyl phenate sulphide.

A supplementary high HLB salixarene emulsifier is shown below.



Where R is approximately a 550 number average molecular weight polyisobutylene oligomer and n is a value between 1 and 10, more desirably between 1 and 4. These salixarene or their metal salts, salixarates, are more generally referred to as detergents and are described as a detergent in this application, but they may also function as an emulsifier or surfactant. These types of compounds are generally taught in US patent 6,200,936, which is hereby incorporated by reference for its teachings on making both linear and cyclic salixarenes and their metal salts, salixarates.

Example 1: Incorporation of a Water-Soluble Inorganic Compound (KOH)

Table 1

Ingredient	% Wt
ESSO 600 SN Oil	43.07
ESSO 150 BS Oil	31.90
Alkenylsuccinic ester salt using dimethylethanol amine HDSA:DMEA	0.31
Polyisobutenyl (about 1000 MW) succinic anhydride OR Polyolefin succinic aminoester/salt (PIBSA:EG:DMEA)	1.19
Polyisobutenylsuccinic anhydride, product with polyethyleneamines	1.34
Calcium dodecylphenatesulfide	2.19
Potassium Hydroxide	13.00
Distilled Water	7.00
TOTAL	100

Procedure:

An aqueous solution of KOH was prepared by adding 154g of KOH flake into 286g of distilled water. The organic blend was prepared by adding the surfactants to the base oil. The aqueous solution (30g) was added with the organic blend (120g) into a Waring blender and blended for 6 minutes. A total of 6 blends were done, to get 900g of emulsified solution. This solution was added into a 2-L four-neck flask equipped with an

overhead stirrer, condenser, collection flask cooled with a dry ice trap, vacuum inlet and thermowell, then slowly evacuated to a pressure of 30 mm Hg. The emulsion was slowly heated to 150C over 1h then held at 150C for 120 minutes. A total of 100.5g of water was collected; the experimentally determined water content was 1.087%. The appearance of the dehydrated emulsion was very clear, with a turbidity (JTU 5% in hexanes) of 20.0. The solids content was low (0.8% volume), while the TBN was as expected (60.9 mg KOH/g).

This procedure was also used to successfully incorporate 5% NaOH in place of 7% KOH to deliver a clear solution of comparable TBN.

EXAMPLE 2: Water-Soluble Organic Compound (Di sodium salt of dimercapto-thiadiazole (DMTD))

Table 2

Ingredient	% Wt
Exxon 600N Oil	88.2
Benzenamine, ar-nonyl-N(nonylphenyl)- & benzenamine, ar-nonyl-N(phenyl)-	0.45
Polyisobutenylsuccinic anhydride, product with polyethyleneamines	0.9
Oil (diluent oil)	0.36
(2-Ethylhexyl/Ethyl) acrylate copolymer	0.072
Polydimethylsiloxane	0.018
1,3,4-thiadiazole, Na salt	4.5
Distilled Water	5.5
TOTAL	100

Procedure:

The emulsion was prepared with a Waring blender as described in Example 1. The emulsion (1409.3 g) was added to a 3L four-neck flask equipped with an overhead stirrer, condenser, collection flask cooled with a dry ice trap, vacuum inlet and thermowell, then slowly evacuated to a pressure of 30 mm Hg. The emulsion was slowly heated to 150C over 1h then held at 150C for 2h. A total of 147.5g of water was collected; the experimentally determined water content was 0.025%. The appearance of the dehydrated emulsion was very clear during heating at 78C, and then suddenly became cloudy. The final appearance of the dehydrated emulsion was the same creamy yellow color as the initial emulsion. Yield was 93%.

Samples of the dispersion of di-sodium salt of DMTD before and after dehydration were tested. Preliminary results indicate improved wear performance using the dehydrated emulsion relative to both the emulsion prior to dehydration and to a conventional baseline formulation (synthetic).

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. While ranges are given for most of the elements of the invention independent of the ranges for other elements, it is anticipated that in more preferred embodiments of the invention, the elements of the invention are to be combined with the various (assorted) desired or preferred ranges for each element of the invention in various combinations. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

Claims

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1. An additive package for a lubricant or functional fluid comprising
 - a) an oil of lubricating viscosity,
 - b) at least one emulsifier capable of forming a water in oil emulsion,
 - c) optionally an oil insoluble solvent(s) and
 - d) at least 0.1 part by weight of an oil insoluble functional lubricant additive selected from friction modifiers including extreme pressure additive, corrosion inhibitor, antioxidant, or metal protectorant characterized as being an oil insoluble dispersed phase partially or completely stabilized as a dispersion by said at least one emulsifier, wherein said oil insoluble functional additive is neither characterized as a detergent (e.g. overbased metals) nor a borate compound, wherein said parts by weight are based upon 100 parts by weight of said additive package, and wherein the amount of said oil-insoluble solvent is less than 20% by weight based on the weight of said package.
2. An additive package according to claim 1, wherein the oil less said functional additive, emulsifier, and optional solvent has a viscosity from about 2 centistokes to about 50 centistokes at 50 °C and said functional additive is in a dispersed phase having less than 30 wt.% of said oil insoluble solvent(s) based on the weight of said additive and wherein said dispersed phase has an intensity average particle size by light scattering of 1 or 5 nanometers to 100 microns.
3. An additive package according to claim 1, wherein said oil insoluble solvent(s) is from about 0 to about 20 weight percent of the weight of said functional additive.
4. An additive package according to claim 3 said functional additive is in a dispersed phase having an intensity average particle size by light scattering of from 1 or 5 nanometers to 100 microns.

