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54 **Improved demulsified lubricating oil compositions.**

57 In accordance with one aspect, the present invention is directed to a lubricating oil additive mixture comprising (A) a lubricating oil dispersant additive comprising at least one of (1) ashless dispersants and/or (2) polymeric viscosity index improver dispersants, and (B) a demulsifier additive comprising the reaction product of an alkylene oxide and an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol. In a preferred embodiment, the lubricating oil additive mixtures further comprises (C) a compatibilizer additive for the demulsifier, which comprises a glycol ester or a hydroxyamide derivative of a carboxylic acid having a total of from 24 to 90 carbon atoms and at least one carboxylic group per molecule, for enhanced solubility, viz. stability, of the demulsifier in the oil solutions containing such dispersants.

Description

IMPROVED DEMULSIFIED LUBRICATING OIL COMPOSITIONS

This invention relates to oleaginous compositions containing high molecular weight ashless dispersant and demulsifier additive having improved demulsibility. Such concentrates are useful in oleaginous compositions, including fuel and lubricating oil compositions.

The Sequence IID is one of the established ASTM tests which define the current standard of crankcase lubricants for gasoline engines (American Society for Testing and Materials Special Technical Publication 315H, Part 1; September 15, 1979). The test, designed to evaluate the rust-preventive properties of the lubricant, creates an environment conducive to rust formation, in part by retaining water vapor from combustion gases in the crankcase with the use of a condenser at the crankcase breather outlet.

A by-product of the wet IID environment is the presence of conditions that are very conducive to emulsion formation. Although emulsions would not necessarily be a matter of concern in themselves, the condenser tubes can become partially blocked with emulsion, leading to a pressure drop across the condenser and resultant pressure development in the crankcase. Engine manufacturers have become concerned that oils which develop emulsions may also tend in the field to plug PCV valves or other lines associated with the crankcase ventilation system, and to coat other internal engine surfaces such as the rocker covers, valve deck, etc. with emulsion. These concerns are particularly directed to internal combustion engines wherein fresh air purge of the crankcase is not employed. In such cases, the absence of fresh air purge can cause build-up of water in the crankcase vapors. In some engines, crankcase vapors are passed to an external separator intended to separate entrained liquids and vapors. The separated liquids are intended to continuously drain back into the crankcase, and the gases passing through the separator are intended to be combined with air and/or fuel (or mixtures thereof) for charging to the engine's cylinder for combustion. The presence of emulsion in the crankcase, and in the entrained vapors passing to the separator, causes plugging of, or at least a buildup in the effective pressure drop across, the separator, decreasing its efficiency. This, in severe cases, may result in an unintended increase in crankcase pressure beyond design limits, which, in turn, can cause oil seepage through crankcase seals, and other problems. In cold climates, and in short-trip or low-engine speed conditions, the above problems may become more pronounced.

Crankcase lubricants for internal combustion engines are required to suspend solids resulting, e.g., from the inevitable oxidation of the oils components during operation of the engine, to minimize both the degree of deposits (e.g., varnish) on engine components and the formation of sludge. Since modern engines operate at high temperatures, as a result of the decreased engine sizes and high power demands, modern crankcase lubricant formulations require the use of high levels of dispersancy (e.g., provided by use of high molecular weight dispersants or increased levels of lower molecular weight dispersants), and the use of other potent engine components, to minimize the adverse consequences on the engine of the oxidation of the lubricant during use.

Therefore, stricter limits on crankcase pressure have been suggested in the Sequence IID test, and it has become very important to prevent emulsion formation in modern lubricating oil formulations.

Unfortunately, the critical components that are necessary to maintain engine cleanliness and control deposit formation in modern lubricating oil formulations, many dispersants and multifunctional viscosity modifiers, can be highly potent emulsion formers.

A large variety of lubricating oil demulsifiers have been suggested heretofore.

U.S. Patent 3,509,052 discloses lubricating oil demulsifiers comprising certain alkylphenoxy poly(ethylene oxy) ethyl-mono- and diesters of phosphoric acid, polyoxyethylated amines, amides and quaternary salts, and polyoxyalkylene polyols and esters of such polyoxyalkylene polyols with lauric acid, stearic acid, succinic acid, and alkyl- or alkenyl-substituted succinic acids (up to 20 carbons in the alkyl or alkenyl group).

U.S. Patent 3,511,882 relates to crude oil petroleum demulsifiers prepared by adding a higher alkylene oxide, e.g., butylene oxide or propylene oxide, to a monohydric, dihydric or trihydric compound (e.g., propylene glycol). Thereafter ethylene oxide is added to the first adduct to form an oxyethylated adduct in which the proportion of primary hydroxyl groups to secondary hydroxyl groups is controlled. The oxyethylated adduct is then reacted with an epoxide of a polyphenol, preferably a diglycidyl ether of bis-phenol A. Demulsification is achieved by use of mixing of the demulsifying agents with the crude oil, emulsions in a ratio of about 1 part of the demulsifying agent to 2000 to 50,000 parts of the emulsion, and thereafter allowing the emulsion to remain in a relatively quiescent state during which separation of the oil and water occurs. It is disclosed that these demulsifiers may be used in combination with other demulsifying agents from classes such as petroleum sulfonate types, of which naphthenene sulfonic acid is an example, the modified fatty acid type, and the amine modified oxyalkylated phenol-formaldehyde type.

Crude oil demulsifiers which have also been heretofore used in the breaking of crude petroleum oil demulsions (e.g., in down well applications) comprise the adducts obtained by reacting diglycidyl ether of bis-phenol A with polypropylene glycol, and the propoxylated derivatives thereof.

However, the environment in which demulsifiers are employed in the breaking of crude oil emulsions, and the manner in which such quiescent state for emulsion phase separation is permitted to occur, are distinct from the dynamic flow and shear environment in which crankcase lubricating oils are employed in internal combustion engines and are also to be contrasted with the variety of other lubricating oil additives which are

employed in crankcase lubricating compositions, as discussed above. Principally among these, the effect of ashless dispersants in crankcase lubricating oils can be counteracted by demulsifiers.

The modern trend to the use of higher molecular-weight ashless dispersants in such formulations, and in additive concentrates therefor, has greatly complicated the search for more potent demulsifier additives. In addition, the frequent simultaneous use in such formulations and concentrates of high total base number metal detergents requires the demulsifier to be compatible with these compositions, that is, the demulsifier should not adversely affect these products' storage stability.

Heretofore, many lubricants and fuels have contained compounds known as friction modifiers (also termed "lubricity additives", which act to reduce the friction of internal engine parts and thereby increase fuel economy. U.S. Patent 3,429,817 relates to the improvement of the lubricity and load carrying ability of a synthetic ester lubricating oil by addition of an ester formed by reacting about 2 moles of C₂ to C₅ glycol with about 1 mole of C₃₆ dicarboxylic acid dimer of a C₁₈ unsaturated fatty acid (e.g., linoleic acid or oleic acid). U.S. Patent 3,273,981 is directed to fuels and lubricating oil containing as lubricating additive a mixture of dimer acids and polyhydric alcohol partial esters. U.S. Patent 4,459,223 relates to lubricating oil friction reducing additives which are the reaction product of a dimer carboxylic acid (e.g., linoleic acid dimers) and a polyhydric alcohol having at least 3 hydroxyl groups. U.S. Patent 4,479,883 relates to lubricating oil compositions having a relatively low level of phosphorous and improved friction reducing properties by use of a mixture of a glycol or glycerol ester of a polycarboxylic acid (e.g., linoleic acid dimers) with Mo, Zn, or Sb dithiocarbamates. U.S. Patent 4,557,846 relates to lubricating oil friction reducing additives comprising oil soluble hydroxyamide compounds prepared by condensing a dimer carboxylic acid (e.g., linoleic acid dimers) with a hydroxyamine. U.S. Patent 4,617,026 relates to fuel friction modifying additives comprising hydroxyl-containing esters of a C₁₂ to C₃₀ monocarboxylic acid and a glycol or trihydric alcohol, wherein the glycol can comprise polyalkylene glycols having 2 to 100 oxyalkylene repeat units. U.S. Patent 4,683,069 relates to lubricating oil fuel economy additives comprising glycerol partial esters of C₁₆-C₁₈ fatty acids.

The instability, and hence the need for a stabilization of, compositions containing polycarboxylic acid-glycol esters, ashless dispersant and certain metal lubricating oil additives has been noted in the art. U.S. Patent 4,105,571 is directed to storage stable lubricating compositions having improved anti-friction and anti-wear properties containing a zinc dihydrocarbyldithiophosphate, an ester of a polycarboxylic acid and a glycol, and an ashless high molecular weight dispersant, wherein either the zinc or ester component, or both, are predispersed with the ashless dispersant prior to adding them to the lubricating composition. The friction modifying esters are disclosed to include linoleic acid dimers which are esterified with glycol such as diethylene glycol.

U.S. Patent 4,388,201 discloses lubricating oil compositions containing such polycarboxylic acid-glycol friction modifier esters in combination with borated or non-borated alkenyl succinimide dispersants, which are stabilized by the addition of small proportions of a co-dispersant comprising an oil-soluble hydrocarbyl substituted mono- or bi-oxazoline or lactone oxazoline.

U.S. Patent 4,505,829 discloses lubricating oil compositions containing polycarboxylic acid, glycol esters as friction modifiers in combination with hydrocarbon soluble alkenyl succinimide dispersants with reduced tendency towards formation of sediment upon storage. The storage stability is improved by the addition thereto of small proportions of polyol or polyol anhydride partial esters of a fatty acid or an ethoxylated fatty acid, amine or amide compound.

U.S. Patent 4,617,134 relates to storage stable lubricating oil compositions comprising an additive combination of a polycarboxylic acid glycol or glycerol ester, as friction modifier, and zinc dihydrocarbyldithiophosphate and an ashless dispersant containing a selected amount of free hydroxyl groups.

U.S. Patent 4,684,473 relates to solubilization of oxygenated (hydroxy) esters of a dimer acid (including linoleic dimer esters of polyhydric alcohols) by the incorporation in the lubricating composition of an C₄-C₂₃ oil soluble alkanol or an oil soluble alkyl phosphate. It is disclosed that the selection of the chain length of the alcohol is critical.

SUMMARY OF THE INVENTION

In accordance with one aspect, the present invention is directed to a lubricating oil additive mixture comprising (A) a lubricating oil dispersant additive comprising at least one of (1) ashless dispersants and/or (2) polymeric viscosity index improver dispersants, and (B) a demulsifier additive comprising the reaction product of an alkylene oxide and an adduct obtained by reacting a bisepoxide with a polyhydric alcohol. In a preferred embodiment, the lubricating oil additive mixtures further comprises (C) a compatibilizer additive for the demulsifier, which comprises an alcohol ester or hydroxyamide derivative of a carboxylic acid having a total of from 24 to 90 carbon atoms and at least one carboxylic group per molecule, for enhanced solubility, viz. stability, of the demulsifier in the oil solutions containing such dispersants.

In accordance with another aspect of this invention, a process is provided for forming a storage-stable lubricating oil additive package comprising the above components A, B, and C and further comprising (D) a lubricating oil metal detergent additive wherein (1) ashless dispersant component A and metal detergent component D are pre-mixed at elevated temperature, (2) components B and C are separately premixed, and the resulting mixtures (1) and (2) are then admixed. It has been surprisingly found that improved storage

stability is achieved if a mixture of demulsifier B and compatibility additive C is first formed and then added to a previously formed mixture comprising ashless dispersant A and metal detergent D, as compared to mixtures of these components which are prepared using different orders of mixing.

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DETAILED DESCRIPTION OF THE INVENTION DISPERSANT COMPONENT A

The dispersant Component A of the oleaginous compositions of this invention can comprise one or more ashless dispersant materials, one or more polymeric viscosity index improver dispersants or mixtures thereof. Ashless dispersants and ashless dispersants admixed with polymeric viscosity index (V.I.) improver dispersants are particularly preferred. When the fully formulated lubricating oil is intended to contain both ashless dispersant and polymeric V.I. improver dispersant, generally they will be introduced to the final oil in separate additive concentrates, since the polymeric V.I. improver dispersants generally are not compatible with concentrates containing ashless dispersants, metal detergents, and many other conventional lubricant additives. Therefore, it will be understood that references herein to amounts and proportions of polymeric VI improver dispersants, unless otherwise indicated, are intended to refer to the final, fully formulated lubricating oil composition, rather than additive concentrates (to be discussed in more detail below).

A-1 Ashless dispersants useful in this invention as Component A comprise nitrogen or ester containing dispersants selected from the group consisting of (i) oil soluble salts, amides, imides, oxazolines and esters, or mixtures thereof, of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; (ii) long chain aliphatic hydrocarbon having a polyamine attached directly thereto; and (iii) Mannich condensation products formed by condensing about a molar proportion of long chain hydrocarbon substituted phenol with about 1 to 2.5 moles of formaldehyde and about 0.5 to 2 moles of polyalkylene polyamine; wherein said long chain hydrocarbon group in (i), (ii) or (iii) is a polymer of a C₂ to C₁₀, e.g., C₂ to C₅, monoolefin, said polymer having a number average molecular weight of at least about 900.

A-1(i) The long chain hydrocarbyl substituted mono or dicarboxylic acid material, i.e. acid, anhydride, or ester, includes long chain hydrocarbon, generally a polyolefin, substituted with an average of at least about 0.8, more generally from about 1.0 to about 2.0, and preferably from about 1.05 to 1.25, e.g., 1.06 to 1.20, (or 1.10 to 1.20) moles, per mole of polyolefin, of an alpha or beta- unsaturated C₄ to C₁₀ dicarboxylic acid, or anhydride or ester thereof. Exemplary of such dicarboxylic acids, anhydrides and esters thereof are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, dimethyl fumarate, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, etc.

Preferred olefin polymers for reaction with the unsaturated dicarboxylic acids to form Component A-1 ashless dispersants are polymers comprising a major molar amount of C₂ to C₁₀, e.g. C₂ to C₅ monoolefin. Such olefins include ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene, etc. The polymers can be homopolymers such as polyisobutylene, as well as copolymers of two or more of such olefins such as copolymers of: ethylene and propylene; butylene and isobutylene; propylene and isobutylene; etc. Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is a C₄ to C₁₈ non-conjugated diolefin, e.g., a copolymer of isobutylene and butadiene; or a copolymer of ethylene, propylene and 1,4-hexadiene; etc.

In some cases, the olefin polymer may be completely saturated, for example an ethylene-propylene copolymer made by a Ziegler-Natta synthesis using hydrogen as a moderator to control molecular weight.

The olefin polymers used in the Component A-1 ashless dispersants will usually have number average molecular weights of at least about 900, more generally within the range of about 1200 and about 5,000, more usually between about 1500 and about 4000. Particularly useful olefin polymers have number average molecular weights within the range of about 1500 and about 3000 with approximately one terminal double bond per polymer chain. An especially useful starting material for highly potent ashless dispersant additives useful in accordance with this invention is polyisobutylene. The number average molecular weight for such polymers can be determined by several known techniques. A convenient method for such determination is by 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.

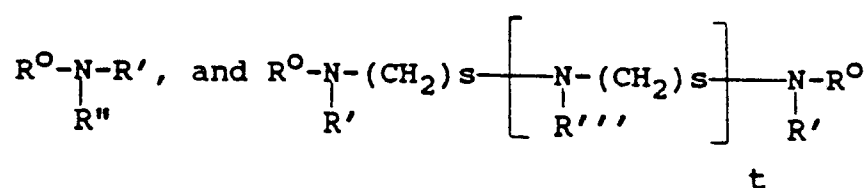
Process for reacting the olefin polymer with the C₄-₁₀ unsaturated dicarboxylic acid, anhydride or ester are known in the art. For example, the olefin polymer and the dicarboxylic acid material may be simply heated together as disclosed in U.S. Patents 3,361,673 and 3,401,118 to cause a thermal "ene" reaction to take place. Or, the olefin polymer can be first halogenated, for example, chlorinated or brominated to about 1 to 8 wt. %, preferably 3 to 7 wt. % chlorine, or bromine, based on the weight of polymer, by passing the chlorine or bromine through the polyolefin, at a temperature of 60 to 250°C, e.g., 120 to 160°C, for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer may then be reacted with sufficient unsaturated acid or anhydride at 100 to 250°C, usually about 180° to 235°C, for about 0.5 to 10, e.g. 3 to 8 hours, so the product obtained will contain the desired number of moles of the unsaturated acid per mole of the halogenated polymer. Processes of this general type are taught in U.S. Patents 3,087,436; 3,172,892; 3,272,746 and others.

Alternatively, the olefin polymer, and the unsaturated acid material are mixed and heated while adding chlorine to the hot material. Processes of this type are disclosed in U.S. patents 3,215,707; 3,231,587; 3,912,764; 4,110,349; 4,234,435; and in U.K. 1,440,219.

