

Sulphurised Phenol Additives and Compositions

The present invention is concerned with a process for preparing sulfurised phenol lubricating oil additives, lubricant oil compositions and concentrates containing such additives and with the use of such additives in lubricant oil formulations.

Power trains, for example, automotive power trains, require shaft and bearing seals to prevent the ingress of contaminants. Seal life depends on, inter alia, the suitability of the chosen seal, the care in installing the seal, the exposure temperature of the seal in use, and the nature of the lubricants and the condition of the surface(s) contacting the seal in use. Seal failure will mostly cause lubricant to leak, which is increasingly regarded as unacceptable, leaking seals must normally be replaced. Thus, the life of seals needs to be prolonged for as long as possible.

Sulfur-containing additives have been widely used in various lubricants, e.g., crankcase lubricating oils, or gear lubricants, and in various functional fluids, e.g., hydraulic fluids, automatic transmission fluids and heat transfer fluids. One of the most common of such sulfur-containing additives are the sulfurised phenols such as alkyl substituted phenolsulfides, disulphides, polysulfides, salts thereof, overbased salts thereof, and mixtures thereof. The additives function as oxidation inhibitors, antiwear additives, load carrying additives and detergents for these different category of fluids.

Although these sulfur-containing additives have been effective for the above mentioned functions, they have generally been found to be corrosive to metals such as copper and copper alloys, which are widely used as bearings and bearing liners. They have also been found to degrade elastomeric materials, which are used as seals or sealant devices, a particular problem with sulfurised phenol additives. The problems associated with copper corrosion and/or seals preclude use of higher levels of sulphurised phenols. It is also desirable that lubricating oil formulations contain as little ash as possible. It is believed the presence of sulphur species, including elemental sulfur, sometimes referred to as labile, free or active sulfur, gives rise to the problems associated with sulphurised phenols.

The art describes attempts to provide sulfurised phenols and other sulfur-containing additives for lubricating oils which do not have a detrimental effect on

the compatibility of elastomeric seals when exposed to such seals in oil formulations and/or which exhibit reduced copper corrosion.

U.S. Patent No. 4 228 022 describes a process in which a sulfurised phenate is reacted with sufficient α -olefin (C₁₅₋₁₈) to ensure that the final product has substantially no residual free sulfur so that the product has anti-corrosive properties; that is, so that it does not corrode metallic engine parts. The level of α -olefin which may be used is up to 25 wt % based on the amount of phenol used to prepare the phenate. More generally, the patent states that the olefins preferably contain 10 to 30 carbon atoms, especially 15 to 20 carbon atoms, and may be straight or branched chain. The patent does not discuss the performance of elastomeric materials.

International Specification No. WO 85/04896 describes obtaining labile sulfur-free additives for lubricants by treating sulfurised phenol additives containing labile or active sulfur with copper, or copper and another material reactive with labile sulfur, or with a mono-olefin, particularly an α -olefin; α -olefins containing 4 to 30 carbon atoms, especially 10 to 20 carbon atoms, being preferred. It is stated that the metal corrosivity and the degradation of elastomeric materials which are caused by labile sulfur-containing additives can be substantially eliminated. There is no reference to specific elastomeric materials and the olefins mentioned in the Examples are C₁₂, C₁₅₋₁₈ or C₁₆₋₁₈ α -olefins.

Also, there is a need for lubricating oil additives having reduced levels of chlorine so that their use in finished oil formulations does not contribute to high levels of chlorine in the finished lubricating oil formulation. The presence of chlorine in lubricating oils creates waste disposal and environmental problems. Thus, destroying lubricating oils containing high levels of chlorine after their use e.g. by incineration, may produce harmful chlorinated and polychlorinated biphenyls.

A problem in the art is to provide ashless sulfurised phenol additives having both a low active sulphur content and also a low chlorine content, to enable the additives to be used at high levels in lubricating oil compositions which are compatible with elastomeric seals, particularly nitrile, and which do not contribute significantly to the chlorine content of the composition.

A first aspect of the invention is a process for preparing an oil-soluble sulphurised phenol containing less than 1000 ppm by weight of chlorine, which comprises the steps of:

- (a) reacting together sulphur monochloride and at least one phenol that is substituted with one or more hydrocarbyl radicals, wherein the mole ratio of phenol to sulphur monochloride is greater than 1.7:1, to produce an oil-soluble phenol intermediate containing less than 1000 ppm by weight of chlorine; and
- (b) completely reacting an unsaturated organic compound having one or more olefinic or acetylenic bonds with the intermediate at elevated temperature to reduce the amount of active sulphur to produce a sulphurised phenol.

A second aspect of the invention is an oil-soluble sulfurised phenol additive compatible with nitrile seals obtained or obtainable by the above process, provided that the additive is not obtainable by:

- (i) reacting together at a temperature of at least 100°C : an oil-soluble active-sulfur containing sulfurised phenol intermediate; and an olefin or an acetylenic compound in an amount in excess of that required to react with the active sulfur present in the sulfurised phenol intermediate; and
- (ii) removing substantially all unreacted olefin or acetylenic compound.

A third aspect of the invention is a lubricating oil composition which comprises lubricating oil as a major component and an oil-soluble sulfurised phenol additive of the second aspect of the invention.

A fourth aspect of the invention is a lubricating oil concentrate which comprises one or more lubricant additives, and an oil soluble sulfurised phenol additive of the second aspect of the invention.

A fifth aspect of the invention is the use of an oil soluble sulfurised phenol additive of the second aspect of the invention to enhance the nitrile elastomer seal compatibility and/or the copper corrosion properties of a lubricating oil composition.

The present invention gives rise, for example, to an additive concentrate suitable for incorporation into a low chlorine oil composition which comprises

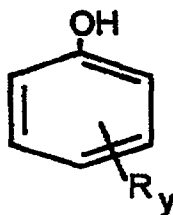
- (a) a lubricating oil, and
- (b) an oil-soluble sulphurised phenol,

the concentrate containing greater than 7% by weight of sulphur and less than 1000 ppm of chlorine, and to a lubricating oil composition comprising an oil-soluble sulphurised phenol, the composition containing greater than 1% by weight of the phenol and less than 50 ppm of chlorine.

The features of the invention will now be discussed in more detail as follows:-

STEP (a)

Preferably, the phenol is represented by the formula II



II

wherein R represents a hydrocarbyl group and y is 1, 2, 3 or 4.

Mixtures of phenols of general formula II may be used.

Preferably, the oil soluble sulfurised phenol intermediate has at least 4% by weight of sulfur.

Preferably, the step comprises reacting together sulfur monochloride and at least one phenol of general formula II in a reaction mixture and at a temperature in the range of -50 to 250°C.