5. An additive package according to claim 1, further comprising at least one conventional lubricating oil additive selected from dispersant(s), detergent(s), viscosity modifier(s), and antioxidant(s) in a total amount of at least 1 part by weight per 100 parts by weight of said additive package.
6. An additive package according to claim 5, wherein said at least one emulsifier comprises a polyisobutylene functionalized succan portion having a number average molecular weight of at least 600 reacted with one or more other chemicals to provide a polar end group or (please give me a list of other emulsifiers e.g. a salixarene, or a Mannich dispersant).
7. An additive package according to claim 5, further comprising at least one antioxidant selected from a metal dithiophosphate, a hindered phenol, an aromatic amine, sulfurized olefin, copper antioxidant, salicylate acid or its derivative or a sulfurized phenol.
8. An additive package according to claim 5, wherein said oil insoluble functional additive is present as a dispersed phase with an intensity average particle diameter by light scattering from about 20 nanometers to about 10 microns and wherein said oil-insoluble solvent is present in an amount of less than 20 weight percent based on the weight of said oil-insoluble functional additive.
9. An additive package according to claim 8, wherein said oil insoluble functional additive is an antioxidant or an antiwear additive.
10. A lubricant comprising;
 - a) from about 50 to about 99 wt.% of one or more oils of lubricating viscosity,
 - b) less than 20 wt.% total of oil insoluble solvent(s)
 - c) from about 0.02 to about 15 wt.% of a emulsifier(s) capable of forming a water in oil emulsion

from about 0.01 to about 40 wt.% of an oil insoluble functional additive selected from extreme pressure additive, corrosion inhibitor, antioxidant, metal protectorant, wherein said oil insoluble functional additive is present as a dispersed phase optionally with said oil insoluble solvent(s) present, wherein said oil insoluble functional additive is neither characterized as a detergent (e.g. overbased metals) nor a borate, and wherein said wt.% is based on the weight of said lubricant.

11. A lubricant according to claim 10, wherein said oil insoluble functional additive is present as a dispersed phase with an intensity average particle diameter by light scattering from about 20 nanometers to about 10 microns and wherein said oil-insoluble solvent is present in an amount of less than 20 weight percent based on the weight of said oil-insoluble functional additive.

12. A lubricant according to claim 11, further comprising at least one conventional lubricating oil additive selected from dispersant(s), detergent(s), viscosity modifier(s), and antioxidant(s) in a total amount of at least 1 part by weight per 100 parts by weight of said additive package.

13. A lubricant according to claim 12, wherein said at least one emulsifier comprises a polyisobutylene functionalized succan portion having a number average molecular weight of at least 600 reacted with one or more other chemicals to provide a polar end group or (please give me a list of other emulsifiers e.g. a salixarene, or a Mannich dispersant).

14. A lubricant according to claim 11, further comprising at least one antioxidant selected from a metal dithiophosphate, a hindered phenol, an aromatic amine, sulfurized olefin, copper antioxidant, salicylate acid or its derivative or a sulfurized phenol.

15. A process for forming an additive package for a functional fluid (including a lubricant) comprising;

- a) dissolving or dispersing an oil insoluble functional additive in an oil insoluble solvent e.g. water forming a dispersion or blend,
- b) adding said dispersion or blend of said oil insoluble functional additive and oil insoluble solvent to a lubricating oil,
- c) dispersing said dispersion or blend of said oil insoluble functional additive and solvent in said lubricating oil as a dispersed phase using a water in oil type emulsifier, and
- d) thereafter removing a portion or all of said solvent(s) so that the total oil insoluble solvent content in the dispersed phase is less than 30 wt.% based on the weight of said functional additive(s)
- e) wherein said insoluble functional additive is neither a borate compound nor an overbased or neutral metal detergent.

16. A process according to claim 15 wherein after step d, the amount of oil insoluble solvent is present at less than 20 wt.%, and preferably less than 10 or 5 wt.% based on the weight of said functional additive.

17. A process according to claim 15 further comprising a step of adding at least one part by weight of a conventional oil soluble additive selected from antioxidant, dispersant, detergent, viscosity modifier, antiwear additive or combinations thereof based on 100 parts by weight of said additive package or lubricant.

18. A process according to claim 15, wherein said oil insoluble functional additive is present after said steps as a dispersed phase with an intensity average particle diameter by light scattering from about 20 nanometers to about 10 microns and wherein said oil-insoluble solvent is present in an amount of less than 20 weight percent based on the weight of said oil-insoluble functional additive.

19. A process according to claim 15, wherein said oil-in-water emulsifier comprises a polyisobutylene functionalized succan portion having a number average molecular weight of at least 600 reacted with one or more other chemicals to provide a polar end

group or (please give me a list of other emulsifiers e.g. a salixarene, or a Mannich dispersant).

20. A process for preparing an oil insoluble component for additive package for a functional fluid or a lubricant comprising;

- a) dissolving or dispersing an oil insoluble functional additive in an oil insoluble solvent(s) (e.g. water) forming a mixture ,
- b) adding said mixture to a lubricating oil,
- c) dispersing said mixture in said lubricating oil as a dispersed phase using a water in oil type emulsifier, and
- d) thereafter removing at least 50 weight percent of the original portion of said oil insoluble solvent(s), so that the total oil insoluble solvent content in the dispersed phase is less than 30 wt.% based on the weight of said functional additive and wherein said oil insoluble functional additive is neither a conventional lubricant detergent nor a borate compound.

21. A process according to claim 20, wherein said oil insoluble functional additive is metal containing antioxidant (e.g. copper).

22. A process according to claim 20, wherein said oil insoluble functional additive is an antiwear or extreme pressure additive.

23. A process according to claim 20, wherein said oil insoluble functional additive is a compound(s) containing bismuth, inorganic phosphates (as opposed to organic phosphates), or molybdenum.