By the use of halogen, about 65 to 95 wt. % of the polyolefin, e.g. polyisobutylene will normally react with the dicarboxylic acid material. Upon carrying out a thermal reaction without the use of halogen or a catalyst, then usually only about 50 to 75 wt. % of the polyisobutylene will react. Chlorination helps increase the reactivity. For convenience, the aforesaid functionality ratios of dicarboxylic acid producing units to polyolefin, e.g., 1.2 to 2.0, etc. are based upon the total amount of polyolefin, that is, the total of both the reacted and unreacted polyolefin, used to make the product.

The dicarboxylic acid producing materials can also be further reacted with amines, alcohols, including polyols, amino-alcohols, etc., to form other useful dispersant additives. Thus, if the acid producing material is to be further reacted, e.g., neutralized, then generally a major proportion of at least 50 percent of the acid units up to all the acid units will be reacted.

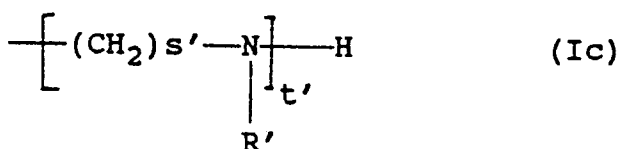
Amine compounds useful as nucleophilic reactants for neutralization of the hydrocarbyl substituted dicarboxylic acid materials include mono- and (preferably) polyamines, most preferably polyalkylene polyamines, of about 2 to 60, preferably 2 to 40 (e.g. 3 to 20), total carbon atoms and about 1 to 12, preferably 3 to 12, and most preferably 3 to 9 nitrogen atoms in the molecule. These amines may be hydrocarbyl amines or may be hydrocarbyl amines including other groups, e.g. hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Hydroxy amines with 1 to 6 hydroxy groups, preferably 1 to 3 hydroxy groups are particularly useful. Preferred amines are aliphatic saturated amines, including those of the general formulas:



(Ia)

(Ib)

wherein R^0 , R' , R'' and R''' are independently selected from the group consisting of hydrogen; C_1 to C_{25} straight or branched chain alkyl radicals; C_1 to C_{12} alkoxy C_2 to C_6 alkylene radicals; C_2 to C_{12} hydroxy amino alkylene radicals; and C_1 to C_{12} alkylamino C_2 to C_6 alkylene radicals; and wherein R''' can additionally comprise a moiety of the formula

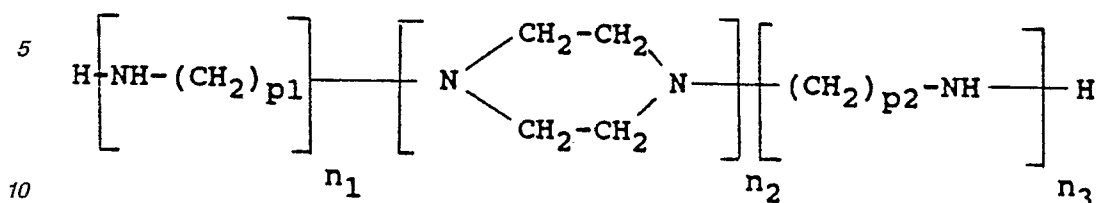


wherein R' is as defined above, and wherein s and s' can be the same or a different number of from 2 to 6, preferably 2 to 4; and t and t' can be the same or different and are numbers of from 0 to 10, preferably 2 to 7, and most preferably about 3 to 7, with the proviso that the sum of t and t' is not greater than 15. To assure a facile reaction, it is preferred that R^0 , R' , R'' , R''' , s , s' , t and t' be selected in a manner sufficient to provide the compounds of Formulas Ia and Ib with typically at least one primary or secondary amine group, preferably at least two primary or secondary amine groups. This can be achieved by selecting at least one of said R^0 , R' , R'' or R''' groups to be hydrogen or by letting t in Formula Ib be at least one when R''' is H or when the Ic moiety possesses a secondary amino group. The most preferred amine of the above formulas are presented by Formula Ib and contain at least two primary amine groups and at least one, and preferably at least three, secondary amine groups.

Non-limiting examples of suitable amine compounds include: 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; polypropylene amines such as 1,2-propylene diamine; di-(1,2-propylene) triamine; di-(1,3-propylene) triamine; N,N-dimethyl-1,3-diaminopropane; N,N-di(2-aminoethyl) ethylene diamine; N,N-di(2-hydroxyethyl)-1,3-propylene diamine; 3-do-decyloxypropylamine; N-dodecyl-1,3-propane diamine; tris hydroxymethylaminomethane (THAM); diisopropanol amine; diethanol amine; triethanol amine; mono-, di-, and tri-tallow amines; amino morpholines such as N-(3-aminopropyl)morpholine; and mixtures thereof.

Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines, and N-aminoalkyl piperazines of the general formula

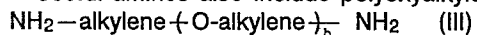
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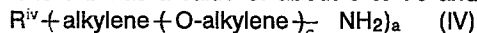
wherein p_1 and p_2 are the same or different and are each integers of from 1 to 4, and n_1 , n_2 and n_3 are the same or different and are each integers of from 1 to 3. Non-limiting examples of such amines include 2-pentadecyl imidazoline: N-(2-aminoethyl) piperazine; etc.

Commercial mixtures of amine compounds may advantageously be used. For example, one process for preparing alkylene amines involves the reaction of an alkylene dihalide (such as ethylene dichloride or propylene dichloride) with ammonia, which results in a complex mixture of alkylene amines wherein pairs of nitrogens are joined by alkylene groups, forming such compounds as diethylene triamine, triethylenetetramine, tetraethylene pentamine and isomeric piperazines. Low cost poly(ethyleneamines) compounds averaging about 5 to 7 nitrogen atoms per molecule are available commercially under trade names such as "Polyamine H", "Polyamine 400", "Dow Polyamine E-100", etc.

Useful amines also include polyoxyalkylene polyamines such as those of the formulae:



where b has a value of about 3 to 70 and preferably 10 to 35; and



where " c " has a value of about 1 to 40 with the provision that the sum of all the c 's is from about 3 to about 70 and preferably from about 6 to about 35, and R^{iv} is a polyvalent saturated hydrocarbon radical of up to ten carbon atoms wherein the number of substituents on the R^{iv} group is represented by the value of " a ", which is a number of from 3 to 6. The alkylene groups in either formula (III) or (IV) may be straight or branched chains containing about 2 to 7, and preferably about 2 to 4 carbon atoms.

The polyoxyalkylene polyamines of formulas (III) or (IV) above, preferably polyoxyalkylene diamines and polyoxyalkylene triamines, may have average molecular weights ranging from about 200 to about 4000 and preferably from about 400 to about 2000. The preferred polyoxyalkylene polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines having average molecular weights ranging from about 200 to 2000. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403", etc. The amine is readily reacted with the selected dicarboxylic acid material, e.g. alkenyl succinic anhydride, by heating an oil solution containing 5 to 95 wt. % of dicarboxylic acid material to about 100 to 250°C., preferably 125 to 175°C., generally for 1 to 10, e.g. 2 to 6 hours until the desired amount of water is removed. The heating is preferably carried out to favor formation of imides or mixtures of imides and amides, rather than amides and salts. Reaction ratios of dicarboxylic material to equivalents of amine as well as the other nucleophilic reactants described herein can vary considerably, depending on the reactants and type of bonds formed. Generally from 0.1 to 1.0, preferably from about 0.2 to 0.6, e.g., 0.4 to 0.6, moles of dicarboxylic acid moiety content (e.g., grafted maleic anhydride content) is used per equivalent of nucleophilic reactant, e.g., amine. For example, about 0.8 mole of a pentaamine (having two primary amino groups and five equivalents of nitrogen per molecule) is preferably used to convert into a mixture of amides and imides, the product formed by reacting one mole of olefin with sufficient maleic anhydride to add 1.6 moles of succinic anhydride groups per mole of olefin, i.e., preferably the pentaamine is used in an amount sufficient to provide about 0.4 mole (that is, 1.6 divided by (0.8 x 5) mole) of succinic anhydride moiety per nitrogen equivalent of the amine.

The nitrogen containing ashless dispersants can be further treated by boration as generally taught in U.S. Patent Nos. 3,087,936 and 3,254,025 (incorporated herein by reference thereto). This is readily accomplished by treating the selected acyl nitrogen dispersant with a boron compound selected from the class 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 said acylated nitrogen composition to about 20 atomic proportions of boron for each atomic proportion of nitrogen of said acylated nitrogen composition. Usefully the dispersants of the inventive combination contain from about 0.05 to 2.0 wt. %, e.g. 0.05 to 0.7 wt. % boron based on the total weight of said borated acyl nitrogen compound. The boron, which appears to be in the product as dehydrated boric acid polymers (primarily $(\text{HBO}_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts, e.g., the metaborate salt of said diimide.

Treating is readily carried out by adding from about 0.05 to 4, e.g., 1 to 3 wt. % (based on the weight of said acyl nitrogen compound) of said boron compound, preferably boric acid which is most usually added as a slurry to said acyl nitrogen compound and heating with stirring at from about 135°C. to 190, e.g., 140-170°C., for from 1 to 5 hours followed by nitrogen stripping at said temperature ranges. Or, the boron treatment can be

carried out by adding boric acid to the hot reaction mixture of the dicarboxylic acid material and amine while removing water.

The tris(hydroxymethyl) amino methane (THAM) can be reacted with the aforesaid acid material to form amides, imides or ester type additives as taught by U.K. 984,409, or to form oxazoline compounds and borated oxazoline compounds as described, for example, in U.S. 4,102,798; 4,116,876 and 4,113,639.

The ashless dispersants may also be esters derived from the aforesaid long chain hydrocarbon substituted dicarboxylic acid material and from hydroxy compounds such as monohydric and polyhydric alcohols or aromatic compounds such as phenols and naphthols, etc. The polyhydric alcohols are the most preferred hydroxy compound and preferably contain from 2 to about 10 hydroxy radicals, for example, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, and other alkylene glycols in which the alkylene radical contains from 2 to about 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.

The 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 the esters of this invention comprise the ether-alcohols and amino-alcohols including, for example, the oxy-alkylene, oxy-arylene-, amino-alkylene-, and amino-arylene-substituted alcohols having one or more oxy-alkylene, amino-alkylene or amino-arylene oxy-arylene radicals. They are exemplified by Cellosolve, Carbitol, N,N,N',N'-tetrahydroxy-trimethylene di-amine, and ether-alcohols having up to about 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to about 8 carbon atoms.

The ester dispersant 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. Mixtures of the above illustrated esters likewise are contemplated within the scope of this invention.

The ester dispersant may be prepared by one of several known methods as illustrated for example in U.S. Patent 3,381,022. The ester dispersants may also be borated, similar to the nitrogen containing dispersants, as described above.

Hydroxyamines which can be reacted with the aforesaid long chain hydrocarbon substituted dicarboxylic acid materials to form dispersants include 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, p-(beta-hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1, 3-propane-diol, 2-amino-2-ethyl-1, 3-propanediol, N-(beta-hydroxy-propyl)-N'-(beta-amino-ethyl)-piperazine, tris(hydroxymethyl) amino-methane (also known as trimethylolaminomethane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)ethylamine, and the like. Mixtures of these or similar amines can also be employed. The above description of nucleophilic reactants suitable for reaction with the hydrocarbyl substituted dicarboxylic acid or anhydride includes amines, alcohols, and compounds of mixed amine and hydroxy containing reactive functional groups, i.e., amino-alcohols.

A preferred group of ashless dispersants are those derived from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines, e.g., tetraethylene pentamine, pentaethylene hexamine, polyoxyethylene and polyoxypropylene amines, e.g., polyoxypropylene diamine, trimethylolaminomethane and pentaerythritol, and combinations thereof. One particularly preferred ashless dispersant combination involves a combination of (i) polyisobutylene substituted with succinic anhydride groups and reacted with (ii) a hydroxy compound, e.g., pentaerythritol, (iii) a polyoxyalkylene polyamine, e.g., polyoxypropylene diamine, and (iv) a polyalkylene polyamine, e.g., polyethylene diamine and tetraethylene pentamine using about 0.3 to about 2 moles each of (ii) and (iv) and about 0.3 to about 2 moles of (iii) per mole of (i) as described in U.S. Patent 3,804,763. Another preferred ashless dispersant combination involves the combination of (i) polyisobutenyl succinic anhydride with (ii) a polyalkylene polyamine, e.g., tetraethylene pentamine, and (iii) a polyhydric alcohol or polyhydroxy-substituted aliphatic primary amine, e.g., pentaerythritol or trimethylolaminomethane as described in U.S. Patent 3,632,511.

A-1(ii) Also useful as ashless nitrogen-containing dispersant in this invention are dispersants wherein a nitrogen containing polyamine is attached directly to the long chain aliphatic hydrocarbon as shown in U.S. Patents 3,275,554 and 3,565,804 where the halogen group on the halogenated hydrocarbon is displaced with various alkylene polyamines.

A-1(iii) Another class of nitrogen containing dispersants which may be used are those containing Mannich base of Mannich condensation products as they are known in the art. Such Mannich condensation products generally are prepared by condensing about 1 mole of a high molecular weight hydrocarbyl substituted mono- or polyhydroxy benzene (e.g., having a number average molecular weight of 1,000 or greater) with about 1 to 2.5 moles of formaldehyde or paraformaldehyde and about 0.5 to 2 moles polyalkylene polyamine as disclosed, e.g., in U.S. Patents 3,442,808; 3,649,229 and 3,798,165 (the disclosures of which are hereby incorporated by reference in their entirety). Such Mannich condensation products may include a long chain, high molecular weight hydrocarbon on the phenol group or may be reacted with a compound containing such a hydrocarbon, e.g., polyalkenyl succinic anhydride as shown in said aforementioned U.S. Patent 3,442,808.

A-2 Examples of suitable polymeric viscosity index improvers dispersants include:

- (i) polymers comprised of C₄ to C₂₄ unsaturated esters of vinyl alcohol or C₃ to C₁₀ unsaturated mono- or dicarboxylic acid with unsaturated nitrogen containing monomers having 4 to 20 carbons;
- (ii) polymers of C₂ to C₂₀ olefin with unsaturated C₃ to C₁₀ mono- or dicarboxylic acid neutralized with

amine, hydroxy amine or alcohols; and

(iii) polymers of ethylene with a C₃ to C₂₀ olefin further reacted either by grafting C₄ to C₂₀ unsaturated nitrogen containing monomers thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting said carboxylic acid groups with amine, hydroxy amine or alcohol.

In these polymers the amine, hydroxy amine or alcohol "mono- or poly-hydric" may be as described above in relation to the ashless dispersant compounds.

It is preferred that the polymeric viscosity index improver dispersant have a number average molecular weight range as by vapor phase osmometry, membrane osmometry, or gel permeation chromatography, of 1000 to 2,000,000; preferably 5,000 to 250,000 and most preferably 10,000 to 200,000. It is also preferred that the polymers of group (i) comprise a major weight amount of unsaturated ester and a minor, e.g., 0.1 to 40, preferably 1 to 20 wt.% of a nitrogen containing unsaturated monomer, said wt.% based on total polymer. Preferably the polymer group (ii) comprises 0.1 to 10 moles of olefin, preferably 0.2 to 5 moles C₂-C₂₀ aliphatic or aromatic olefin moieties per mole of unsaturated carboxylic acid moiety and that from 50% to 100% of the acid moieties are neutralized. Preferably the polymer of group (iii) comprises an ethylene copolymer of 25 to 80 wt.% ethylene with 75 to 20 wt.% C₃ to C₂₀ mono- and/or diolefin, 100 parts by weight of ethylene copolymer being grafted with either 0.1 to 40, preferably 1 to 20 parts by weight unsaturated nitrogen containing monomer, or being grafted with 0.01 to 5 parts by weight of unsaturated C₃ to C₁₀ mono- or dicarboxylic acid, which acid is 50% or more neutralized.

The unsaturated carboxylic acids used in (i), (ii) and (iii) above will preferably contain 3 to 10, more usually 3 or 4 carbon atoms, and may be mono carboxylic such as methacrylic and acrylic acids or dicarboxylic such as maleic acid, maleic anhydride, fumaric acid, etc.

Examples of unsaturated esters that may be used include aliphatic saturated mono alcohols of at least 1 carbon atom, and preferably of from 12 to 20 carbon atoms such as decyl acrylate, lauryl acrylate, stearyl acrylate, eicosanyl acrylate, docosanyl acrylate, decyl methacrylate, diamyl fumarate, lauryl methacrylate, cetyl methacrylate, stearyl methacrylate, and the like and mixtures thereof.

Other esters include the vinyl alcohol esters of C₂ to C₂₂ fatty or mono carboxylic acids, preferably saturated such as vinyl acetate, vinyl laurate, vinyl palmitate, vinyl stearate, vinyl oleate, and the like and mixtures thereof.