Preferably, R contains 5 to 30 and most preferably 8 to 20, carbon atoms and y is 1 or 2. It is preferred that the phenol is a mixture of phenols and as such has an average molecular weight of 164 or greater, preferably 200 or greater and most

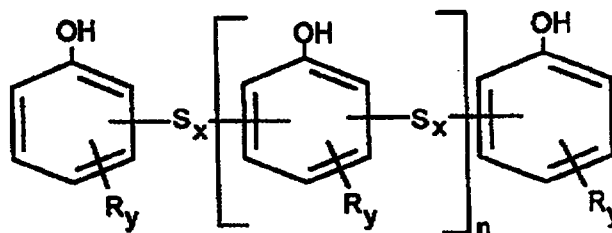
preferably 220 or greater, e.g. 250 or greater. Most preferred mixtures are mixtures of mono- and di-substituted phenols of general formula II e.g. mixtures of para- and ortho/para substituted phenols. Preferably, the phenolic compound comprises between 20 and 90% by weight of para mono-substituted phenolic compound and between 10 and 80% by weight of at least one di-substituted phenolic compound which has at least one reactive ortho position free and preferably is an ortho-/para-di-substituted phenolic compound. It is preferred that the phenols are not hindered phenols although they may be mixtures of phenols which comprise a minor proportion such as less than 45 wt %. e.g. less than 35 or 25 wt % e.g. less than 10 wt % of hindered phenol. By hindered phenols is meant phenols in which all the ortho and para reactive sites are substituted, or sterically hindered phenols in which, either both ortho positions are substituted or only one ortho position and the para position are substituted and, in either case, the substituent is a tertiary alkyl group e.g. t-butyl. It is preferred that for a given mixture of mono and di-alkyl substituted phenols e.g. nonyl substituted, that the monosubstituted phenol is present in at least 20 wt % and preferably in the range 10 to 65 wt %. When the average molecular weight is greater than 250 but less than 300 it is preferred that the mixture of phenols, when used, comprises 50 wt % or greater preferably 60 wt % or greater e.g. 65 wt % of mono-substituted phenol. When the average molecular weight is greater than 300 it is preferred that the phenol mixture, when used, comprises 50 wt % or greater preferably 70 wt % or greater e.g. 80 wt % of di-substituted phenol. It is preferred that the mole ratio of phenol to sulfur monochloride is 2 or greater and most preferably is 2.2 or greater.

Step (a) produces intermediates which have low levels of chlorine whilst allowing for the required levels of sulfur and conversion of phenolic material to be achieved. Preferably the chlorine content is 900 ppm or less e.g. 800 or less and most preferably 500 ppm or less. The level of sulphur, the required conversion of phenolic material to keep the un-sulphurised material to a minimum and the chlorine levels are linked. It is difficult to keep chlorine levels low whilst increasing sulphur content and achieving the desired conversion, because more chlorine-containing starting material i.e. S_2Cl_2 is usually required to achieve these targets; the task is to be able to achieve low chlorine whilst at the same time not having a detrimental effect on the other two factors. In this process for producing the intermediate it is preferred that the reaction is carried out in the temperature range of -15 or -10 to 150°C e.g. 20 to 150°C and preferably 60 to 150°C. It is most preferred that the reaction is carried out at less than 110 °C; the use of reaction temperatures below 110°C with certain phenols results in

intermediates with lower levels of chlorine. Typically the reaction temperature is between 60 and 90°C. Preferably the sulfur monochloride is added to the reaction mixture at a rate of 4×10^{-4} to $15 \times 10^{-4} \text{ cm}^3 \text{ min}^{-1} \text{ g}^{-1}$ phenol. If the reaction mixture is not adequately mixed during this addition the chlorine content of the intermediate may increase. The resultant product preferably has a sulphur content of at least 4% e.g. between 4 and 16%, more preferably 4 to 14 % and most preferably at least 6% e.g. 7 to 12%. The process has the advantage of not requiring complicated post reaction purification steps in order to reduce the levels of chlorine in the intermediate product.

The oil-soluble phenol intermediates, which contain active sulphur, include mono-, di- and polysulfides of phenols or hydrocarbyl group substituted phenols such as alkyl phenols. The hydrocarbyl group substituted phenols may contain one or more hydrocarbyl substituent groups per aromatic ring.

Suitable intermediates may be represented by the general formula I:



wherein R represents a hydrocarbyl radical, n is an integer of 0 to 20, y is an integer of 0 to 4 and may be different for each aromatic nucleus and x is an integer of from 1 to 7 typically 1 to 4. The average number of carbon atoms per hydrocarbyl radical being sufficient to ensure adequate solubility in oil of the sulfurised hydrocarbyl group substituted phenol intermediate. The individual groups represented by R may be the same or different and may contain from 1 to 50, preferably 5 to 30 and most preferably 8 to 20, carbon atoms. Preferably the hydrocarbyl radical R represents an alkyl group. Preferred sulfurised alkyl phenol intermediates are those wherein n is 0 to 4, y is 1 or 2 and may be different for each aromatic nucleus, x is 1 to 4 and R is 8 to 20 carbon atoms most preferably 9 to 12 carbon atoms. These intermediates may be mixtures of intermediates of the above general formula and may include un-sulfurised phenolic material. It is

preferred that the level of un-sulfurised phenolic material is kept to a minimum. The final product may contain up to 20% preferably up to 12% by weight of un-sulfurised phenolic material. One preferred group of sulfurised hydrocarbyl group substituted phenol intermediates are those with a sulfur content of between 4 and 16 mass % preferably 4 to 14% and most preferably 6 to 12 mass %. The sulfurised intermediates, which will normally comprise a mixture of different compounds, typically contain at least some sulfur which is either free, or is only loosely bonded; the sulfur thus being available to attack nitrile elastomeric seals and is referred to as active sulfur. This active sulfur may be present in the form of polysulfides for example when x is three or greater in formula I ; in this form the active sulfur may be present at levels which are typically up to 2 wt % or more.

In step (a), the sulphur monochloride acts as a sulfurising agent, being an agent which introduces S_x bridging groups between phenols where x is 1 to 7.

STEP (b)

By 'completely reacting' is meant that all of the unsaturated organic compound reacts with active sulphur present in the intermediate. This does not necessarily mean that the organic compound cannot be detected in the final product. Thus, small amounts of residual organic compound, for example, less than 3 or 1% weight, such as up to 0.5% by weight, for example, up to 0.4% or 0.1%, may be present in the final product, provided such residual organic compound does not need to be removed before the final product can be used as a lubricating oil additive.

The process of the invention may be used to reduce the level of active sulphur in the final product to, for example, less than 1% by weight, preferably less than 0.5%, more preferably less than 0.4%, most preferably less than 0.2 or 0.1%.

The organic compound may be an unsaturated hydrocarbon such as an olefin or an acetylene. Suitable olefins include mono-olefins, di-olefins, tri-olefins or higher homologues. By "suitable" is meant olefins which are capable of reacting with active sulfur. Preferred olefins are those with a boiling point of up to 200°C and most preferably have a boiling point in the range of 150°C to 200°C.

Any mono-olefin meeting the above requirements may be used in the preparation of additives of the present invention. The mono-olefins may be unsubstituted aliphatic mono-olefins meaning that they contain only carbon and hydrogen atoms, or they may be substituted with one or more heteroatoms and/or heteroatom containing groups e.g. hydroxyl, amino, cyano. An example of a suitable cyano substituted mono-olefin is fumaronitrile. The mono-olefins may also be substituted with aromatic functionality as for example in styrene. The mono-olefins may contain for example ester, amide, carboxylic acid, carboxylate, alkaryl, amidine, sulfinyl, sulfonyl or other such groups. It is preferred that the mono-olefins are aliphatic and are not substituted with heteroatoms and/or heteroatom containing groups other than hydroxyl or carboxylate groups. The mono-olefins may be branched or non-branched it is preferred that they are branched. By branched is meant that the olefin contains one or more tertiary carbon atoms i.e. carbon atoms that are bound to at least three other carbon atoms or when one or more heteroatoms or heteroatom containing groups are present in the olefin one or more of these carbon atoms may be a heteroatom.

The mono-olefin preferably has from 4 to 36 carbon atoms and most preferably 8 to 20 carbon atoms. The mono-olefin may for example be an α -olefin. Examples of α -olefins which may be used in the process of the present invention include; 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1 tetracosene, 1-pentacosene, 1-hexacosene, 1-octacosene, and 1-nanocosene. The α -olefin may be a mixture of α -olefins such as the following commercially available mixtures; C₁₅-C₁₈, C₁₂-C₁₆, C₁₄-C₁₆, C₁₄-C₁₈, C₁₆-C₂₀, C₂₂-C₂₈, and C₃₀+ (Gulftene available from the Gulf Oil Company).

Another class of mono-olefins are those containing a saturated alicyclic ring and one double bond e.g. an exocyclic double bond. The alicyclic ring preferably contains at least six carbon atoms, and, advantageously, the alicyclic ring is substituted by a methylene bridging group that forms a four-membered ring with three of the ring carbon atoms. The methylene carbon atom in such a bridging group may be substituted, preferably by two methyl groups e.g. as in β -pinene. Other examples of mono-olefins include α -pinene, methylene cyclohexane, camphene, and methylene cyclopentane etc. and unsaturated compounds such as the various derivatives of acrylic acid such as acrylate, methacrylate and acrylamide derivatives.

An example of a suitable mono-olefin is the C₁₂ tetramer of propylene. Other suitable mono-olefins include oligomers of for example ethylene. Typically oligomeric olefins are mixtures; therefore mixtures of oligomeric mono-olefins may be used such as mixtures of propylene oligomers.

The di-olefins, tri-olefins and higher homologues may be any such olefins which meet the above identified performance requirement for the olefin. Preferred di-olefins, tri-olefins and higher homologues are those selected from;

- (a) an acyclic olefin having at least two double bonds, adjacent double bonds being separated by two saturated carbon atoms; or
- (b) an olefin comprising an alicyclic ring, which ring comprises at least eight carbon atoms and at least two double bonds, each double bond being separated from the closest adjacent double bond(s) by two saturated carbon atoms.

The preferred olefins of group (a) are unsubstituted or substituted linear terpenes. Unsubstituted linear terpenes for use in accordance with the invention may be represented by the formula (C₅H₈)_n wherein n is at least 2, that is, a terpene containing carbon and hydrogen atoms only. An example of an unsubstituted linear terpene is squalene (in which n in the above formula is 6). Possible substituents for linear terpenes to be used in accordance with the invention are, for example, hydroxyl groups. Suitable substituted terpenes include farnasol and geraniol with geraniol being preferred. Other examples of suitable di-olefins include dicyclopentadiene, dipentene, 1,3-cyclohexadiene, 1,5-cyclooctadiene, methylcyclopentadiene, limonene and 1,4-cyclohexadiene and polybutadiene etc.

If desired, the group (b) olefins may contain at least three double bonds, each end of each double bond being separated from each adjacent double bond by two saturated carbon atoms. An example of a suitable group (b) olefin having three double bonds is 1,5,9-cyclododecatriene. An example of another tri-olefin is cycloheptatriene.

Acetylenic compounds for use in Step (b) are compounds which are capable of reacting with active sulfur. An example of a suitable acetylene material is phenyl acetylene.

The preferred olefins for use in the process of the present invention are di-olefins such as those as defined in a) above; most preferably they are 1,5-di-olefins such as 1,5-cyclooctadiene and geraniol.

Olefins are preferred to acetylenic compounds.

More than one olefin may be used if desired. Where two or more olefins are used, they need not necessarily each be from the same class of olefin. Thus, for example mixtures of mono and diolefins may be used although not as a preference.

In carrying out step (b), the unsaturated organic compound and phenol intermediate may be added in any order. Thus, for example, the organic compound may be introduced into a vessel already containing the intermediate, or vice versa, or the two materials may be introduced simultaneously into the vessel. This process may be carried out in a suitable solvent for the reactants and/or products whose removal does not affect product stability. An example of such a solvent is SN150 basestock. In some instances, an olefin when used in a sufficient amount as the organic compound may act as a solvent for the reaction.

In the present process the exact levels of unsaturated organic compound used will depend on its nature, e.g. when an olefin, whether is it a mono-di or tri olefin, its molecular weight, its level of sulfur, and the level of active sulfur of the sulphurised phenol intermediate.

Preferably, the reaction between the sulfurised phenol intermediate and the organic compound is carried out at an elevated temperature of at least 100°C such as greater than 120°C, most preferably between 120°C to 250°C, and for 0.5 to 60 hours.

The intermediate need not necessarily be isolated from its reaction mixture before being used in Step (b). On completion of the reaction between sulfur monochloride and the phenol, the temperature of the intermediate reaction mixture may be increased to the reaction temperature with the organic compound and the reaction carried out. This increase in temperature may be achieved by means of a ramped temperature increase to the reaction temperature. The organic compound may be added to the intermediate reaction mixture before, during or after the temperature increase.

This invention has been found to be particularly effective in reducing the levels of chlorine in the phenols intermediates. Thus chlorine levels of 500 ppm or less and as low as 300 ppm and even 100 ppm may be achieved in the final product after reaction with the organic compound. The magnitude of this reduction is increased with the use of higher reaction temperatures between the sulfurised additive and the organic compound.

The process of the invention not only results in additives which have low chlorine levels, that is less than 1000 ppm, preferably 900 ppm or less e.g. 800 ppm or less and most preferably 500 ppm or less, but also in nitrile seal compatible additives.