Such ester polymers may be grafted with, or the ester copolymerized with, polymerizable unsaturated nitrogen-containing monomers to impart dispersancy to the V.I. improvers. Examples of suitable unsaturated nitrogen-containing monomers include those containing 4 to 20 carbon atoms such as amino substituted olefins as p-(beta-diethylaminoethyl)styrene; basic nitrogen-containing heterocycles carrying a polymerizable ethylenically unsaturated substituent, e.g., the vinyl pyridines and the vinyl alkyl pyridines such as 2-vinyl-5-ethyl pyridine, 2-methyl-5-vinyl pyridine, 2-vinyl-pyridine, 4-vinyl-pyridine, 3-vinyl-pyridine, 3-methyl-5-vinyl-pyridine, 4-methyl-2-vinyl-pyridine, 4-ethyl-2-vinyl-pyridine and 2-butyl-1-5-vinyl-pyridine and the like.

N-vinyl lactams are also suitable, e.g., N-vinyl pyrrolidones or N-vinyl piperidones. The vinyl radical preferably is unsubstituted (CH₂=CH-), but it may be mono substituted with an aliphatic hydrocarbon group of 1 to 2 carbon atoms, such a methyl or ethyl.

The vinyl pyrrolidones are preferred and are exemplified by N-vinyl pyrrolidone, N(1-methylvinyl) pyrrolidone, N-vinyl-5-methyl pyrrolidone, N-vinyl-3, 3-dimethylpyrrolidone, N-vinyl-5-ethyl pyrrolidone, N-vinyl-4-butyl pyrrolidone N-ethyl-3-vinyl pyrrolidone, N-butyl-5-vinyl pyrrolidone, 3-vinyl pyrrolidone, 4-vinyl pyrrolidone, 5-vinyl pyrrolidone and 5-cyclohexyl-N-vinyl pyrrolidone, and the like.

Examples of olefins which could be used to prepare the copolymers of (ii) and (iii) above include mono-olefins such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-decane, 1-dodecene, styrene, etc.

Representative non-limiting examples of diolefins that can be used in (iii) include 1,4-hexadiene, 1,5-heptadiene, 1,6-octadiene, 5-methyl-1-4-hexadiene, 1,4-dicyclohexadiene, 1,5-cyclo-octadiene, vinyl-cyclohexane, dicyclopentenyl and 4,4'-dicyclohexenyl such as tetrahydroindene, methyl tetrahydroindene, dicyclopentadiene, bicyclo(2,2,1)-hepta-2,5-diene, alkenyl, alkylidene, 5-methylene-2-norbornene, 5-ethylidene-2-norbornene.

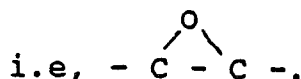
Typical polymeric viscosity index improver-dispersants include copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminolalkyl methacrylate, alkyl fumarate-vinyl acetate N-vinyl pyrrolidone copolymers, post-grafted interpolymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine, e.g., see U.S. Patents 4,089,794; 4,160,739; 4,137,185; or copolymers of ethylene and propylene reacted or grafted with nitrogen compounds such as shown in U.S. Patents 4,068,056; 4,068,058; 4,146,489; 4,149,984; styrene/maleic anhydride polymers post-reacted with alcohols and amines, ethoxylated derivatives of acrylate polymers, for example, see U.S. Patent 3,702,300. Also useful are styrene-isobutylene, and styrene-maleic anhydride copolymers and terpolymers and the like substituted with nitrogen-containing compounds (e.g., polyalkylene polyamines, piperidines, morpholines, hydrazines, and the like) and Mannich base condensation product derivatives, as disclosed in U.S. Patents 3,493,520; 3,558,743; 3,634,493; 3,684,713; 3,933,761; 3,956,149; 3,959,159; 4,029,702; and 4,424,317; Hungarian Patent 25,896; Soviet Patents 235,232, and 1,121,268; and British Patent 2,124,633, the disclosures of all of which are hereby incorporated by reference.

DEMULSIFIER COMPONENT B

The lubricating oil demulsifier additives of this invention are the water insoluble, at least partially oil soluble product of the reaction of (i) an alkylene oxide, and (ii) an adduct obtained by reacting a bis- epoxide, 5

preferably a diglycidyl ether of bis-phenol A, and a polyhydric alcohol, preferably a polyoxyalkylene glycol. In making the demulsifiers of this invention, a first adduct is made by reacting a bis- epoxide with a polyhydric alcohol.

The bis-epoxides are compounds containing at least two oxirane rings, i.e., 10



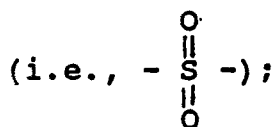
These oxirane rings are connected or joined by hydrocarbon moieties or hydrocarbon moieties containing at least one hetero atom or group. The hydrocarbon moieties generally contain from 1 to about 100 carbon atoms. They include the alkylene, cycloalkylene, alkenylene, arylene, aralkenylene and alkarylene radicals. Typical alkylene radicals are those containing from 1 to about 100 carbon atoms, more typically from 1 to about 50 carbon atoms. The alkylene radicals may be straight chain or branched and may contain from 1 to about 100 carbon atoms, preferably from 1 to about 50 carbon atoms. Typical cycloalkylene radicals are those containing from 4 to about 16 ring carbon atoms. The cycloalkylene radicals may contain alkyl substituents, e.g., C₁ - C₈ alkyl, on one or more ring carbon atoms. Typical arylene radicals are those containing from 6 to 12 ring carbons, e.g., phenylene, naphthylene and biphenylene. Typical alkarylene and aralkylene radicals are these containing from 7 to about 100 carbon atoms, preferably from 7 to about 50 carbon atoms. The hydrocarbon moieties joining the oxirane rings may contain substituent groups thereon. The substituent groups are those which are substantially inert or unreactive at ambient conditions with the oxirane ring. As used in the specification and appended claims the term "substantially inert and unreactive at ambient conditions" is intended to mean that the atom or group is substantially inert to chemical reactions at ambient temperatures and pressure with the oxirane ring so as not to materially interfere in an adverse manner with the preparation and/or functioning of the compositions, additives, compounds, etc. of this invention in the context of its intended use. For example, small amounts of these atoms or groups can undergo minimal reaction with the oxirane ring without preventing the making and using of the invention as described herein. In other words, such reaction, while technically discernable, would not be sufficient to deter the practical worked of ordinary skill in the art from making and using the invention for its intended purposes. Suitable substituent groups include, but are not limited to, alkyl groups, hydroxyl groups, tertiary amino groups, halogens, and the like. When more than one substituent is present they may be the same or different. 30

It is to be understood that while many substituent groups are substantially inert or unreactive at ambient conditions with the oxirane ring, they will react with the oxirane ring under conditions effective to allow reaction of the oxirane ring with the reactive hydroxy groups of the polyhydric alcohols. Whether these groups are suitable substituent groups which can be present on the bis-epoxide depends, in part, upon their reactivity with the oxirane ring. Generally, if they are substantially more reactive with the oxirane ring than the oxirane ring is with the reactive hydroxy group, they will tend to materially interfere in an adverse manner with the preparation of the intended demulsifiers of this invention and are, therefore, unsuitable. If, however, their reactivity with the oxirane ring is less than or generally similar to the reactivity of the oxirane ring with the reactive hydroxy groups, they will not materially interfere in an adverse manner with the preparation of the demulsifiers of the present invention and may be present on the bis-epoxide, particularly if the epoxide groups are present in excess relative to the substituent groups. An example of such a reactive but suitable group is the hydroxyl group. An example of an unsuitable substituent group is a primary amino group. 40

The hydrocarbon moieties containing at least one hetero atom or group are the hydrocarbon moieties described above which contain at least one hetero atom or group in the chain. The hetero atoms or groups are those that are substantially unreactive at ambient conditions with the oxirane rings. When more than one hetero atom or group is present they may be the same or different. The hetero atoms or groups are separated from the carbon atom of the oxirane ring by at least one intervening carbon atom. These hetero atom or group containing hydrocarbon moieties may contain at least one substituent group on at least one carbon atom. These substituent groups are the same as those described above as being suitable for the hydrocarbon moieties. 45

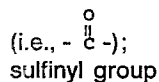
Some illustrative non-limiting examples of suitable hetero atoms or groups include: oxygen atoms (i.e., -O- or ether linkages in the carbon chain); sulfur atoms (i.e., -S- or thioether linkages in the carbon chain); carboxy groups 50

(i.e.,  - O - ; sulfonyl group 55

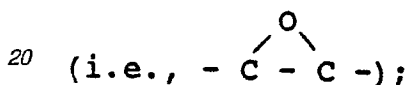


5

10 ketone group



15 (i.e., $-\overset{\text{O}}{\parallel}{\text{S}}-$);
an oxirane ring



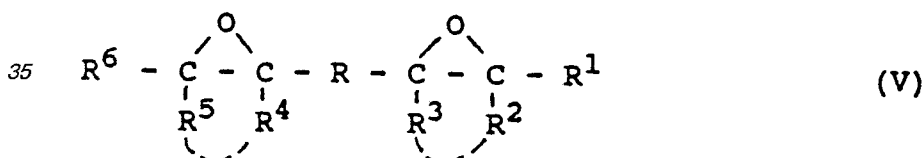
and

25 nitro group.

As mentioned hereinafore the bis-epoxides of the present invention contain at least two oxirane rings or epoxide moieties. It is critical that the bis-epoxide contain at least two oxirane rings in the same molecule.

The bis-epoxides useful in the instant invention are well known in the art and are generally commercially available or may readily be prepared by conventional and well known methods.

30 The bis-epoxides include those represented by the general formula



40

wherein:

R is a divalent hydrocarbon radical, a substituted divalent hydrocarbon radical containing at least one hetero atom or group, and a substituted divalent hydrocarbon radical containing at least one hetero atom or group;

45 R¹ and R⁶ are independently selected from hydrogen, monovalent hydrocarbon radicals, substituted monovalent hydrocarbon radicals, monovalent hydrocarbon radicals containing at least one hetero atom or group, substituted monovalent hydrocarbon radicals containing at least one hetero atom or group, and oxirane containing radicals;

50 R² and R³ are independently selected from hydrogen, monovalent hydrocarbon radicals, substituted monovalent hydrocarbon radicals, monovalent hydrocarbon radicals containing at least one hetero atom or group, substituted monovalent hydrocarbon radicals containing at least one hetero atom or group, monovalent oxirane containing radicals, divalent hydrocarbon radicals, and substituted divalent hydrocarbon radicals, with the proviso that if R² or R³ is a divalent hydrocarbon radical or substituted divalent hydrocarbon radical then both R² and R³ must be divalent hydrocarbon radicals or substituted divalent hydrocarbon radicals that together with the two carbon atoms of the oxirane ring form a cyclic structure; and

55 R⁴ and R⁵ are independently selected from hydrogen, monovalent hydrocarbon radicals, substituted monovalent hydrocarbon radicals, monovalent hydrocarbon radicals containing at least one hetero atom or group, substituted monovalent hydrocarbon radicals containing at least one hetero atom or group, monovalent oxirane containing radicals, divalent hydrocarbon radicals, and substituted divalent hydrocarbon radicals, with the proviso that if R⁴ or R⁵ is a divalent hydrocarbon radical or substituted divalent hydrocarbon radical then both R⁴ and R⁵ must be divalent hydrocarbon radicals or substituted divalent hydrocarbon radicals that together with the two carbon atoms of the oxirane ring form a cyclic structure.

60 The monovalent hydrocarbon radicals represented by R¹ - R⁶ generally contain from 1 to about 100 carbon atoms. These hydrocarbon radicals include alkyl, alkenyl, cycloalkyl, aryl, aralkyl, and alkaryl radicals. The alkyl radicals may contain from 1 to about 100, preferably from 1 to about 50, carbon atoms and may be straight

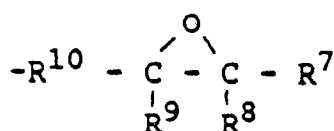
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chain or branched. The alkenyl radicals may contain from 2 to about 100 carbons, preferably from 2 to about 50 carbon atoms, and may be straight chain or branched. Preferred cycloalkyl radicals are those containing from about 4 to about 12 ring carbon atoms, e.g., cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, etc. These cycloalkyl radicals may contain substituent groups, preferably alkyl groups, on the ring carbon atoms, e.g., methylcyclohexyl, 1,3-dimethylcyclopentyl, etc. The preferred alkenyl radicals are those containing from 2 to about 30 carbon atoms, e.g., ethenyl, 1-propenyl, 2-propenyl, etc. The preferred aryl radicals are those containing from 6 to about 12 ring carbon atoms, i.e., phenyl, naphthyl, and biphenyl. The preferred aralkyl and alkaryl radicals are those containing from 7 to about 30 carbon atoms, e.g., p-tolyl, 2,6-xylyl, 2,4-trimethylphenyl, 2-isopropylphenyl, benzyl, 2-phenylethyl, 4-phenylbutyl, etc. The substituted monovalent hydrocarbon radicals represented by $R^1 - R^6$ are the monovalent hydrocarbon radicals described hereinabove which contain at least one substituent group thereon. The substituent groups are such that they are substantially unreactive under ambient conditions with the oxirane moieties. When more than one substituent group is present they may be the same or different.

The monovalent hydrocarbon radicals containing at least one hetero atom or group are the monovalent hydrocarbon radicals described hereinabove which contain at least one hetero atom or group in the carbon chain. The hetero atom or group is separated from the carbon of the oxirane ring by at least one intervening carbon atom. When more than one hetero atom or group is present they may be the same or different. The hetero atoms or groups are those that are substantially unreactive under ambient conditions with the oxirane ring. These hetero atoms or groups are those described hereinabove.

The substituted monovalent hydrocarbon radicals containing at least one hetero atom or group are the substituted monovalent hydrocarbon radicals containing at least one hetero atom or group described above which contain at least one substituent group on at least one carbon atom. The substituent groups are those described hereinabove.

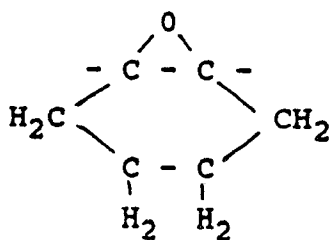
The oxirane radicals represented by $R^1 - R^6$ may be represented by the formula



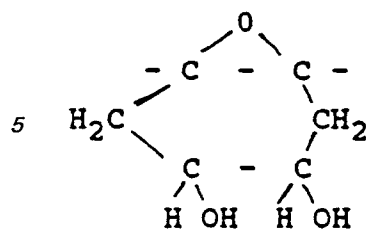
(VI)

wherein:

R^7 has the same meaning as R^1 , $R^8 - R^9$ have the same meaning as $R^2 - R^3$, and R^{10} has the same meaning as R in Formula V. The divalent hydrocarbon radicals represented by $R^2 - R^5$ and $R^8 - R^9$ generally are aliphatic acyclic radicals and contain from 1 to about 5 carbon atoms. Preferred divalent hydrocarbon radicals are the alkylene radicals. Preferred alkylene radicals are those that, together with the two carbon atoms of the oxirane ring, form a cyclic structure containing from 4 to about 8 ring carbon atoms. Thus, for example, if R^3 and R^4 are both ethylene radicals the resultant cyclic structure formed with the two carbon atoms of the oxirane ring is a cyclohexylene oxide, i.e.,



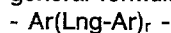
The divalent substituted hydrocarbon radicals represented by $R^2 - R^5$ and $R^8 - R^9$ are the divalent hydrocarbon radicals described above which contain at least one substituent group on at least one carbon atom. Thus, for example, if R^3 and R^4 are both hydroxy substituted ethylene radicals, the resultant cyclic structure formed with the two carbon atoms of the oxirane ring may be represented by the formula:



15 The divalent hydrocarbon radicals represented by R and R¹⁰ generally contain from 1 to about 100 carbon atoms, preferably from 1 to about 50 carbon atoms. They may be aliphatic, aromatic or aliphatic-aromatic. If they are aliphatic they may be saturated or unsaturated, acyclic or alicyclic. They include alkylene, cycloalkylene, alkenylene, arylene, aralkylene, and alkarylene radicals. The alkylene radicals may be straight chain or branched. Preferred alkylene radicals are those containing from 1 to about 50 carbon atoms. Preferred alkenylene radicals are those containing from 2 to about 50 carbon atoms. Preferred cycloalkylene radicals are those containing from 4 to about 12 ring carbon atoms. The cycloalkylene radicals may contain substituents, preferably alkyls, on the ring carbon atoms.

20 It is to be understood that the term "arylene" as used in the specification and the appended claims is not intended to limit the divalent aromatic moiety represented by R and R¹⁰ to benzene. Accordingly, it is to be understood that the divalent aromatic moiety can be a single aromatic nucleus such as a benzene nucleus, a pyridine nucleus, a thiophene nucleus, a 1,2,3,4-tetrahydronaphthalene nucleus, etc., or a poly-nuclear aromatic moiety. Such polynuclear moieties can be of the fused type; that is, wherein at least one aromatic nucleus is fused at two points to another nucleus such as found in naphthalene, anthracene, the azanaphthalenes, etc. Alternatively, such polynuclear aromatic moieties can be of the linked type wherein at least two nuclei (either mono- or polynuclear) are linked through bridging linkages to each other. Such bridging linkages can be chosen from the group consisting of carbon-to-carbon single bonds, ether linkages, keto linkages, sulfide linkages, polysulfide linkages of 2 to 6 sulfur atoms, sulfinyl linkages, sulfonyl linkages, methylene linkages, alkylene linkages, di-(lower alkyl)-methylene linkages, lower alkylene ether linkages, alkylene keto linkages, lower alkylene sulfur linkages, lower alkylene polysulfide linkages of 2 to 6 carbon atoms, amino linkages, polyamino linkages and mixtures of such divalent bridging linkages.