USE OF ADDITIVES

The additives of the invention may be used to prepare phenates and overbased phenates by reaction with alkali or alkaline earth metal salts or compounds. The phenates and overbased phenates derived from the additives may also have low levels of chlorine e.g. less than 1000 ppm and as low as or lower levels than those present in the additive used in their preparation. Phenates may contain a substantially stoichiometric amount of the metal when they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased phenates comprise neutralised detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased phenates may have a TBN of 150 or greater, and typically of from 250 to 450 or more. The metals are in particular the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in phenates used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient phenates are neutral and overbased calcium phenates and sulfurized phenates having a TBN of from 50 to 450.

Metal salts of phenols and sulfurised phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods known in the art.

Lubricating oil additives of the invention are oil-soluble or (in common with certain other additives referred to below) are dissolvable in oil with the aid of a suitable solvent, or are stably dispersible materials.

Preferably, the low chlorine lubricating oil composition of the invention contains 50 ppm or less and most preferably 10 ppm or less e.g. 5 ppm or less of chlorine. It is preferred that the concentrate of the invention further comprises one or more ashless dispersants prepared from non-halogenated polymers.

The terms "oil-soluble", "dissolvable", or "stably dispersible" used herein do not necessarily indicate that the additives are soluble, dissolvable, miscible, or capable of being suspended in oil in all proportions. They do mean, however, that they are, for instance, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

Additives of the invention can be incorporated into the oil in any convenient way. Thus, they can be added directly to the oil by dispersion or by dissolution in the oil at the desired concentration, optionally with the aid of a suitable solvent such as, for example, toluene, cyclohexane, or tetrahydrofuran. In some cases blending may be effected at room temperature: in other cases elevated temperatures are advantageous such as up to 100°C.

Base oils with which the additives may be used include those suitable for use in crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, for example, automobile and truck engines, marine and railroad diesel engines.

Synthetic base oils include alkyl esters of dicarboxylic acids, polyglycols and alcohols, poly- α -olefins, polybutenes, alkyl benzenes, organic esters of phosphoric acids and polysilicone oils.

Natural base oils include mineral lubricating oils whose crude source, for example, paraffinic, naphthenic, mixed, or paraffinic-naphthenic, and method of production, for example, distillation range, straight run or cracked, hydrotreated, solvent extracted, may vary widely.

More specifically, natural lubricating oil base stocks which can be used may be straight mineral lubricating oil or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crude oils. Alternatively, if desired, various blended oils may be employed as well as residual oils, particularly those from which asphaltic constituents have been removed. The oils may be refined by any suitable method, for example, using acid, alkali, and/or clay or other agents such as aluminium chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents, for example, phenol, sulfur dioxide, furfural, dichlorodiethylether, nitrobenzene, or crotonaldehyde.

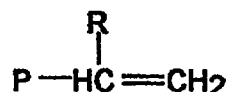
The lubricating oil base stock conveniently has a viscosity of from 2.5 to 12 cSt or mm²/sec and preferably from 3.5 to 9 cSt or mm²/sec at 100°C.

Additives of the invention may be employed in a lubricating oil composition which comprises lubricating oil, typically in a major proportion, and the additives, typically in a minor proportion. Additional additives may be incorporated into the composition to enable it to meet particular requirements. Examples of additives which may be included in lubricating oil compositions are viscosity index improvers, corrosion inhibitors, oxidation inhibitors, friction modifiers, dispersants, detergents, metal rust inhibitors, anti-wear agents, pour point depressants, and anti-foaming agents.

Ashless dispersants comprise an oil soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless dispersant may be, for example, selected from oil soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

The oil soluble polymeric hydrocarbon backbone is typically an olefin polymer or polyene, especially polymers comprising a major molar amount (i.e., greater than 50 mole %) of a C₂ to C₁₈ olefin (e.g., ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a C₂ to C₅ olefin. The oil soluble polymeric hydrocarbon backbone may be a homopolymer (e.g., polypropylene or polyisobutylene) or a copolymer of two or more of such olefins (e.g., copolymers of ethylene and an alpha-olefin such as propylene or butylene, or copolymers of two different alpha-olefins). Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is an α,ω -diene, such as a C₃ to C₂₂ non-conjugated diolefin (e.g., a copolymer of isobutylene and butadiene, or a copolymer of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene). Atactic propylene oligomer typically having $\overline{M}_n$ of from 700 to 5000 may also be used, as described in EP-A-490454, as well as heteropolymers such as polyepoxides.

One preferred class of olefin polymers is polybutenes and specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C₄ refinery stream. Other preferred classes of olefin polymers are ethylene alpha-olefin (EAO) copolymers and alpha-olefin homo- and copolymers having in each case a high degree (e.g., >30%) of terminal vinylidene unsaturation. That is, the polymer has the following structure:



wherein P is the polymer chain and R is a C₁ - C₁₈ alkyl group, typically methyl or ethyl. Preferably the polymers will have at least 50% of the polymer chains with terminal vinylidene unsaturation. EAO copolymers of this type preferably contain 1 to 50 wt% ethylene, and more preferably 5 to 48 wt% ethylene. Such polymers may contain more than one alpha-olefin and may contain one or more C₃ to C₂₂ diolefins. Also usable are mixtures of EAO's of varying ethylene content. Different polymer types, e.g., EAO and PIB, may also be mixed or blended, as well as polymers differing in $\overline{M}_n$; components derived from these also may be mixed or blended.

Suitable olefin polymers and copolymers may be prepared by various catalytic polymerization processes. In one method, hydrocarbon feed streams, typically C₃

- C₅ monomers, are cationically polymerized in the presence of a Lewis acid catalyst and, optionally, a catalytic promoter, e.g., an organoaluminum catalyst such as ethylaluminum dichloride and an optional promoter such as HCl. Most commonly, polyisobutylene polymers are derived from Raffinate I refinery feedstreams. Various reactor configurations can be utilised, e.g., tubular or stirred tank reactors, as well as fixed bed catalyst systems in addition to homogeneous catalysts. Such polymerization processes and catalysts are described, e.g., in US-A 4,935,576; 4,952,739; 4,982,045; and UK-A 2,001,662.

Conventional Ziegler-Natta polymerization processes may also be employed to provide olefin polymers suitable for use in preparing dispersants and other additives. However, preferred polymers may be prepared by polymerising the appropriate monomers in the presence of a particular type of Ziegler-Natta catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl-transition metal compound) and, preferably, a cocatalyst or an activator, e.g., an alumoxane compound or an ionising ionic activator such as tri (n-butyl) ammonium tetra (pentafluorophenyl) boron.

Metallocene catalysts are, for example, bulky ligand transition metal compounds of the formula:



where L is a bulky ligand; A is a leaving group, M is a transition metal and m and n are such that the total ligand valency corresponds to the transition metal valency. Preferably the catalyst is four co-ordinate such that the compound is ionizable to a 1⁺ valency state.

The ligands L and A may be bridged to each other, and if two ligands A and/or L are present, they may be bridged. The metallocene compound may be a full sandwich compound having two or more ligands L which may be cyclopentadienyl ligands or cyclopentadienyl derived ligands, or they may be half sandwich compounds having one such ligand L. The ligand may be mono- or polynuclear or any other ligand capable of η -5 bonding to the transition metal.