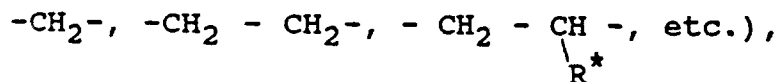
35 When the divalent aromatic moiety, Ar, is a linked polynuclear aromatic moiety it can be represented by the general formula



40 wherein r is an integer of 1 to about 10, preferably 1 to about 8, more preferably 1, 2 or 3; Ar is a divalent aromatic moiety as described above, and each Lng is a bridging linkage individually chosen from the group consisting of carbon-to-carbon single bonds, ether linkages (e.g. -O-), keto linkages (e.g.,



45 sulfide linkages (e.g., -S-), polysulfide linkages of 2 to 6 sulfur atoms (e.g., -S₂-), sulfinyl linkages (e.g., -S(O)-), sulfonyl linkages (e.g., -S(O)₂-), lower alkylene linkages (e.g.,



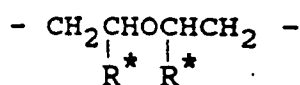
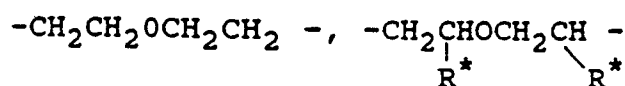
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di (lower alkyl) -methylene linkages (e.g., -CR²-), lower alkylene ether linkages (e.g.,

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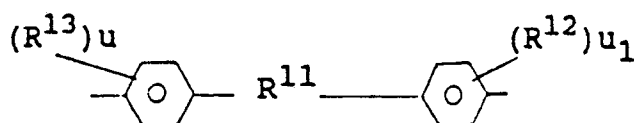
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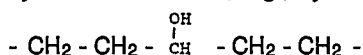
etc.) lower alkylene sulfide linkages (e.g., wherein one or more -O-'s in the lower alkylene ether linkages is replaced with an -S- atom), lower alkylene polysulfide linkages (e.g., wherein one or more -O-'s is replaced with a -S₂ to -S₆- group), with R* being a lower alkyl group.

Illustrative of such linked polynuclear aromatic moieties are those represented by the formula



wherein R¹² and R¹³ are independently selected from hydrogen and alkyl radicals, preferably alkyl radicals containing from 1 to about 20 carbon atoms; R¹¹ is selected from alkylene, alkylidene, cycloalkylene, and cycloalkylidene radicals; and u and u¹ are independently selected from integers having a value of from 1 to 4.

The divalent substituted hydrocarbon radicals represented by R and R¹⁰ are those divalent hydrocarbon radicals described above which contain at least one substituent group of the type described hereinafore. Thus, for example, if the divalent hydrocarbon radical is a C₅ alkylene, the corresponding divalent substitute hydrocarbon radical, e.g., hydroxyl substituted radical, may be

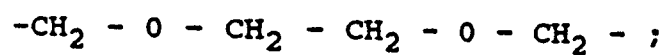


When more than one substituent group is present they may be the same or different.

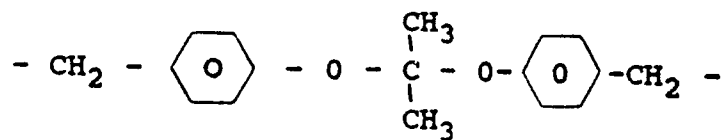
The divalent hydrocarbon radicals containing at least one hetero atom or group are those divalent hydrocarbon radicals described hereinafore which contain at least one hetero atom or group. These hetero atoms or groups are those described hereinafore. Some illustrative non-limiting examples of divalent hydrocarbon radicals containing at least one hetero atom or group include:



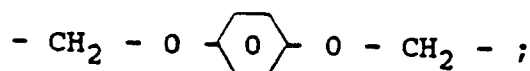
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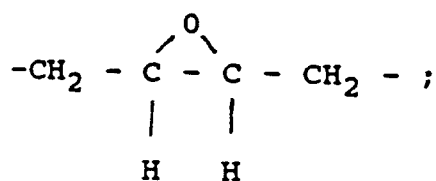
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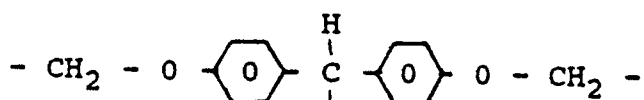


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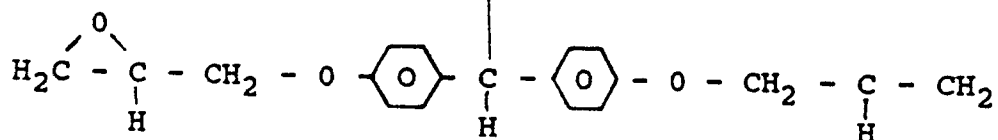


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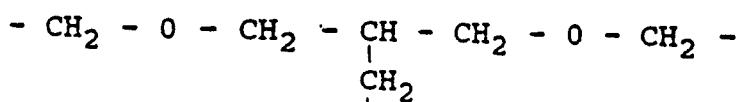
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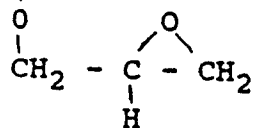
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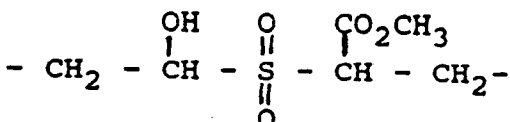
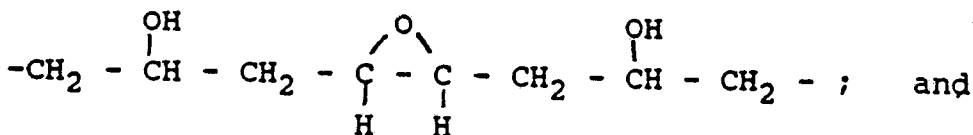
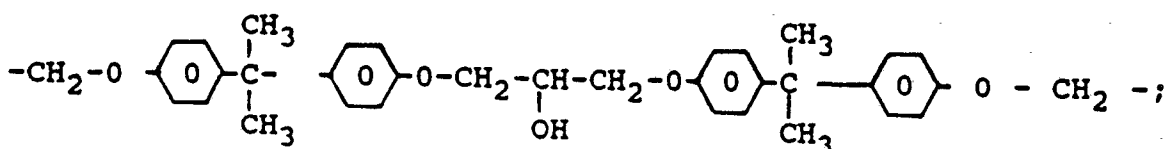
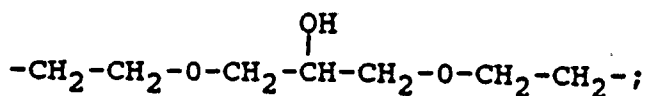
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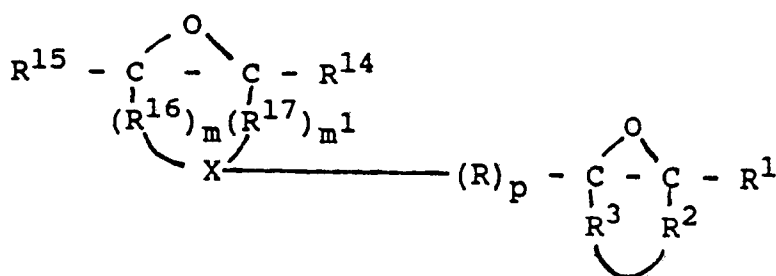
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The divalent substituted hydrocarbon radicals containing at least one hetero atom or group are those divalent hydrocarbon radicals containing at least one hetero atom or group described above which contain at least one substituent group of the type described hereinafore. Some illustrative non-limiting examples of divalent substituted hydrocarbon radicals containing at least one hetero atom or group include:



Also included within the scope of the bis-epoxides of the instant invention are these represented by the formula (VII)



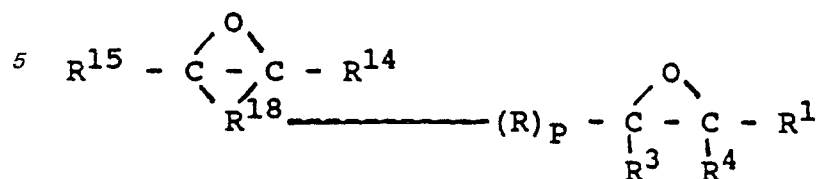
wherein:

R and R¹-R³ are as defined hereinafore; R¹⁴ and R¹⁵ independently have the same meaning as R¹; X is an aromatic moiety; R¹⁶ and R¹⁷ are independently selected from divalent aliphatic acyclic hydrocarbon radicals and divalent substituted aliphatic acyclic hydrocarbon radicals which together with the two carbon atoms of the oxirane ring and the two adjacent ring carbon atoms of the aromatic moiety X form a cyclic structure; m and m¹ are independently zero or one with the proviso that the sum of m plus m¹ is at least one; and p is zero or one.

The aromatic moieties represented by X are preferably those containing from 6 to 12 ring carbon atoms, e.g., benzene, naphthalene, and biphenyl. The aromatic moieties may contain one or more substituents on one or more ring carbon atoms. These substituents are those which are substantially unreactive at ambient conditions, e.g., temperature and pressure, with the oxirane ring. They include, for example, alkyl, hydroxyl, nitro, and the like.

Also falling within the scope of the bis-epoxides of the instant invention are those represented by the

formula (VIII):



wherein:

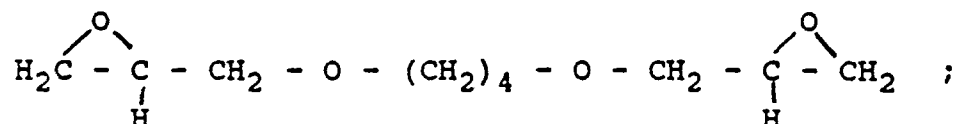
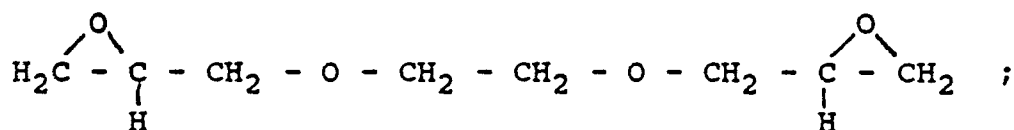
R, R¹-R³, R¹⁴-R¹⁵ and p are as defined hereinafore; and R¹⁸ is independently selected from divalent hydrocarbon radicals or a substituted divalent hydrocarbon radicals which together with the two carbon atoms of the oxirane ring forms a cyclic preferably cycloaliphatic, structure.

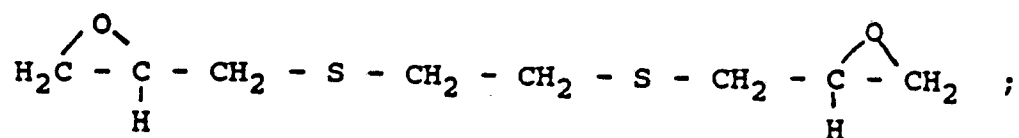
The divalent hydrocarbon or substituted divalent hydrocarbon radicals represented by R¹⁸ preferably contain from 2 to about 14 carbon atoms so as to form, together with the two carbon atoms of the oxirane ring, a 4 to about 16 membered ring structure, preferably a cycloaliphatic ring. The preferred divalent hydrocarbon radicals are the divalent aliphatic hydrocarbon radicals, preferably the alkylene radicals.

The divalent aliphatic hydrocarbon radicals represented by R¹⁸ may contain one or more substituent groups on one or more ring carbon atoms. The substituents are selected from those that are substantially unreactive under ambient conditions with the oxirane ring, e.g., alkyl, hydroxyl, and the like.

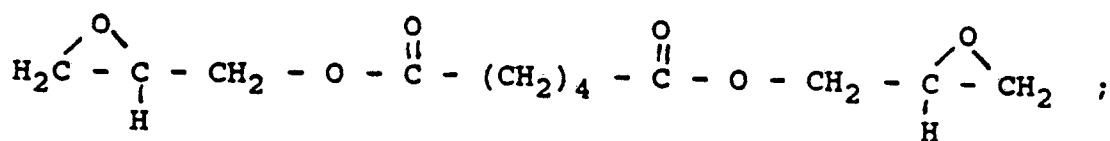
Preferred bis-epoxides of the instant invention are those wherein the oxirane rings (preferably at least one of which is a terminal or end oxirane ring) are unhindered. By unhindered is meant that the oxirane ring contains one secondary carbon atom, i.e., having two hydrogens bonded thereto, and preferably contains one secondary carbon atom and one tertiary carbon atom, i.e., having one hydrogen bonded thereto. Thus, for example, an unhindered bis-epoxide of Formula V is one wherein R¹, R², R⁵, and R⁶ are hydrogen preferably one wherein R¹-R³ and R⁴-R⁶ are all hydrogen.

Some illustrative non-limiting Examples of the bis-epoxides of the instant invention include:

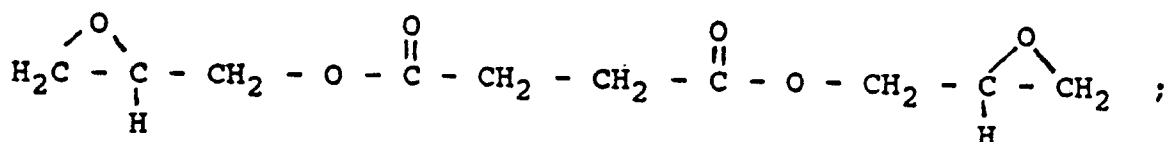




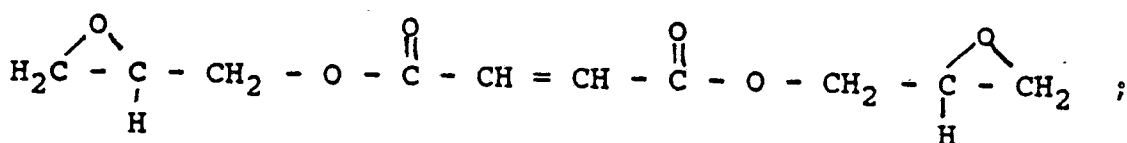
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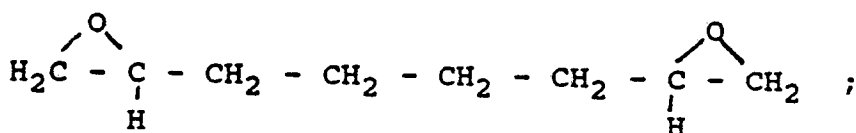


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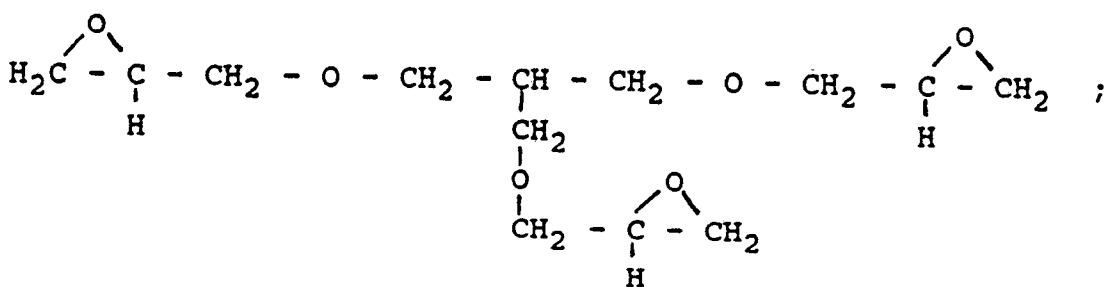


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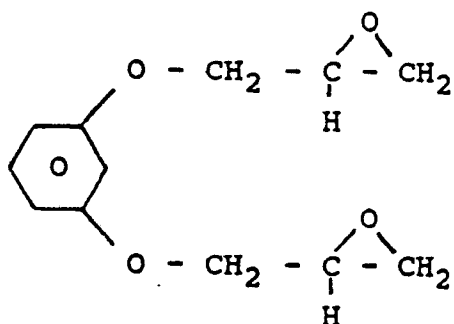
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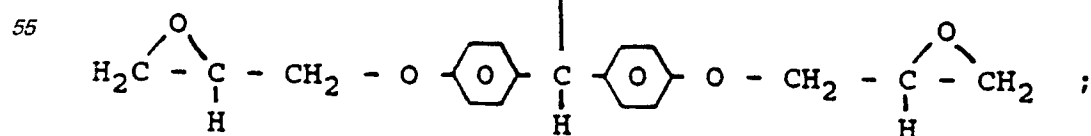
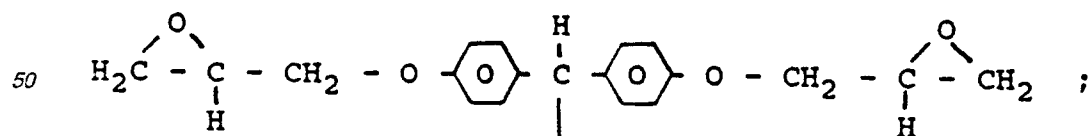
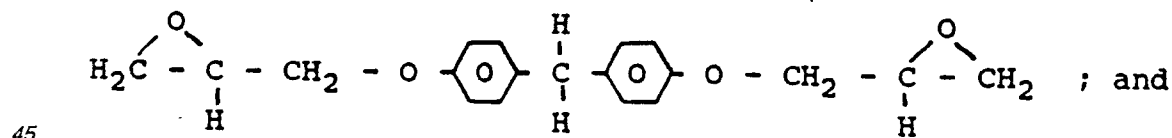
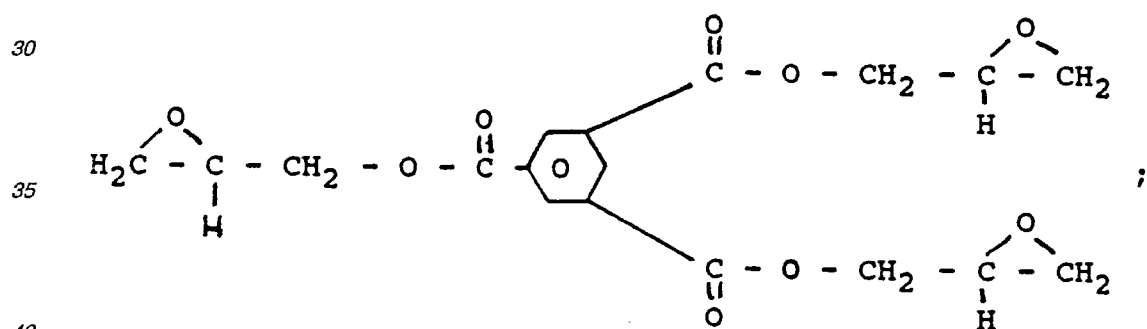
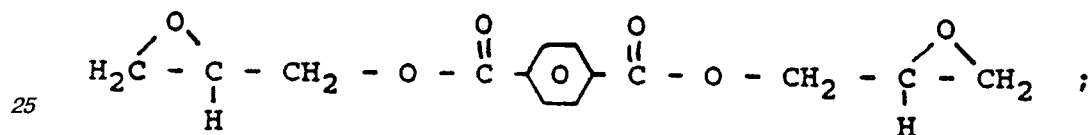
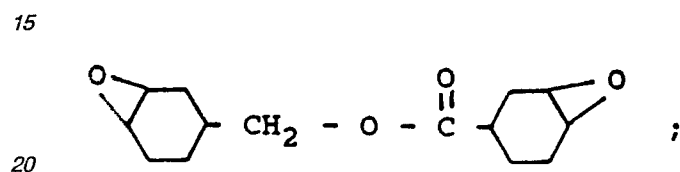
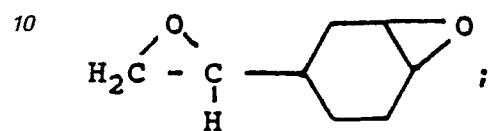
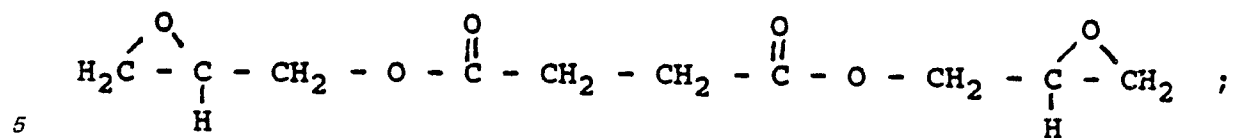


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The bis-epoxides useful in the instant invention also include the epoxy resins. These epoxy resins are well known in the art and are generally commercially available. They are described, for example, in Billmeyer, F. W. Jr., Textbook of Polymer Science, 2nd edition, Wiley-Interscience, New York, 1971, pp. 479-480; Lee, H and Neville, K., "Epoxy Resins", pp. 209-271 in Mark, H. F., Gaylord, N. G. and Bikales, N. M., eds., Encyclopedia of Polymer Science and Technology, Vol. 6, Interscience Div., John Wiley and Sons, New York, 1967; and in U.S. Patent Nos. 3,477,990 and 3,408,422; all of which are incorporated herein by reference.

The epoxy resins include those compounds possessing one or two terminal epoxy groups. These bis-epoxides are saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic, and are substituted, if desired, with non-interfering substituents, such as halogen atoms, hydroxyl groups, ether radicals, and the like.

Preferred bis-epoxides are the glycidyl polyethers of polyhydric phenols and polyhydric alcohols, especially the glycidyl polyethers of 2,2-bis(4-hydroxyphenyl) propane having an average molecular weight between about 300 and 3,000 and an epoxide equivalent weight (WPE) between about 140 and 2,000. Especially preferred are the diglycidyl polyethers of 2,2-bis(4-hydroxyphenyl) propane having a WPE between about 140 and 500 and an average molecular weight of from about 300 to about 900.

Other suitable epoxy compounds include those compounds derived from polyhydric phenols and having at least one vicinal epoxy group wherein the carbon-to-carbon bonds within the six-membered ring are saturated. Such epoxy resins may be obtained by at least two well-known techniques, i.e., by the hydrogenation of glycidyl polyethers of polyhydric phenols of (2) by the reaction of hydrogenated polyhydric phenols with epichlorohydrin in the presence of a suitable catalyst such as Lewis acids, i.e., boron trihalides and complexes thereof, and subsequent dehydrochlorination in an alkaline medium. The method of preparation forms no part of the present invention and the resulting saturated epoxy resins derived by either method are suitable in the present compositions.

Briefly, the first method comprises the hydrogenation of glycidyl polyethers of polyhydric phenols with hydrogen in the presence of a catalyst consisting of rhodium and/or ruthenium supported on an inert carrier at a temperature below about 50°C. This method is thoroughly disclosed and described in U.S. Pat. No. 3,336,241, issued Aug. 15, 1967.

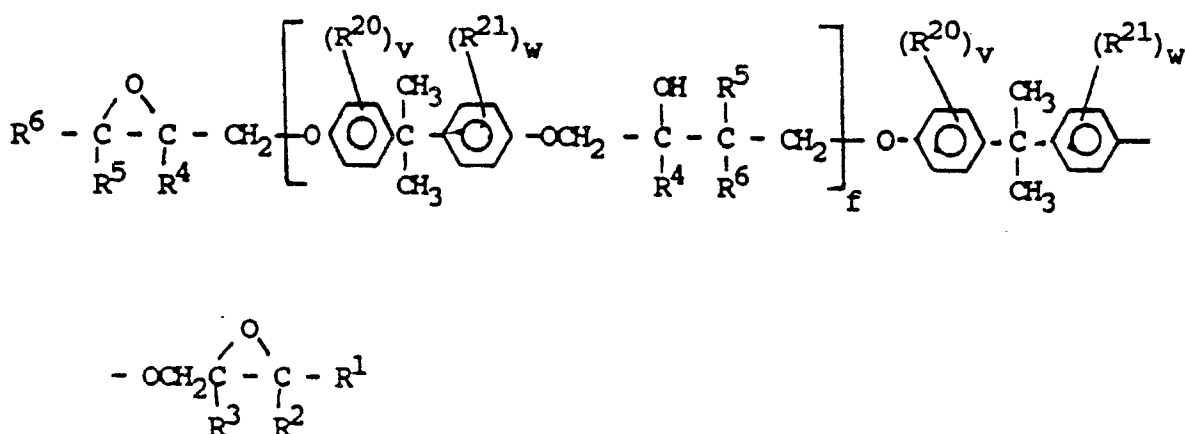
The hydrogenated epoxy compounds prepared by the process disclosed in U.S. Pat. No. 3,336,241 are suitable for use in the present compositions. Accordingly, the relevant disclosure of U.S. pat. No. 3,336,241 is incorporated herein by reference.

The second method comprises the condensation of a hydrogenated polyphenol with an epihalohydrin, such as epichlorohydrin, in the presence of a suitable catalyst such as BF₃, followed by dehydrohalogenation in the presence of caustic. When the phenol is hydrogenated Bisphenol A, the resulting saturated epoxy compound is sometimes referred to as "diepoxidized hydrogenated Bisphenol A," or more properly as the diglycidyl ether of 2,2-bis(4-cyclohexanol) propane.

In any event, the term "saturated epoxy resin," as used herein shall be deemed to mean the glycidyl ethers of polyhydric phenols wherein the aromatic ring structure of the phenols have been or are saturated.

Preferred saturated epoxy resins are the hydrogenated resins prepared by the process described in U.S. Pat. No. 3,336,241. More preferred are the hydrogenated glycidyl ethers of 2,2-bis(4-hydroxyphenyl) propane, sometimes called the diglycidyl ethers of 2,2-bis(4-cyclohexanol) propane.

One class of useful epoxy resins are those prepared by condensing epichlorohydrin with bisphenol-A. They include resins represented by the general structural formula (IX):



wherein:

R¹-R⁶ are defined hereinafore, and preferably are all hydrogen;

R²⁰ is independently selected from alkyl radicals, preferably alkyl radicals containing from 1 to about 10 carbon atoms, hydroxyl, or halogen radicals;

R^{21} is independently selected from alkyl radicals, preferably alkyl radicals containing from 1 to about 10 carbon atoms, hydroxyl, or halogen radicals;

v is independently selected from integers having a value of from 0 to 4 inclusive;

w is independently selected from integers having a value of from 0 to 4 inclusive; and

- 5 f has a value of at least one, and varies according to the molecular weight of the resin, with the upper-limit of f preferably not exceeding about 10, more preferably not exceeding about 5.

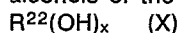
Preferred compounds of Formula IX are those wherein $R^1 - R^6$ are all hydrogen, and v and w are all zero.

An example of commercially available and useful epoxy resins are the EPON resins of Shell Oil Company.

- 10 As mentioned hereinafore those bis-epoxides, including the epoxy resins, wherein the two carbon atoms of the oxirane ring are bonded to three hydrogen atoms, e.g., wherein $R^1 - R^6$ in Formula V are all hydrogen, are preferred. Preferred bis-epoxides of this type are those wherein the hydrocarbon moieties bridging the epoxide moieties, e.g., R in Formula V, contain polar groups or atoms. These polar groups or atoms include, but are not limited to, the polar hetero atoms or groups described hereinafore. Particularly preferred bis-epoxides are the epoxy resins, especially those devised from polyhydric phenols.

- 15 In the preferred compositions of the invention, the epoxide equivalent of the epoxide of the polyphenol is preferably limited to a minimum of 145 and a maximum below 250. The epoxide equivalent is defined as the number of grams of material containing one epoxide group. Thus, a suitable starting material is a substance known as Epon 828 which is a commercial epoxidized dihydroxy-di-phenyldimethylmethane having an average epoxide equivalent of 175 to 210. Other similar commercial products are available and can be employed as the bis-epoxide. Exemplary of these commercial products are the bis-epoxides of polynuclear phenol. These products for the most part consist principally of the diglycidyl ether of diphenyldimethylmethane. The diglycidyl ether of diphenylmonomethylmethane and the diphenylmethane diglycidyl ether can be employed as reactants.

- 20 The polyhydric alcohol reactants can comprise at least one member selected from the group consisting of alcohols of the formula:



wherein R^{22} is a hydrocarbyl group or represents a hydrocarbyl chain, optionally containing one or more hetero chain atoms (e.g., O, S or N), and x is a number of from 2 to 8, e.g., 1 to 5 (preferred). Preferred polyhydric alcohols are polyoxyalkylene glycols of the formula:

- 30 $HO-(MO)_y(TO)_qH \quad (XI)$

- wherein M and T are the same or different and are alkylene groups of at least 2 carbon atoms wherein the sum of y and q is in the range of from 15 to 250, such that the total average molecular weight of the polyoxyalkylene glycol is at least 1,000, preferably from 1,000 to 10,000, more preferably from 2,000 to 8,000. Preferably M and T are either 3 or 4 carbon atoms, and therefore preferably the polyoxyalkylene glycol comprises polypropylene glycol, polybutylene glycol or block copolymer mixtures thereof.

- 35 The selected polyhydric alcohol and bis-epoxide reactants are contacted for reaction in a weight:weight ratio of polyhydric alcohol to bis-epoxide of from about 10:1 to about 20:1, preferably from about 14:1 to 18:1.

- The conditions of reaction in forming the first adduct will vary depending upon such factors as the polyhydric alcohol and bis-epoxide used, the presence of solvent for the reaction and other factors. In general, 40 temperatures within the range of from about 110 to 200°C, preferably from about 120 to 170°C, will be employed.

- The reaction for formation of the first adduct may be conducted in the presence of a reaction solvent, such as a hydrocarbon solvent, e.g., toluene, xylene and the like. The quantity of the selected solvent is not critical, although the solvent, e.g., toluene will be usually within the range from about 25 to 75 parts of solvent per 100 45 parts of the first adduct, calculated by weight.

The pressure employed in the reaction for formation of the first adduct is not critical, and may be subatmospheric, atmospheric or superatmospheric.

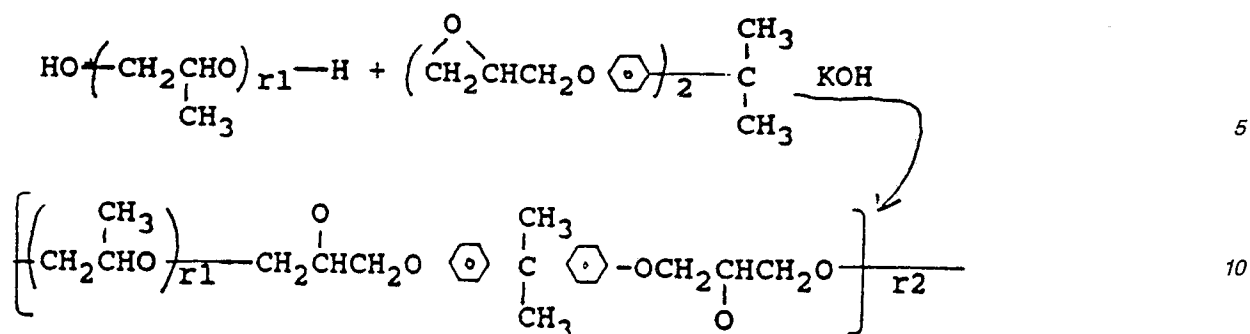
- The reaction of the selected polyhydric alcohol and bis-epoxide may be conducted in the presence of a small amount of catalyst for the reaction, such as a Lewis base, e.g., caustic soda or caustic potash, which can 50 be employed in the range of from about 0.2 to 0.5 wt. % of all the components charged to the reaction mixture.

The desired adduct formed by the reaction of the polyhydric alcohol and bis-epoxide can be illustrated by reference to the following equation, wherein the reaction of polypropylene glycol and the diglycidyl ether of bis-phenol A is illustrated.

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wherein r_1 has the value sufficient to satisfy the number average molecular weight of the polypropylene glycol. For example, r_2 will range generally from about 5 to about 120 for polypropylene glycols having number average molecular weights of from about 4000 to about 7000.

It is not essential that the reaction to form the first adduct be carried to completion and it will be understood that the reaction mass can also contain by-product and unreacted starting material. Illustrative of by-product are dimers, trimers and higher "homologues" formed by reactions of molecules of the selected bis-epoxide with the desired polyhydric alcohol.

The product mixture obtained for preparation of the first adduct can, if desired, be directly charged to a separate reaction vessel for reaction in the second step with the selected amount of the alkylene oxide, e.g., propylene oxide. Alternatively, the alkylene oxide can be directly introduced into the reaction vessel containing the adduct product mixture.

The alkylene oxide reactant for use in the oxyalkylation of the thus-formed bis-epoxide/polyhydric alcohol adduct product mixture comprise alkylene oxides having from 2 to 10, preferably from 2 to 5, carbon atoms. Exemplary of such alkylene oxides are ethylene oxide, propylene oxide, 1,2-epoxy butane, 2,3-epoxy butane, 1,2-epoxy pentane, 2,3-epoxy pentane, 1,2-epoxy hexane, 2,3-epoxy hexane, 3,4-epoxy hexane, 1,2-epoxy-3-methylbutane, and the like. Particularly preferred alkylene oxides are propylene oxide and butylene oxide. Most preferably, the alkylene oxide comprises propylene oxide.