One or more of the ligands may π -bond to the transition metal atom, which may be a Group 4, 5 or 6 transition metal and/or a lanthanide or actinide transition metal, with zirconium, titanium and hafnium being particularly preferred.

The ligands may be substituted or unsubstituted, and mono-, di-, tri, tetra- and penta-substitution of the cyclopentadienyl ring is possible. Optionally the substituent(s) may act as one or more bridge between the ligands and/or leaving groups and/or transition metal. Such bridges typically comprise one or more of a carbon, germanium, silicon, phosphorus or nitrogen atom-containing radical, and preferably the bridge places a one atom link between the entities being bridged, although that atom may and often does carry other substituents.

The metallocene may also contain a further displaceable ligand, preferably displaced by a cocatalyst - a leaving group - that is usually selected from a wide variety of hydrocarbyl groups and halogens.

Such polymerizations, catalysts, and cocatalysts or activators are described, for example, in US 4,530,914; 4,665,208; 4,808,561; 4,871,705; 4,897,455; 4,937,299; 4,952,716; 5,017,714; 5,055,438; 5,057,475; 5,064,802; 5,096,867; 5,120,867; 5,124,418; 5,153,157; 5,198,401; 5,227,440; 5,241,025; USSN 992,690 (filed Dec. 17, 1992; EP-A- 129,368; 277,003; 277,004; 420436; 520,732; WO91/04257; 92/00333; 93/08199 and 93/08221; and 94/07928.

The oil soluble polymeric hydrocarbon backbone will usually have a number average molecular weight ($\overline{M}_n$) within the range of from 300 to 20,000. The $\overline{M}_n$ of the polymer backbone is preferably within the range of 500 to 10,000, more preferably 700 to 5,000 where its use is to prepare a component having the primary function of dispersancy. Polymers of both relatively low molecular weight (e.g., $\overline{M}_n$ = 500 to 1500) and relatively high molecular weight (e.g., $\overline{M}_n$ = 1500 to 5,000 or greater) are useful to make dispersants. Particularly useful olefin polymers for use in dispersants have $\overline{M}_n$ within the range of from 1500 to 3000. Where the oil additive component is also intended to have a viscosity modifying effect it is desirable to use a polymer of higher molecular weight, typically with $\overline{M}_n$ of from 2,000 to 20,000; and if the component is intended to function primarily as a viscosity modifier then the molecular weight may be even higher, e.g., $\overline{M}_n$ of from 20,000 up to 500,000 or greater. Furthermore, the olefin polymers used to prepare dispersants preferably have approximately one double bond per polymer chain, preferably as a terminal double bond.

Polymer molecular weight, specifically $\overline{M}_n$, can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC),

which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). Another useful method, particularly for lower molecular weight polymers, is vapour pressure osmometry (see, e.g., ASTM D3592).

The oil soluble polymeric hydrocarbon backbone may be functionalized to incorporate a functional group into the backbone of the polymer, or as one or more groups pendant from the polymer backbone. The functional group typically will be polar and contain one or more hetero atoms such as P, O, S, N, halogen, or boron. It can be attached to a saturated hydrocarbon part of the oil soluble polymeric hydrocarbon backbone via substitution reactions or to an olefinic portion via addition or cycloaddition reactions. Alternatively, the functional group can be incorporated into the polymer in conjunction with oxidation or cleavage of the polymer chain end (e.g., as in ozonolysis).

Useful functionalization reactions include: halogenation of the polymer at an olefinic bond and subsequent reaction of the halogenated polymer with an ethylenically unsaturated functional compound (e.g., maleation where the polymer is reacted with maleic acid or anhydride); reaction of the polymer with an unsaturated functional compound by the "ene" reaction absent halogenation; reaction of the polymer with at least one phenol group (this permits derivatization in a Mannich base-type condensation); reaction of the polymer at a point of unsaturation with carbon monoxide using a Koch-type reaction to introduce a carbonyl group in an iso or neo position; reaction of the polymer with the functionalizing compound by free radical addition using a free radical catalyst; reaction with a thiocarboxylic acid derivative; and reaction of the polymer by air oxidation methods, epoxidation, chloroamination, or ozonolysis. It is preferred that the polymer is not halogenated.

The functionalized oil soluble polymeric hydrocarbon backbone is then further derivatized with a nucleophilic reactant such as an amine, amino-alcohol, alcohol, metal compound or mixture thereof to form a corresponding derivative.

Useful amine compounds for derivatizing functionalized polymers comprise at least one amine and can comprise one or more additional amine or other reactive or polar groups. These amines may be hydrocarbyl amines or may be predominantly hydrocarbyl amines in which the hydrocarbyl group includes other

groups, e.g., hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Particularly useful amine compounds include mono- and polyamines, e.g., polyalkylene and polyoxyalkylene polyamines of about 2 to 60, conveniently 2 to 40 (e.g., 3 to 20), total carbon atoms and about 1 to 12, conveniently 3 to 12, and preferably 3 to 9 nitrogen atoms in the molecule. Mixtures of amine compounds may advantageously be used such as those prepared by reaction of alkylene dihalide with ammonia. Preferred amines are aliphatic saturated amines, including, e.g., 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; and polypropyleneamines such as 1,2-propylene diamine; and di-(1,2-propylene)triamine.

Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines. A particularly useful class of amines are the polyamido and related amido-amines as disclosed in US 4,857,217; 4,956,107; 4,963,275; and 5,229,022. Also usable is tris(hydroxymethyl)amino methane (THAM) as described in US 4,102,798; 4,113,639; 4,116,876; and UK 989,409. Dendrimers, star-like amines, and comb-structure amines may also be used. Similarly, one may use the condensed amines disclosed in US 5,053,152. The functionalized polymer is reacted with the amine compound according to conventional techniques as described in EP-A 208,560; US 4,234,435 and US 5,229,022.

The functionalized oil soluble polymeric hydrocarbon backbones also may be derivatized with hydroxy compounds such as monohydric and polyhydric alcohols or with aromatic compounds such as phenols and naphthols. Polyhydric alcohols are preferred, e.g., alkylene glycols in which the alkylene radical contains from 2 to 8 carbon atoms. Other useful polyhydric alcohols include glycerol, mono-oleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, and mixtures thereof. An ester dispersant may also be derived from unsaturated alcohols such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexane-3-ol, and oleyl alcohol. Still other classes of the alcohols capable of yielding ashless dispersants comprise the ether-alcohols and including, for example, the oxy-alkylene, oxy-arylene. They are exemplified by ether-alcohols having up to 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to 8 carbon atoms. The ester dispersants may be di-esters of succinic acids or acidic esters, i.e., partially esterified succinic acids; as well as

partially esterified polyhydric alcohols or phenols, i.e., esters having free alcohols or phenolic hydroxyl radicals. An ester dispersant may be prepared by one of several known methods as illustrated, for example, in US 3,381,022.