The quantity of the alkylene oxide introduced into the second reaction stage for reaction with the adduct can vary widely, but preferably from about 0.1 to 20 parts by weight of alkylene oxide, more preferably from about 0.4 to 10 parts by weight of alkylene oxide, and most preferably from about 1 to 4 parts by weight of alkylene oxide, are reacted with the adduct product mixture per part by weight of the first adduct product mixture. Preferably, the alkylene oxide charged to this reaction stage will comprise less than about 50 wt.%, still more preferably less than about 40 wt.%, and most preferably less than about 30 wt.% (e.g., 0-20 wt.%), ethylene oxide, with the balance of the charged alkylene oxide comprising propylene oxides and higher epoxides, as described above. The contact of the selected alkylene oxide and the first adduct reaction mixture will be made under conditions for reaction of the alkylene oxide with the hydroxy groups of the first adduct. Conditions effective to achieve such reaction can vary widely, and this second stage reaction will typically employ a reaction temperature within the range of from about 110 to 180°C, preferably 130 to 160°C. Any convenient pressure may be used, that is, subatmospheric, atmospheric or superatmospheric, although superatmospheric will be typically preferred.

A mixture of alkylene oxides may be employed, e.g., a mixture of ethylene oxide and a higher alkylene oxide (e.g., propylene oxide or butylene oxide). Alternatively, different alkylene oxides can be charged in any sequence, to form "blocks" of the separately charged alkylene oxide. The order of such sequential oxyalkylation, or the number of repeats of any such oxyalkylation, can be varied widely. For example, the first adduct can be oxyethylated, followed by charging of propylene oxide for oxypropylation, or the first adduct can be first treated with propylene oxide followed by oxyethylation of the oxypropylated adduct. If such sequential alkylations are used with ethylene oxide, propylene or a higher alkylene oxide is preferably charged second (if two alkylation stages are used) or last (in the case of 3 or more alkylation stages), to alkoxyate substantially all of the oxyethylene chain ends.

The reaction of the selected bis-epoxide and polyhydric alcohol, and the alkoxylation of the resulting adduct, are preferably conducted under substantially anhydrous conditions.

The oxyalkylation reaction stage(s) may be conducted in the presence of the Lewis Base catalyst employed in the formation of the first adduct so that it is not necessary to remove the Lewis Base catalyst prior to the introduction of the alkylene oxide. Similarly, the oxyalkylation may be conducted under the presence of the same or different solvent as employed in the first reaction wherein the first adduct of the bis-epoxide and polyhydric phenol is formed. If desired, additional reaction solvent (e.g., toluene) may be added. The Lewis Base catalyst is preferably neutralized (e.g., by addition of acetic acid or similar alkanolic acid) to a substantially neutral pH (e.g., pH of 5-8).

Preferably, the demulsifiers of this invention will contain from about 10 to 80 wt.%, and more preferably from about 20 to 70 wt.%, of oxyalkylene units derived from the selected alkylene oxide(s) used to oxyalkylate the bis-epoxide/polyhydric phenol adduct, and preferably will contain at least about 25 wt.%, and more preferably

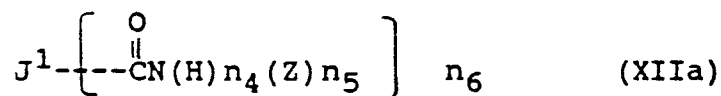
at least 40 wt.%, of oxyalkylene units derived from alkylene oxides of 3 carbon atoms or greater (e.g., propylene oxide, butylene oxide, and the like) used in the oxyalkylation step.

One of the preferred demulsifiers of this invention can be described as the propoxylated copolymer of a diglycidyl ether of bis-phenol A with polypropylene glycol wherein the polypropylene glycol has a molecular weight of from 2000 to 8000, the weight ratio of the polypropylene glycol to the diglycidyl ether of bis-phenol A is within the range of from 14 to 1 to 18 to 1, and the weight ratio of propylene oxide reacted with the first adduct is within the range of from about 2.5:1 to 3.5:1.

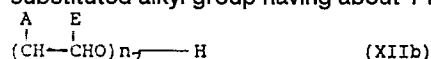
COMPATIBILITY ADDITIVE C

Preferably, the lubricating oil additive mixtures of this invention further comprise a compatibilizing effective amount of at least one alcohol ester or hydroxyamide derivative of a carboxylic acid having a total of from 24 to 90 carbon atoms and at least 1, e.g., about 2 to 3, carboxylic acid groups per molecule. These ester compatibility additives are generally derived from the esterification of a monocarboxylic or polycarboxylic acid with a mono-, di- or trihydric alcohol (e.g., glycol, glycerol, oxa-alkane diols). Such esters have been heretofore used in lubricating oils as friction modifiers, and the methods of preparation thereof, and structures, are described in U.S. Patents 3,429,817; 4,459,223; 4,479,883; 4,617,026; and 4,683,069, the disclosures of which are hereby incorporated by reference in their entirety. The hydroxyamide derivatives of such mono- and polycarboxylic acids can be prepared by condensing the acid at elevated temperature with a hydroxyamine (e.g. alkanol amines or aminoalcohols, such as ethanolamine, diethanol-amine, propanolamine, 3-amino-1,1-propanediol), employing the methods disclosed in U.S. Patent 4,557,846, which is hereby incorporated by reference in its entirety.

The carboxylic acid may be an aliphatic saturated or unsaturated acid and will generally have a total of about 24 to 90, preferably about 24 to 60, carbon atoms and at least 1, e.g., about 2 to 3, preferably about 2, carboxylic acid groups with at least about 9 carbon atoms, preferably about 12 to 42, especially 16 to 22 carbon atoms between the carboxylic acid groups. Exemplary of the hydroxyamide compatibilizers are oil soluble hydroxyamide compounds having the formula:

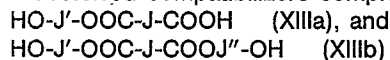


wherein J^1 is the hydrocarbon radical or skeleton of a dimer carboxylic acid having a total of about 24 to about 90 carbon atoms with about 9 to about 42 carbon atoms between carboxylic acid groups; Z is (a) a hydroxy substituted alkyl group having about 1 to about 20 carbon atoms, or (b) an oxyalkylene group of the formula:



where A and E are each alkyl of 1 to 2 carbon atoms or hydrogen and n_7 is an integer of 1 to 50; n_4 is 0 or 1; n_5 is 1 or 2 and n_6 is 1 or 2.

Preferred compatibilizers comprise partial esters or diesters of dicarboxylic acids of the formulas:

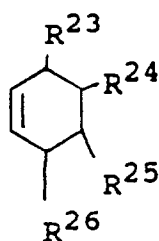


wherein J is the hydrocarbon radical of the acid and J' and J'' is either the hydrocarbon radical of an alkane diol or the oxy-alkylene radical from an oxa-alkane diol as defined hereinbelow. Generally about 1-3 moles of glycol, preferably 1-2 moles of glycol, are used per mole of acid to provide either a complete or partial ester.

Also, esters can be obtained by esterifying a mono- or dicarboxylic acid or mixture of such acids with a mixture of diols, in which case J would then be the hydrocarbon radical of the dicarboxylic acid(s) and J' and J'' would be the hydrocarbon radicals associated with the diols.

The compatibility additives are typically used in amounts ranging from about 0.1 to 5 parts by weight, more preferably 0.5 to 1.5 parts by weight based upon the weight of the Component B demulsifier additive in the lubricating oil composition. If desired, higher amounts of the compatibility additive may be employed, since such polycarboxylic acid-glycol esters may also serve as friction modifiers in the lubricating oil composition. Therefore, the compatibility additives will be generally employed in an amount of from about 0.0005 to 2, more preferably from about 0.001 to 0.25, and most preferably from about 0.005 to 0.1, weight percent.

Especially preferred compatibilizer additives are the dimer acid esters. The term dimer acid used herein is meant to refer to those substituted cyclohexene dicarboxylic acids formed by a Diels-Alder-type reaction (which is a thermal condensation) of C_{18} - C_{22} unsaturated fatty acids, such as tall oil fatty acids, which typically contain about 85 to 90 percent oleic or linoleic acids. Such dimer acids typically contain about 36 carbon atoms. The dimer acid structure can be generalized as follows:



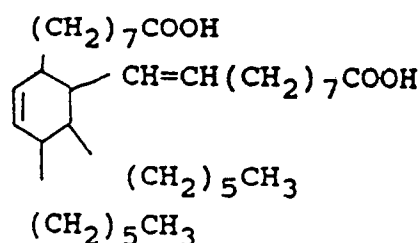
(XIV)

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with two of the R^{23} - R^{26} groups containing carboxyl groups and two being hydrocarbon groups depending upon how the condensation of the carboxylic acid has occurred. The carboxyl groups can be $-(CH_2)_8COOH$; $-CH=CH(CH_2)_8COOH$; $-(CH_2)_7COOH$; $-CH_2-CH=CH(CH_2)_7COOH$; $-CH=CH(CH_2)_7COOH$ and the hydrocarbon terminating group can be represented by: $CH_3(CH_2)_4-$; $CH_3(CH_2)_5-$; $CH_3(CH_2)_7-$; $CH_3(CH_2)_4CH=CH-$; $CH_3(CH_2)_4CH=CHCH_2-$, and the like. The dimer of linoleic acid which is the preferred embodiment can be expressed in the following formula:

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(XV)

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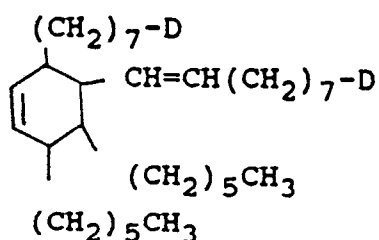
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Also the term dimer acid as used herein necessarily includes products containing trimers (and higher homologues), e.g., up to about 24 percent by weight trimer, but more typically about 10 percent by weight trimer since, as is well known in the art, the dimerization reaction provides a product containing a trimer acid having molecular weight of about three times the molecular weight to the starting fatty acid.

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The polycarboxylic acids or dimer acids noted above are esterified with a glycol, the glycol being an alkane diol or oxa-alkane diol represented by the formula $HO(R^{27}CHCH_2O)_{x^1}H$ wherein R^{27} is H or CH_3 and x^1 is about 1 to 100, preferably 1 to 25 with ethylene glycol and diethylene glycol particularly preferred. A preferred embodiment is formation of the ester with about 1 to 2 moles of glycol per mole of dimer acid or polycarboxylic acid, such as the ester of diethylene glycol with dimerized linoleic acid. Illustrative of such esters are compounds of the formula (XVI):

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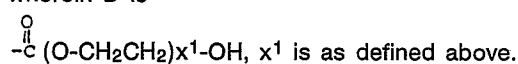


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wherein D is



The preparation and use of the foregoing polycarboxylic acid glycol esters as friction reducing esters (viz., friction modifiers) is disclosed in U.S. Patent 4,505,829, the disclosure of which is hereby incorporated by reference in its entirety.

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METAL DETERGENT COMPONENT D

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The lubricating oil metal detergent additives are also frequently referred to as rust inhibitors and include the metal salts of sulphonic acids, alkyl phenols, sulphurized alkyl phenols, alkyl salicylates, naphthenates, and other oil soluble mono- and di-carboxylic acids. Highly basic, that is overbased metal salts, are frequently used as detergents and appear particularly prone to interaction with the ashless dispersant. Usually these metal

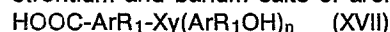
containing rust inhibitors and detergents are used in lubricating oil in amounts of about 0.01 to 10, e.g. 0.1 to 5 wt. %, based on the weight of the total lubricating composition. Marine diesel lubricating oils typically employ such metal-containing rust inhibitors and detergents in amounts of up to about 20 wt.%.
Highly basic alkaline earth metal sulfonates are frequently used as detergents. They are usually produced by heating a mixture comprising an oil-soluble sulfonate or alkaryl sulfonic acid, with an excess of alkaline earth metal compound above that required for complete neutralization of any sulfonic acid present and thereafter forming a dispersed carbonate complex by reacting the excess metal with carbon dioxide to provide the desired overbasing. The sulfonic acids are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum by distillation and/or extraction or by the alkylation of aromatic hydrocarbons as for example those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl and the 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 30 carbon atoms. For example haloparaffins, olefins obtained by dehydrogenation of paraffins, polyolefins produced from ethylene, propylene, etc. are all suitable. The alkaryl sulfonates usually contain from about 9 to about 70 or more carbon atoms, preferably from about 16 to about 50 carbon atoms per alkyl substituted aromatic moiety.

The alkaline earth metal compounds which may be used in neutralizing these alkaryl sulfonic acids to provide the sulfonates includes the oxides and hydroxides, alkoxides, carbonates, carboxylate, sulfide, hydrosulfide, nitrate, borates and ethers of magnesium, calcium, and barium. Examples are calcium oxide, calcium hydroxide, magnesium acetate and magnesium borate. As noted, the alkaline earth metal compound is used in excess of that required to complete neutralization of the alkaryl sulfonic acids. Generally, the amount ranges from about 100 to 220%, although it is preferred to use at least 125%, of the stoichiometric amount of metal required for complete neutralization.

Various other preparations of basic alkaline earth metal alkaryl sulfonates are known, such as U.S. Patents 3,150,088 and 3,150,089 wherein overbasing is accomplished by hydrolysis of an alkoxide-carbonate complex with the alkaryl sulfonate in a hydrocarbon solvent-diluent oil.

A preferred alkaline earth sulfonate additive is magnesium alkyl aromatic sulfonate having a total base number ASTM D2896 ranging from about 300 to about 400 with the magnesium sulfonate content ranging from about 25 to about 32 wt. %, based upon the total weight of the additive system dispersed in mineral lubricating oil.

Neutral metal sulfonates are frequently used as rust inhibitors. Polyvalent metal alkyl salicylate and naphthenate materials are known additives for lubricating oil compositions to improve their high temperature performance and to counteract deposition of carbonaceous matter on pistons (U.S. Patent 2,744,069). An increase in reserve basicity of the polyvalent metal alkyl salicylates and naphthenates can be realized by utilizing alkaline earth metal, e.g. calcium, salts of mixtures of C₈-C₂₆ alkyl salicylates and phenates (see U.S. Patent 2,744,069) or polyvalent metal salts of alkyl salicyclic acids, said acids obtained from the alkylation of phenols followed by phenation, carboxylation and hydrolysis (U.S. Patent 3,704,315) which could then be converted into highly basic salts by techniques generally known and used for such conversion. The reserve basicity of these metal-containing rust inhibitors is usefully at TBN levels of between about 60 and 150. Included with the useful polyvalent metal salicylate and naphthenate materials are the methylene and sulfur bridged materials which are readily derived from alkyl substituted salicylic or naphthenic acids or mixtures of either or both with alkyl substituted phenols. Basic sulfurized salicylates and a method for their preparation is shown in U.S. Patent 3,595,791. Such materials include alkaline earth metal, particularly magnesium, calcium, strontium and barium salts of aromatic acids having the general formula:



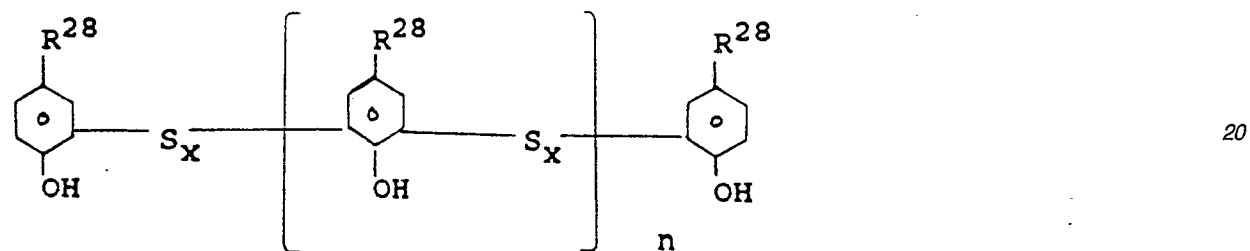
where Ar is an aryl radical of 1 to 6 rings, R₁ is an alkyl group having from about 8 to 50 carbon atoms, preferably 12 to 30 carbon atoms (optimally about 12), X is a sulfur (-S-) or methylene (-CH₂-) bridge, y is a number from 0 to 4 and n is a number from 0 to 4.

Preparation of the overbased methylene bridged salicylate-phenate salt is readily carried out by conventional techniques such as by alkylation of a phenol followed by phenation, carboxylation, hydrolysis, methylene bridging a coupling agent such as an alkylene dihalide followed by salt formation concurrent with carbonation. An overbased calcium salt of a methylene bridged phenol-salicylic acid of the general formula (XVIII):



with a TBN of 60 to 150 is highly useful in this invention.

The sulfurized metal phenates can be considered the "metal salt of a phenol sulfide" which thus refers to a metal salt whether neutral or basic, of a compound typified by the general formula (XIX):



where $x = 1$ or 2 , $n = 0, 1$ or 2 ; or a polymeric form of such a compound, where R^{28} is an alkyl radical, n and x are each integers from 1 to 4 , and the average number of carbon atoms in all of the R^{28} groups is at least about 9 in order to ensure adequate solubility in oil. The individual R^{28} groups may each contain from 5 to 40 , preferably 8 to 20 , carbon atoms. The metal salt is prepared by reacting an alkyl phenol sulfide with a sufficient quantity of metal containing material to impart the desired alkalinity to the sulfurized metal phenate.

Regardless of the manner in which they are prepared, the sulfurized alkyl phenols which are useful generally contain from about 2 to about 14% by weight, preferably about 4 to about 12 wt. % sulfur based on the weight of sulfurized alkyl phenol.

The sulfurized alkyl phenol may be converted by reaction with a metal containing material including oxides, hydroxides and complexes in an amount sufficient to neutralize said phenol and, if desired, to overbase the product to a desired alkalinity by procedures well known in the art. Preferred is a process of neutralization utilizing a solution of metal in a glycol ether.

The lubricating oil additive mixtures of the present invention can be incorporated into a lubricating oil in any convenient way. Thus, these mixtures can be added directly to the oil by dispersing or dissolving the same in the oil at the desired level of concentrations of the ashless dispersant, demulsifier, compatibility additive, and metal detergent (where employed), respectively. Such blending into the additional lube oil can occur at room temperature or elevated temperatures. Alternatively, the ashless dispersant, demulsifier, compatibility additive, and metal detergent (where employed) can be blended with a suitable oil-soluble solvent or base oil to form a concentrate, and which can then be blended with a lubricating oil basestock to obtain the final formulation. Such concentrates will typically contain (on an active ingredient (A.I.) basis) from about 3 to about 45 wt. %, and preferably from about 10 to about 35 wt. %, ashless dispersant additive A; typically from about 0.01 to 3 wt.%, and preferably from about 0.05 to 0.3 wt.% demulsifier additive B; (where present) typically from about 0.0005 to 2 wt.%, preferably from about 0.001 to 0.25 wt.%, and most preferably from about 0.005 to 0.1 wt.% compatibility additive C; (where present) typically from about 2 to 45 wt.%, and preferably from about 2 to 14 wt.%, metal detergent D; and typically from about 30 to 90 wt. %, preferably from about 40 to 60 wt. %, base oil, based on the concentrate weight.

Additive packages of this invention comprising ashless dispersant, metal detergent, demulsifier and compatibility additive (alone or together with other lubricating oil additives as discussed below, e.g., antiwear additives, corrosion inhibitors, antioxidants, etc.) are preferably prepared in the following manner. The ashless dispersant and metal detergent components (in the selected baseoil or solvent) are preferably first blended together at elevated temperature (e.g., from 70 to 130°C) for a time and under stirring sufficient to intimately contact these components, followed by cooling of the dispersant/detergent mixture to 65°C or below, as disclosed in co-pending EP-A-0294-096. The selected demulsifier and compatibility additive are separately admixed in the selected baseoil or solvent for a time and under conditions sufficient to intimately contact these components (e.g., from 50 to 130°C , for 1 to 5 hours, with stirring), and then introduced as a mixture to the dispersant/detergent mixture, e.g., at 50 to 130°C with stirring to provide intimate blending, for 1 to 5 hours. The remaining lubricating oil additives can be added (separately or simultaneously) prior to, during or after the mixing of the dispersant/detergent mixture with the demulsifier/compatibility additive mixture.

The lubricating oil basestock for the lubricating oil mixture typically is adapted to perform a selected function by the incorporation of additional additives therein to form lubricating oil compositions (i.e., formulations).

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LUBRICATING COMPOSITIONS

The additive mixtures of the present invention possess very good demulsified properties as measured herein in a wide variety of environments. Accordingly, the additive mixtures are used by incorporation and dissolution into an oleaginous material such as fuels and lubricating oils. When the additive mixtures of this invention are used in normally liquid petroleum fuels such as middle distillates boiling from about 65° to 430° C, including kerosene, diesel fuels, home heating fuel oil, jet fuels, etc., a concentration of the additives in the fuel in the range of typically from about 0.001 to about 0.5, and preferably 0.005 to about 0.15 weight percent, based on the total weight of the composition, will usually be employed.

The additive mixtures of the present invention find their primary utility in lubricating oil compositions which employ a base oil in which the additives are dissolved or dispersed. Such base oils may be natural or synthetic. Base oils suitable for use in preparing the lubricating oil compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Advantageous results are also achieved by employing the additive mixtures of the present invention in base oils conventionally employed in and/or adapted for use as power transmitting fluids such as automatic transmission fluids, tractor fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil compositions can also benefit from the incorporation therein of the additive mixtures of the present invention.

These lubricating oil formulations conventionally contain several different types of additives that will supply the characteristics that are required in the formulations. Among these types of additives are included viscosity index improvers, antioxidants, corrosion inhibitors, detergents, dispersants, pour point depressants, antiwear agents, friction modifiers, etc.

In the preparation of lubricating oil formulations it is common practice to introduce the additives in the form of 10 to 80 wt. %, e.g., 20 to 80 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent. Usually these concentrates may be diluted with 3 to 100, e.g. 5 to 40 parts by weight of lubricating oil, per part by weight of the additive package, in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend. Thus, a metal hydrocarbyl sulfonate or a metal alkyl phenate would be usually employed in the form of a 40 to 50 wt. % concentrate, for example, in a lubricating oil fraction.

The ashless dispersant and demulsifier mixtures of the present invention, alone or with compatibilizer and metal detergent (where present), will be generally used in admixture with a lube oil basestock, comprising an oil of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof.

Natural base oils include animal oils and vegetable oils (e.g., castor, lard oil) liquid petroleum oils and hydrotreated, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

Alkylenoxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-poly isopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of poly-ethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricants; they include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butylphenyl)silicate, hexa-(4-methyl-2-pentoxyl)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic

lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and rerefined oils can be used in the lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

The ashless dispersant demulsifier mixtures of the present invention can also be used with V.I. improvers to form multi-grade automobile engine lubricating oil formulations. Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain relatively viscous at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. Viscosity modifiers are generally high molecular weight hydrocarbon polymers including polyesters. The viscosity modifiers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties. These oil soluble viscosity modifying polymers will generally have number average molecular weights of from 10^3 to 10^6 , preferably 10^4 to 10^6 , e.g., 20,000 to 250,000, as determined by gel permeation chromatography or osmometry.

Examples of suitable hydrocarbon polymers include homopolymers and copolymers of two or more monomers of C_2 to C_{30} , e.g. C_2 to C_8 olefins, including both alpha olefins and internal olefins, which may be straight or branched, aliphatic, aromatic, alkyl-aromatic, cycloaliphatic, etc. Frequently they will be of ethylene with C_3 to C_{30} olefins, particularly preferred being the copolymers of ethylene and propylene. Other polymers can be used such as polyisobutylenes, homopolymers and copolymers of C_6 and higher alpha olefins, atactic polypropylene, hydrogenated polymers and copolymers and terpolymers of styrene, e.g. with isoprene and/or butadiene and hydrogenated derivatives thereof. The polymer may be degraded in molecular weight, for example by mastication, extrusion, oxidation or thermal degradation, and it may be oxidized and contain oxygen.

The preferred hydrocarbon polymers are ethylene copolymers containing from 15 to 90 wt. % ethylene, preferably 30 to 80 wt. % of ethylene and 10 to 85 wt. %, preferably 20 to 70 wt. % of one or more C_3 to C_{28} , preferably C_3 to C_{18} , more preferably C_3 to C_8 , alpha-olefins. While not essential, such copolymers preferably have a degree of crystallinity of less than 25 wt. %, as determined by X-ray and differential scanning calorimetry. Copolymers of ethylene and propylene are most preferred. Other alpha-olefins suitable in place of propylene to form the copolymer, or to be used in combination with ethylene and propylene, to form a terpolymer, tetrapolymer, etc., include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, etc.; also branched chain alpha-olefins, such as 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methylpentene-1, 4,4-dimethyl-1-pentene, and 6-methylheptene-1, etc., and mixtures thereof.

Terpolymers, tetrapolymers, etc., of ethylene, said C_3 - C_{28} alpha-olefin, and a non-conjugated diolefin or mixtures of such diolefins may also be used. The amount of the non-conjugated diolefin generally ranges from about 0.5 to 20 mole percent, preferably from about 1 to about 7 mole percent, based on the total amount of ethylene and alpha-olefin present.

The polyester V.I. improvers are generally polymers of esters of ethylenically unsaturated C_3 to C_8 mono- and dicarboxylic acids such as methacrylic and acrylic acids, maleic acid, maleic anhydride, fumaric acid, etc.

Examples of unsaturated esters that may be used include those of aliphatic saturated mono alcohols of at least 1 carbon atom and preferably of from 12 to 20 carbon atoms, such as decyl acrylate, lauryl acrylate, stearyl acrylate, eicosanyl acrylate, docosanyl acrylate, decyl methacrylate, diamyl fumarate, lauryl methacrylate, cetyl methacrylate, stearyl methacrylate, and the like and mixtures thereof.

Other esters include the vinyl alcohol esters of C_2 to C_{22} fatty or mono carboxylic acids, preferably saturated such as vinyl acetate, vinyl laurate, vinyl palmitate, vinyl stearate, vinyl oleate, and the like and mixtures thereof. Copolymers of vinyl alcohol esters with unsaturated acid esters such as the copolymer of vinyl acetate with dialkyl fumarates, can also be used.

The esters may be copolymerized with still other unsaturated monomers such as olefins, e.g. 0.2 to 5 moles of C_2 - C_{20} aliphatic or aromatic olefin per mole of unsaturated ester, or per mole of unsaturated acid or anhydride followed by esterification. For example, copolymers of styrene with maleic anhydride esterified with alcohols and amines are known, e.g., see U.S. Patent 3,702,300.

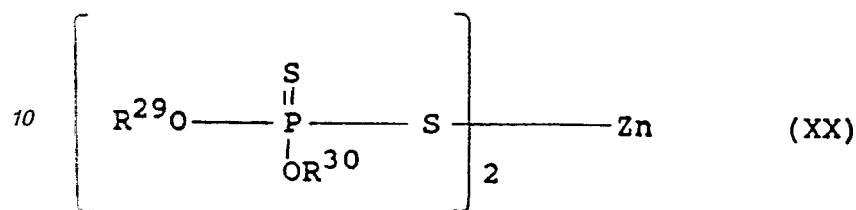
Dihydrocarbyl dithiophosphate metal salts are frequently used as anti-wear agents and also provide antioxidant activity. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 wt. %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dithiophosphoric acid, usually by reaction of an alcohol or a phenol with P_2S_5 and then neutralizing the dithiophosphoric acid with a suitable zinc compound.

Mixtures of alcohols may be used including mixtures of primary and secondary alcohols, secondary generally for imparting improved anti-wear properties, with primary giving improved thermal stability properties. Mixtures of the two are particularly useful. In general, 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 neutralization reaction.

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

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wherein R^{29} and R^{30} 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, aralkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R^{29} and R^{30} 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 etc. In order to obtain oil solubility, the total number of carbon atoms (i.e. R^{29} and R^{30} in formula XX) in the dithiophosphoric acid will generally be about 5 or greater.

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The antioxidants useful in this invention include copper compounds. A copper compound may be blended into the oil (e.g., an oil soluble copper compound) to provide copper in an oil-solubilized form. By oil soluble we mean the compound is oil soluble under normal blending conditions in the oil or additive package. The copper compound may be in the cuprous or cupric form. The copper may be in the form of the copper dihydrocarbyl thio- or dithio-phosphates wherein copper may be substituted for zinc in the compounds and reactions described above although one mole of cuprous or cupric oxide may be reacted with one or two moles of the dithiophosphoric acid, respectively. Alternatively the copper may be added as the copper salt of a synthetic or natural carboxylic acid. Examples include C_{10} to C_{18} fatty acids such as stearic or palmitic, but unsaturated acids such as oleic or branched carboxylic acids such as naphthenic acids of molecular weight from 200 to 500 or synthetic carboxylic acids are preferred because of the improved handling and solubility properties of the resulting copper carboxylates. Also useful are oil soluble copper dithiocarbamates of the general formula $(\text{R}^{31}\text{R}^{32}\text{NCSS})_n\text{Cu}$, where n is 1 or 2 and R^{31} and R^{32} are the same or different hydrocarbyl radicals containing from 1 to 18 and preferably 2 to 12 carbon atoms and including radicals such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R^{31} and R^{32} 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-heptyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl, etc. In order to obtain oil solubility, the total number of carbon atoms (i.e. R^{31} and R^{32}) will generally be about 5 or greater. Copper sulphonates, phenates, and acetylacetonates may also be used.

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Exemplary of useful copper compounds are copper (Cu^I and/or Cu^{II}) salts of alkenyl succinic acids or anhydrides. The salts themselves may be basic, neutral or acidic. They may be formed by reacting (a) any of the materials discussed above in the Ashless Dispersant section, which have at least one free carboxylic acid (or anhydride) group with (b) a reactive metal compound. Suitable acid (or anhydride) reactive metal compounds include those such as cupric or cuprous hydroxides, oxides, acetates, borates, and carbonates or basic copper carbonate.

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Examples of the metal salts of this invention are Cu salts of polyisobutenyl succinic anhydride (hereinafter referred to as Cu-PIBSA), and Cu salts of polyisobutenyl succinic acid. Preferably, the selected metal employed is its divalent form, e.g., Cu^{+2} . The preferred substrates are polyalkenyl succinic acids in which the alkenyl group has a molecular weight greater than about 700. The alkenyl group desirably has a $\bar{M}_n$ from about 900 to 1400, and up to 2500, with a $\bar{M}_n$ of about 950 being most preferred. Especially preferred, of those listed above in the section on Dispersants, is polyisobutylene succinic acid (PIBSA). These materials may desirably be dissolved in a solvent, such as a mineral oil, and heated in the presence of a water solution (or slurry) of the metal bearing material. Heating may take place between 70° and about 200°C . Temperatures of 100° to 140°C are entirely adequate. It may be necessary, depending upon the salt produced, not to allow the reaction to remain at a temperature above about 140°C for an extended period of time, e.g., longer than 5 hours, or decomposition of the salt may occur.

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The copper antioxidants (e.g., Cu-PIBSA, Cu-oleate, or mixtures thereof) will be generally employed in an amount of from about 50-500 ppm by weight of the metal, in the final lubricating or fuel composition.

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The copper antioxidants used in this invention are inexpensive and are effective at low concentrations and therefore do not add substantially to the cost of the product. The results obtained are frequently better than those obtained with previously used antioxidants, which are expensive and used in higher concentrations. In the amounts employed, the copper compounds do not interfere with the performance of other components of the lubricating composition, in many instances, completely satisfactory results are obtained when the copper

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compound is the sole antioxidant in addition to the ZDDP. The copper compounds can be utilized to replace part or all of the need for supplementary antioxidants. Thus, for particularly severe conditions it may be desirable to include a supplementary conventional antioxidant. However, the amounts of supplementary antioxidant required are small, far less than the amount required in the absence of the copper compound.

While any effective amount of the copper antioxidant can be incorporated into the lubricating oil composition, it is contemplated that such effective amounts be sufficient to provide said lube oil composition with an amount of the copper antioxidant of from about 5 to 500 (more preferably 10 to 200, still more preferably 10 to 180, and most preferably 20 to 130 (e.g., 90 to 120)) part per million of added copper based on the weight of the lubricating oil composition. Of course, the preferred amount may depend amongst other factors on the quality of the basestock lubricating oil.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C₂ to C₆ olefin polymer such as polyisobutylene, with from 5 to 30 weight percent of a sulfide of phosphorus for 1/2 to 15 hours, at a temperature in the range of 65° to 315°C. Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner taught in U.S. Patent No. 1,969,324.

Oxidation inhibitors 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 alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, barium t-octylphenyl sulfide, dioctylphenylamine, phenylalphanaphthylamine, phosphosulfurized or sulfurized hydrocarbons, etc.

Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions such as automatic transmission fluids.

Representative examples of suitable friction modifiers are found in U.S. Patent No. 3,933,659 which discloses fatty acid esters and amides; U.S. Patent No. 4,176,074 which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; U.S. Patent No. 4,105,571 which discloses glycerol esters of dimerized fatty acids; U.S. Patent No. 3,779,928 which discloses alkane phosphonic acid salts; U.S. Patent No. 3,778,375 which discloses reaction products of a phosphonate with an oleamide; U.S. Patent No. 3,852,205 which discloses S-carboxy-alkylene hydrocarbyl succinimide, S-carboxy-alkylene hydrocarbyl succinamic acid and mixtures thereof; U.S. Patent No. 3,879,306 which discloses N-(hydroxyalkyl) alkenyl-succinamic acids or succinimides; U.S. Patent No. 3,932,290 which discloses reaction products of di-(lower alkyl) phosphites and epoxides; and U.S. Patent No. 4,028,258 which discloses the alkylene oxide adduct of phosphosulfurized N-(hydroxyalkyl) alkenyl succinimides. The disclosures of the above references are herein incorporated by reference. The most preferred friction modifiers are glycerol mono and dioleates, and succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides and thiobis-alkanols such as described in U.S. Patent No. 4,344,853.