A preferred group of ashless dispersants includes those derived from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines (e.g., tetraethylene pentamine, pentaethylene (di)(pent)amine, polyoxypropylene diamine) aminoalcohols such as trimethylolaminomethane and optionally additional reactants such as alcohols and reactive metals e.g., pentaerythritol, and combinations thereof). Also useful are dispersants wherein a polyamine is attached directly to the long chain aliphatic hydrocarbon as shown in US 3,275,554 and 3,565,804 where a halogen group on a halogenated hydrocarbon is displaced with various alkylene polyamines.

Another class of ashless dispersants comprises Mannich base condensation products. Generally, these are prepared by condensing about one mole of an alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compounds (e.g., formaldehyde and paraformaldehyde) and about 0.5 to 2 moles polyalkylene polyamine as disclosed, for example, in US 3,442,808. Such Mannich condensation products may include a long chain, high molecular weight hydrocarbon (e.g., $\overline{M}_n$ of 1,500 or greater) on the benzene group or may be reacted with a compound containing such a hydrocarbon, for example, polyalkenyl succinic anhydride, as shown in US 3,442,808.

Examples of functionalized and/or derivatized olefin polymers based on polymers synthesized using metallocene catalyst systems are described in US 5,128,056; 5,151,204; 5,200,103; 5,225,092; 5,266,223; USSN 992,192 (filed Dec. 17, 1992); 992,403 (filed Dec. 17, 1992); 070,752 (filed Jun. 2, 1993); EP-A-440,506; 513,157; 513,211. The functionalization and/or derivatizations and/or post treatments described in the following patents may also be adapted to functionalize and/or derivatize the preferred polymers described above: US 3,087,936; 3,254,025; 3,275,554; 3,442,808, and 3,565,804.

The dispersant can be further post-treated by a variety of conventional post treatments such as boration, as generally taught in US 3,087,936 and 3,254,025. This is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from the group consisting of boron oxide, boron

halides, boron acids and esters of boron acids, in an amount to provide from about 0.1 atomic proportion of boron for each mole of the acylated nitrogen composition to about 20 atomic proportions of boron for each atomic proportion of nitrogen of the acylated nitrogen composition. Usefully the dispersants contain from about 0.05 to 2.0 wt. %, e.g. 0.05 to 0.7 wt. % boron based on the total weight of the borated acyl nitrogen compound. The boron, which appears to be in the product as dehydrated boric acid polymers (primarily $(HBO_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts e.g., the metaborate salt of the diimide. Boration is readily carried out by adding from about 0.05 to 4, e.g., 1 to 3 wt. % (based on the weight of acyl nitrogen compound) of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and heating with stirring at from 135° to 190° C, e.g., 140°-170° C, for from 1 to 5 hours followed by nitrogen stripping. Alternatively, the boron treatment can be carried out by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine while removing water.

Viscosity modifiers (or viscosity index improvers) impart high and low temperature operability to a lubricating oil. Viscosity modifiers that also function as dispersants are also known and may be prepared as described above for ashless dispersants. In general, these dispersant viscosity modifiers are functionalized polymers (e.g. inter polymers of ethylene-propylene post grafted with an active monomer such as maleic anhydride) which are then derivatized with, for example, an alcohol or amine.

The lubricant may be formulated with or without a conventional viscosity modifier and with or without a dispersant viscosity modifier. Suitable compounds for use as viscosity modifiers are generally high molecular weight hydrocarbon polymers, including polyesters. Oil soluble viscosity modifying polymers generally have weight average molecular weights of from about 10,000 to 1,000,000, preferably 20,000 to 500,000, which may be determined by gel permeation chromatography (as described above) or by light scattering.

Representative examples of suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially

hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralisers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises neutralised detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically of from 250 to 450 or more.

Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates having TBN of from 20 to 450 TBN, and neutral and overbased calcium phenates and sulfurized phenates having TBN of from 50 to 450.

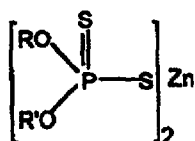
Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 wt % (preferably at least 125 wt %).

Dihydrocarbyl dithiophosphate metal salts are frequently used as anti-wear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 wt. %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralising the formed DDPA with a zinc compound. The zinc dihydrocarbyl dithiophosphates can be made from mixed DDPA which in turn may be made from mixed alcohols. Alternatively, multiple zinc dihydrocarbyl dithiophosphates can be made and subsequently mixed.

Thus the dithiophosphoric acid containing secondary hydrocarbyl groups used in this invention may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralisation reaction.

The preferred zinc dihydrocarbyl dithiophosphates useful in the present invention are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. At least 50 (mole) % of the alcohols used to introduce hydrocarbyl groups into the dithiophosphoric acids are secondary alcohols.

Additional additives are typically incorporated into the compositions of the present invention. Examples of such additives are antioxidants, anti-wear agents, friction modifiers, rust inhibitors, anti-foaming agents, demulsifiers, and pour point depressants.

Oxidation inhibitors or antioxidants reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, ashless oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in US 4,867,890, and molybdenum containing compounds. Examples of molybdenum compounds include molybdenum salts of inorganic and organic acids (see, for example, US 4,705,641), particularly molybdenum salts of monocarboxylic acids having from 1 to 50, preferably 8 to 18, carbon atoms, for example, molybdenum octoate (2-ethyl hexanoate), naphthenate or stearate; overbased molybdenum-containing complexes as disclosed in EP 404 650A; molybdenum dithiocarbamates and molybdenum dithiophosphates; oil-soluble molybdenum xanthates and thioxanthates as disclosed in US 4,995,996 and 4,966,719; oil-soluble molybdenum- and sulfur-containing complexes; and aromatic amines, preferably having at least two aromatic groups attached directly to the nitrogen.

Typical oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen contain from 6 to 16 carbon atoms. The amines may contain more than two aromatic groups. Compounds having a total of at least three aromatic groups in which two aromatic groups are linked by a covalent bond or by an atom or group (e.g., an oxygen or sulfur atom, or a -CO-, -SO₂- or alkylene group) and two are directly attached to one amine nitrogen also considered aromatic amines having at least two aromatic groups attached directly to the nitrogen. The aromatic rings are typically substituted by one or more substituents selected from alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups.

Friction modifiers may be included to improve fuel economy. In addition to the oil soluble aliphatic, oxyalkyl, or arylalkyl amines described above to add nitrogenous TBN, other friction modifiers are known. Among these are esters formed by reacting carboxylic acids and anhydrides with alkanols. Other conventional friction modifiers generally consist of a polar terminal group (e.g. carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. Esters of carboxylic acids and anhydrides with alkanols are described in US 4,702,850. Examples of other conventional friction modifiers are described by M. Belzer in the "Journal of Tribology" (1992), Vol. 114, pp. 675-682 and M. Belzer and S. Jahanmir in "Lubrication Science" (1988), Vol. 1, pp. 3-26.

Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used. When the formulation of the present invention is used, these anti-rust inhibitors are not generally required.

Copper and lead bearing corrosion inhibitors may be used, but are typically not required with the formulation of the present invention. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1,3,4 thiadiazoles such as those described in U.S. Pat. Nos. 2,719,125; 2,719,126; and 3,087,932; are typical. Other similar materials are described in U.S. Pat. Nos. 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882. Other additives are the thio and polythio sulfenamides of thiadiazoles such as those described in UK Patent Specification No. 1,560,830. Benzotriazoles derivatives also fall within this class of additives. When these compounds are included in the lubricating

composition, they are preferably present in an amount not exceeding 0.2 wt % active ingredient.

A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP 330,522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers and polyalkylmethacrylates.

Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

Some of the above-mentioned additives, as is known, can provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor.

When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount which enables the additive to provide its desired function. Representative effective amounts of such additives, when used in crankcase lubricants, are listed below. All the values listed are stated as mass percent active ingredient.

ADDITIVE	MASS %	MASS %
	(Broad)	(Preferred)
Ashless Dispersant	0.1 - 20	1 - 8
Metal detergents	0.1 - 6	0.2 - 4
Corrosion Inhibitor	0 - 5	0 - 1.5
Metal dihydrocarbyl dithiophosphate	0.1 - 6	0.1 - 4
Supplemental anti-oxidant	0 - 5	0.01 - 1.5
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Anti-Foaming Agent	0 - 5	0.001 - 0.15
Supplemental Anti-wear Agents	0 - 0.5	0 - 0.2
Friction Modifier	0 - 5	0 - 1.5
Viscosity Modifier ¹	0.01 - 6	0 - 4
Mineral or Synthetic Base Oil	Balance	Balance

1. Viscosity modifiers are used only in multi-graded oils.

For non-crankcase applications, the quantities and/or proportions of the above additives may be varied; for example, marine diesel cylinder lubricants use relatively higher amounts of metal detergents, which may form 10 - 50 wt% of the lubricant.

The components may be incorporated into a base oil in any convenient way. Thus, each of the components can be added directly to the oil by dispersing or dissolving it in the oil at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature.

Preferably all the additives except for the viscosity modifier and the pour point depressant are blended into a concentrate or additive package that is subsequently blended into basestock to make finished lubricant. Use of such concentrates is conventional. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the concentrate is combined with a predetermined amount of base lubricant.

Preferably the concentrate is made in accordance with the method described in US 4,938,880. That patent describes making a premix of ashless dispersant and metal detergents that is pre-blended at a temperature of at least about 100°C.

Thereafter the pre-mix is cooled to at least 85°C and the additional components are added.

The final formulations may employ from 2 to 15 mass % and preferably 5 to 10 mass %, typically about 7 to 8 mass % of the concentrate or additive package with the remainder being base oil.

EXAMPLES

The invention will now be described by way of illustration only with reference to the following examples. In the examples, unless otherwise noted, all treat rates of all additives are reported as mass percent active ingredient.

The intermediate and final products were tested for seals performance by the following procedure:

The effect of the additive compositions on nitrile seals was tested by immersing samples of a nitrile elastomer in a lubricating oil composition containing a proprietary package of additives and the additive to be tested, and comparing the elongation at break (EAB) and/or tensile strength (TS) of the samples after immersion with the corresponding figures before immersion. The most suitable additives are those giving the smallest percentage loss in the elongation at break and/or tensile strength. Test Methods DIN 53521 and DIN 53504 were used.

It should be noted that a UV technique that functions as a surrogate for the nitrile seals test, and as a process endpoint indicator in the manufacture of sulphurised alkyl phenols, may be used.

The technique is the use of the UV absorbance properties of the different sulphurised alkyl phenol species as a tool for determining the manufacturing process endpoint and predicting the nitrile seals compatibility of the product. The technique is characterised by its use of absorbances at specific wavelengths of the spectrum and the use of ratios of absorbances. The wavelengths were chosen from within 190 to 450 nm, based on the UV maxima of certain components in the product and its intermediates. The absorbance ratio values of process samples are then compared against a correction to the conventional nitrile seals test performance.

Step (a) Preparation of Sulfurised Intermediates

Sulfur monochloride (100 parts by weight) was added to a reaction vessel containing 385 parts by weight of a nonyl phenol (Phenol 1) being a mixture of dinonyl phenol and nonylphenol (35:65 wt%) and having an average molecular weight of 253. This addition was made over a period of 3 hours and 45 minutes. The reaction mixture was stirred efficiently during the addition and the temperature was ramped from 60°C to 90°C. When the addition of sulfur monochloride was completed the temperature was raised to 110°C and held at this temperature for 2 hours whilst the reaction mixture was purged with nitrogen at a rate of 200 cm³ min⁻¹.

The intermediate product was characterised as follows:

Chlorine content by X-ray fluorescence: 612 ppm
Total sulphur content by X-ray fluorescence 11.6% by weight
by ASTM D4927:
Copper corrosion at 2.5% by weight in base oil 3B
by ASTM D130:
Active sulphur content by procedure described 2.76 % by weight
below*

Seals performance at 1.1 mass %:	Tensile strength loss (%) = 62
	Elongation at break loss (%) = 68

*The sample is reduced with zinc and acetic acid to yield mercaptans and hydrogen sulphide:



Potentiometric titration with silver nitrate solution is used to quantify the mercaptans and H₂S yielded, the active sulphur content being derived from the potentiometric titration of the sodium hydroxide scrubber solution as described in "The Analytical Chemistry of Sulphur and Its Compounds Part II", pages 357-360 by J. H. Karchmer, John Wiley and Sons, 1972.

Step (b) Preparation of Additives by Olefin Treatment

The above intermediate (562 parts by weight) was introduced into a stirred reaction vessel with 1-decene (90 parts) and diluent solvent neutral base oil (160 parts). The temperature was raised to 175°C and maintained at that temperature for 8 hours. The temperature was then lowered to ambient while 30 mmHg vacuum and nitrogen purge was applied to remove dissolved H₂S.

The final product was characterised as follows:

Chlorine content by X-ray fluorescence: 158 ppm

Total sulphur content by X-ray fluorescence by 7.6% by weight

ASTM D4927:

Residual olefin by Gas Chromatography: 0.33% by weight

Copper corrosion at 2.5% in base oil by ASTM 1A

D130:

Active sulphur content by procedure described above <0.1% by weight

Seals performance at 1.1 mass %:

Tensile strength loss (%) = 21%

Elongation at break loss (%) =
41%



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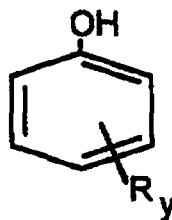
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CLAIMS

1. A process for preparing an oil-soluble sulphurised phenol containing less than 1000 ppm by weight of chlorine, which comprises the steps of:
 - (a) reacting together sulphur monochloride and at least one phenol that is substituted with one or more hydrocarbyl radicals, wherein the mole ratio of phenol to sulphur monochloride is greater than 1.7:1, to produce an oil-soluble phenol intermediate containing less than 1000 ppm by weight of chlorine; and
 - (b) completely reacting an unsaturated organic compound having one or more olefinic or acetylenic bond with the intermediate at elevated temperature to reduce the amount of active sulphur to produce a sulphurised phenol.
2. The process of claim 1 wherein the phenol is represented by the formula II:



II

wherein R represents a hydrocarbyl radical and y is 1, 2, 3 or 4.

3. The process of claim 2 wherein R contains 5 to 30 carbon atoms, and y is 1 or 2.
4. The process of claims 2 or 3 wherein the phenol is a mixture of phenols having an average molecular weight of 164 or greater.
5. The process of any of the preceding claims wherein Step (a) is carried out at a temperature in the range of -50 to 250°C.

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6. The process of any of the preceding claims wherein the mole ratio of phenol to sulphur monochloride is 2 or greater, preferably 2.2 or greater.
7. The process of any of the preceding claims wherein the unsaturated organic compound is a mono-olefin.
8. The process of claim 7 wherein the mono-olefin is an α -olefin.
9. The process of claim 8 wherein the α -olefin is straight chain and has from 8 to 20 carbon atoms.
10. The process of any of the preceding claims wherein Step (b) is carried out at a temperature of at least 100°C.
11. An oil-soluble sulphurised phenol obtained or obtainable by the process of any of claims 1 to 10, provided that the phenol is not obtainable by:
 - (i) reacting together at a temperature of at least 100°C: an oil-soluble active-sulphur containing sulphurised phenol intermediate; and an olefin or an acetylenic compound in an amount in excess of that required to react with the active sulphur present in the sulphurised phenol intermediate; and
 - (ii) removing substantially all unreacted olefin or acetylenic compound.
12. A lubricating oil composition which comprises lubricating oil as a major component and an oil-soluble sulphurised phenol of claim 11.
13. A lubricating oil concentrate which comprises one or more lubricant additives, and an oil soluble sulphurised phenol of claim 11.
14. The use of an oil soluble sulphurised phenol of claim 11 to enhance the nitrile elastomer seal compatibility or the copper corrosion properties or both of a lubricating oil composition.

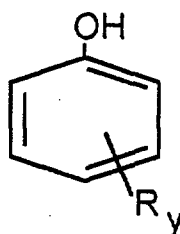
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CLAIMS

1. A process for preparing an oil-soluble sulphurised phenol containing less than 1000 ppm by weight of chlorine, which comprises the steps of:
 - (a) reacting together sulphur monochloride and at least one phenol that is substituted with one or more hydrocarbyl radicals, wherein the mole ratio of phenol to sulphur monochloride is greater than 1.7:1, to produce an oil-soluble phenol intermediate containing less than 1000 ppm by weight of chlorine; and
 - (b) completely reacting all of an unsaturated organic compound having one or more olefinic or acetylenic bonds with the intermediate at elevated temperature to reduce the amount of active sulphur to produce a sulphurised phenol.
2. The process of claim 1 wherein the phenol is represented by the formula II:



II

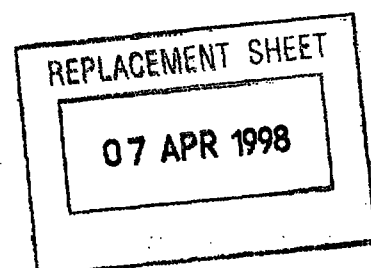
wherein R represents a hydrocarbyl radical and y is 1, 2, 3 or 4.

3. The process of claim 2 wherein R contains 5 to 30 carbon atoms, and y is 1 or 2.
4. The process of claims 2 or 3 wherein the phenol is a mixture of phenols having an average molecular weight of 164 or greater.



5. The process of any of the preceding claims wherein Step (a) is carried out at a temperature in the range of -50 to 250°C.
6. The process of any of the preceding claims wherein the mole ratio of phenol to sulphur monochloride is 2 or greater, preferably 2.2 or greater.
7. The process of any of the preceding claims wherein the unsaturated hydrocarbon is a mono-olefin.
8. The process of claim 7 wherein the mono-olefin is an α -olefin.
9. The process of claim 8 wherein the α -olefin is straight chain and has from 8 to 20 carbon atoms.
10. The process of any of the preceding claims wherein Step (b) is carried out at a temperature of at least 100°C.
11. An oil-soluble sulphurised phenol obtained by the process of any of claims 1 to 10.
12. A lubricating oil composition which comprises lubricating oil as a major component and an oil-soluble sulphurised phenol of claim 11.
13. A lubricating oil concentrate which comprises one or more lubricant additives, and an oil soluble sulphurised phenol of claim 11.
14. The use of an oil soluble sulphurised phenol of claim 11 to enhance the nitrile elastomer seal compatibility or the copper corrosion properties or both of a lubricating oil composition.

AMENDED SHEET



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International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C10M 135/30, 177/00, 159/12, C07C 319/22 // (C10M 159/12, 127:02, 135:30), C10N 30:00, 70:00	A1	(11) International Publication Number: WO 97/24417 (43) International Publication Date: 10 July 1997 (10.07.97)
(21) International Application Number: PCT/EP96/05881 (22) International Filing Date: 20 December 1996 (20.12.96) (30) Priority Data: 9526713.4 29 December 1995 (29.12.95) / GB (71) Applicant (for all designated States except US): EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BAULA, Cezar, Sagmit [US/US]; 5 Daphne Court, Edison, NJ 08820 (US). BUTTS, Timothy, James [US/US]; 235 East 73rd Street, New York, NY 10021 (US). DUNLEAVY, B., E. [US/US]; 613 Summit Avenue, Westfield, NJ 07090 (US). GOMES, Joe, M., G. [GB/GB]; 16 Colegrove Manor, Colegrove Down, Cumnor Hill, Oxford, Oxfordshire OX2 9HT (GB). SKINNER, Philip [GB/GB]; 24 Whitehorse Crescent, Grove, Wantage, Oxfordshire OX12 0PY (GB). (74) Agents: MANSELL, Keith, Rodney et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).	(81) Designated States: BR, CA, JP, MX, <u>SG</u> , US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: SULPHURISED PHENOL ADDITIVES AND COMPOSITIONS		
(57) Abstract Sulphur monochloride and a phenol are reacted to produce an oil-soluble intermediate which is then reacted with an unsaturated organic compound having one or more olefinic or acetylenic bonds to reduce the amount of active sulphur in the intermediate and to leave no excess of hydrocarbon, thereby to produce a low-chlorine, low-active sulphur content oil-soluble sulphurised phenol.		