Pour point depressants lower the temperature at which the fluid will flow or can be poured. Such depressants are well known. Typical of those additives which usefully optimize the low temperature fluidity of the fluid are C₈-C₁₈ dialkylfumarate vinyl acetate copolymers, polymethacrylates, and wax naphthalene.

Foam control can be provided by an antifoamant of the polysiloxane type, e.g. silicone oil and polydimethyl siloxane.

Organic, oil-soluble compounds useful as rust inhibitors in this invention comprise nonionic surfactants such as polyoxyalkylene polyols and esters thereof, and anionic surfactants such as salts of alkyl sulfonic acids. Such anti-rust compounds are known and can be made by conventional means. Nonionic surfactants, useful as anti-rust additives in the oleaginous compositions of this invention, usually owe their surfactant properties to a number of weak stabilizing groups such as ether linkages. Nonionic anti-rust agents containing ether linkages can be made by alkoxylating organic substrates containing active hydrogens with an excess of the lower alkylene oxides (such as ethylene and propylene oxides) until the desired number of alkoxy groups have been placed in the molecule.

The preferred rust inhibitors are polyoxyalkylene polyols and derivatives thereof. This class of materials are commercially available from various sources: Pluronic Polyols from Wyandotte Chemicals Corporation; Polyglycol 112-2, a liquid triol derived from ethylene oxide and propylene oxide available from Dow Chemical Co.; and Tergitol, dodecylphenyl or monophenyl polyethylene glycol ethers, and Ucon, polyalkylene glycols and derivatives, both available from Union Carbide Corp. These are but a few of the commercial products suitable as rust inhibitors in the improved composition of the present invention.

In addition to the polyols per se, the esters thereof obtained by reacting the polyols with various carboxylic acids are also suitable. Acids useful in preparing these esters are lauric acid, stearic acid, succinic acid, and alkyl- or alkenyl-substituted succinic acids wherein the alkyl- or alkenyl group contains up to about twenty carbon atoms.

The preferred polyols are prepared as block polymers. Thus, a hydroxy-substituted compound, Q-(OH)_n (wherein n is 1 to 6, and Q is the residue of a mono- or polyhydric alcohol, phenol, naphthol, etc.) is reacted with propylene oxide to form a hydrophobic base. This base is then reacted with ethylene oxide to provide a

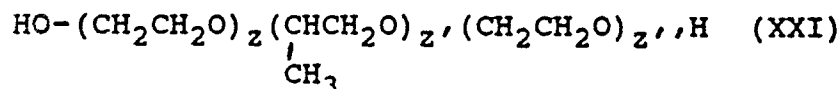
hydrophilic portion resulting in a molecule having both hydrophobic and hydrophilic portions. The relative sizes of these portions can be adjusted by regulating the ratio of reactants, time of reaction, etc., as is obvious to those skilled in the art. Thus it is within the skill of the art to prepare polyols whose molecules are characterized by hydrophobic and hydrophilic moieties which are present in a ratio rendering rust inhibitors suitable for use

in any lubricant composition regardless of differences in the base oils and the presence of other additives. If more oil-solubility is needed in a given lubricating composition, the hydrophobic portion can be increased and/or the hydrophilic portion decreased. If greater oil-in-water emulsion breaking ability is required, the hydrophilic and/or hydrophobic portions can be adjusted to accomplish this.

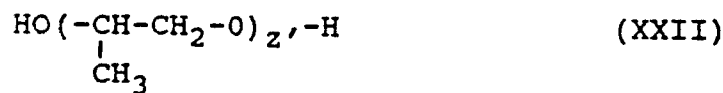
Compounds illustrative of $Q-(OH)_n$ include alkylene polyols such as the alkylene glycols, alkylene triols, alkylene tetrols, etc., such as ethylene glycol, propylene glycol, glycerol, pentaerythritol, sorbitol, mannitol, and the like. Aromatic hydroxy compounds such as alkylated mono- and polyhydric phenols and naphthols can also be used, e.g., heptylphenol, dodecylphenol, etc.

Other suitable demulsifiers include the esters disclosed in U.S. Patents 3,098,827 and 2,674,619.

The liquid polyols available from Wyandotte Chemical Co. under the name Pluronic Polyols and other similar polyols are particularly well suited as rust inhibitors. These Pluronic Polyols correspond to the formula:



wherein z , z' and z'' are integers greater than 1 such that the $-CH_2CH_2O-$ groups comprise from about 10% to about 40% by weight of the total molecular weight of the glycol, the average molecule weight of said glycol being from about 1000 to about 5000. These products are prepared by first condensing propylene oxide with propylene glycol to produce the hydrophobic base



This condensation product is then treated with ethylene oxide to add hydrophilic portions to both ends of the molecule. For best results, the ethylene oxide units should comprise from about 10 to about 40% by weight of the molecule. Those products wherein the molecular weight of the polyol is from about 2500 to 4500 and the ethylene oxide units comprise from about 10% to about 15% by weight of the molecule are particularly suitable. The polyols having a molecular weight of about 4000 with about 10% attributable to (CH_2CH_2O) units are particularly good. Also useful are alkoxyated fatty amines, amides, alcohols and the like, including such alkoxyated fatty acid derivatives treated with C_9 to C_{16} alkyl-substituted phenols (such as the mono- and di-heptyl, octyl, nonyl, decyl, undecyl, dodecyl and tridecyl phenols), as described in U.S. Patent 3,849,501, which is also hereby incorporated by reference in its entirety.

These compositions of our invention may also contain other additives such as those previously described, and other metal containing additives, for example, those containing barium and sodium.

The lubricating composition of the present invention may also include copper lead bearing corrosion inhibitors. Typically such compounds are the thiadiazole polysulphides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Preferred materials are the derivatives of 1,3,4 thiadiazoles such as those described in U.S. Patents 2,719,125; 2,719,126; and 3,087,932; especially preferred is the compound 2,5 bis (t-octadithio)-1,3,4 thiadiazole commercially available as Amoco 150. Other similar materials also suitable are described in U.S. Patents 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882.

Other suitable additives are the thio and polythio sulphenamides of thiadiazoles such as those described in U.S. Patent Specification 1,560,830. When these compounds are included in the lubricating composition, we prefer that they be present in an amount from 0.01 to 10, preferably 0.1 to 5.0 weight percent based on the weight of the composition.

Some of these numerous additives can provide a multiplicity of effects, e.g., a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

Compositions when containing these conventional additives are typically blended into the base oil in amounts effective to provide their normal attendant function. Representative effective amounts of such additives (as the respective active ingredients) in the fully formulated oil are illustrated as follows:

<u>Compositions</u>	<u>Wt.% A.I.</u> <u>(Preferred)</u>	<u>Wt.% A.I.</u> <u>(Broad)</u>	
Ashless Dispersant (Component A)	0.1- 8	0.1-20	5
Polymeric Viscosity Index Improver (Component A)	0.01-2	0.001-10	10
Demulsifier (Component B)	0.001-0.03	0.001-0.3	15
Compatibilizer (Component C)	0.001-0.25	0.0005-2	
Metal Detergents (Component D)	0.01-3	0.01-20	20
Viscosity Modifier	0.01-4	0.01-12	
Corrosion Inhibitor	0.01-1.5	0.01-5	25
Oxidation Inhibitor	0.01-1.5	0.01-5	
Pour Point Depressant	0.01-1.5	0.01-5	30
Anti-Foaming Agents	0.001-0.15	0.001-3	
Anti-Wear Agents	0.001-1.5	0.001-5	35
Friction Modifiers	0.01-1.5	0.01-5	
Mineral Oil Base	Balance	Balance	40

When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the novel ashless dispersant/demulsifier mixtures of this invention (in concentrate amounts hereinabove described), together with one or more of said other additives (including metal detergent, compatibilizer, etc.) (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition or formulation. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the mixtures of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from about 2.5 to about 90%, and preferably from about 15 to about 75%, and most preferably from about 25 to about 60% by weight additives in the appropriate proportions with the remainder being base oil.

The final formulations may employ typically about 10 wt. % of the additive-package with the remainder being base oil.

All of said weight percents expressed herein (unless otherwise indicated) are based on active ingredient (A.I.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the A.I. weight of each additive plus the weight of total oil or diluent.

This invention will be further understood by reference to the following examples, wherein all parts are parts by weight, unless otherwise noted and which include preferred embodiments of the invention.

EXAMPLES

A series of test lubricating oil formulations are prepared containing ashless dispersant, metal detergent, viscosity modifier and the demulsifiers of this invention, or other test materials, identified in Tables I and II

below. To measure the crankcase pressure generated, the indicated compositions were tested in a shortened version of the Sequence IID test (referred to as the IID Screener) in which the ASTM Sequence IID procedure is followed for 12 hours using an Oldsmobile V8 engine which is not rebuilt but is instead carefully flushed between runs. Crankcase pressure is monitored for the 12 hours to produce an integrated (cumulative) crankcase pressure value. The data thereby obtained are summarized in Table III. This test can thus be used to predict tendency of lubricants to form emulsions and generate crankcase pressure in the Sequence IID.

Table 1

Formulations

	<u>Component</u>	<u>(Wt. % a.i.)</u>
	Ashless dispersant ⁽¹⁾	3.0
	Metal detergent ⁽²⁾	0.74
15	Demulsifier	(See Table III)
	Base oil ⁽³⁾	Balance
	Notes:	
20	(1) Borated polyisobutenyl (PIB $\overline{M}_n = 2200$) succinimide of polyethylene polyamine.	
	(2) Overbased magnesium sulfonate detergent, TBN=400.	
25	(3) Solvent (about 130) Neutral mineral baseoil, also containing copper antioxidant, zinc dialkyl dithiophosphate antiwear agent, and ethylene-propylene copolymer viscosity index improver.	

Table II
Demulsifier

Example No.	Demulsi- fier(1)	EO:PO Wt. Ratio(2)	Alkylene Oxide:Ad- duct Wt.Ratio(- 3)
1	Propoxy- lated adduct of polypro- pylene glycol and diglycidyl ether of bis-phenol A	0:100	3:1
2	Propoxy- lated adduct of polypro- pylene glycol and diglycidyl ether of bis-phenol A	0:100	0.6:1
3	Ethoxy- lated propoxy- lated adduct of polypro- pylene glycol and diglycidyl ether of bis-phenol A	30:70	0.6:1

Notes:

(1) Polypropylene glycol, Average
Mol.Wt. = 5000.

(2) EO = ethylene oxide; PO = propylene oxide;
wt. ratio based on ethylene oxide and propylene
oxide reacted with polypropylene glycol/diglycidyl
ether of bis-phenol A adduct ("adduct").

(3) Alkylene oxide:adduct ratio based on weight of
alkylene oxide and adduct charged.

Table III

Example No.	Demulsifier	Demulsifier		Integrated Crankcase Pressure Units
		(Wt.%)	(wppm)	
5	4 Prepared as in Example 1	0.01	100	21.2
10	5 Prepared as in Example 1	0.015	150	5.8
	6 Prepared as in Example 1	0.02	200	6.0
15	7 Prepared as in Example 1	0.05	500	4.0
	8 Prepared as in Example 2	0.02	200	18.3
	9 Prepared as in Example 2	0.05	500	4.7
20	10 Prepared as in Example 2	0.15	1,500	21.0
	11 Prepared as in Example 3	0.05	500	47.2
25	Comp.A Polypropylene glycol ⁽¹⁾	0.015	150	97.3
	Comp.B Polypropylene glycol/diglycidyl ether adduct ⁽²⁾	0.015	150	82.4
30	Comp.C ⁽³⁾ None	-	-	112.4

Notes:

(1) Corresponds to the polypropylene glycol used as feed to Example 1.

(2) Prepared as in Example 1(a).

(3) Composition as in Table I with no added demulsifier.

The pressure data in Table III indicate the surprisingly reduced crankcase pressure resulting from the use of the demulsifiers of this invention in Examples 4-11 as compared to the polypropylene glycol and polypropylene glycol/diglycidyl ether adduct in Comparative Examples A and B, respectively, and as compared to the much higher crankcase pressure generated by the control, non-demulsified control (Comparative Example C). The propoxylated demulsifiers of Examples 1 - 2 provided particularly reduced crankcase pressure, and were superior in this respect to the demulsifier of Example 3 which contained equal weights of oxyalkylene units derived from ethylene oxide and propylene oxide. Comparative B illustrates the criticality to the alkoxylation step in preparing the demulsifiers of this invention.

While not wishing to be bound thereby, it is believed that the alkyoxylation step serves both to chain extend the bis-epoxide/polyhydric alcohol adduct by the addition of oxyalkylene moieties to chain ends of the adduct, and to alkoxyate hydroxy groups in the adduct which are formed by ring opening of the epoxy groups of the bis-epoxide, but some of which are not further reacted during the adduct preparation stage.

EXAMPLES 12-18

In a separate series of tests, additive packages for crankcase lubricating oils were prepared having the following components identified in Table IV. Each additive package was stored at 66°C and observed to determine the onset of any formation of haze, an indication of additive package stability. The data thereby obtained are summarized in Table V below:

Table IV

Additive Concentrates

<u>Component</u>	<u>Wt. % (a.i.)</u>	
Ashless dispersant(1)	26-27	5
Metal detergent(2)	6-7	
Demulsifier	(see Table V)	
Compatibility additive(3)	0, 0.5, 1.0	10
Base oil(4)	Balance	
Notes		
(1) Polyisobutenyl (PIB $\overline{M}_n = 2200$) succinimide of polyethylene polyamine.		15
(2) Overbased Mg sulfonate detergent (TBN=400).		
(3) Diethylene glycol ester of dimer and trimer of linoleic acid.		
(4) Solvent (about 150) neutral mineral oil base oil, also containing copper antioxidant, zinc dialkyldithiophosphate antiwear agent, ethylene propylene copolymer viscosity index improver and supplemental nonylphenol sulfide antioxidant.		20
		25
		30
		35
		40
		45
		50
		55
		60
		65

Table V

<u>Example No.</u>	<u>Demulsifier</u>		<u>Compatibility Additive (wt. 0/0)</u>	<u>Adpack Stability at 66° C</u>	
	<u>Prepared as in Example:</u>	<u>(Wt. 0/0)</u>		<u>No. Days</u>	<u>Appearance</u>
12	2	1	None	5	haze
13	2	1	1.0	96	ok
14	1	1	None	5	haze
15	1	1	1.0	5	slight haze
16	1	0.3	None	33	haze
				4	slight haze
17	1	0.3	0.5	39	haze
18	1	0.3	1.0	95	ok
				95	ok

The data in Table V illustrate the improved additive package stability observed in use of the demulsifiers and compatibility additives of this invention. Substantial improvements in reduced haze were achieved when the propoxylated demulsifier of Example 2, wherein a propylene oxide:adduct weight:weight ratio of 0.6:1 was employed, in combination with a compatibility additive of this invention. Whereas haze was observed after 5 days in Example 12, no haze appeared in the additive package of Example 13 even after 96 days of storage at 66°C. Similar improvements in the haze appearance using the propoxylated demulsifier of Example 1, having a PO:adduct ratio of 3:1, in combination with a compatibility additive of this invention, as may be seen by comparing Example 15 to the additive package of Example 14, wherein a compatibility additive was not employed, and by comparing Examples 17 and 18 (employing varying amounts of the compatibility additive), to the additive package of Example 16.

EXAMPLES 19 -24.

In separate runs, a series of lubricating oil concentrates ("additive packages") are prepared by blending 10 parts of S150N lubricating oil, 55 parts of an ashless dispersant (polyisobutennyl succinimide of a polyethylene polyamine having about 7 carbon atoms and 5 to 6 nitrogen atoms per polyamine molecule) and 11 parts of metal detergent additive (overbased Mg sulfonate, TBN = 400), for 3 hours at a temperature of 100°C. Aliquots of each blend are then taken and are observed to be clear of any visible haze or sediment.

The temperature of each blend is cooled to 75°C, and then the following additional components are introduced, with the indicated components being used in the same concentrations in each blend: zinc dialkyl dithiophosphate antiwear agent, nonyl phenol sulfide oxidation inhibitor, and copper antioxidant, to form a partial adpack (95.3 parts).

Into each partial adpack (at 75°C) is introduced the selected amount of demulsifier and compatibility additives of this invention, together with sufficient lubricating oil to make up the balance of 100 parts of the weight of the lubricating oil concentrate. The order of mixing these additional components is varied as follows:

Method A.

The additional required baseoil, the demulsifier of Example 1 and indicated compatibility additives are introduced into the partial adpack separately with stirring for 1.5 hours at 75°C.

Method B-1.

The additional required baseoil, the demulsifier of Example 1 and compatibility additive I are first premixed together at 75°C for 1 hour, and the resulting premix is introduced into the partial adpack with mixing for an additional 1.5 hours at 75°C.

Method B-2.

The additional required baseoil, the demulsifier of Example 1 and compatibility additive II are first premixed together at 75°C for 1 hour, and the resulting premix is introduced into the partial adpack with mixing for an additional 1.5 hours at 75°C.

Each lubricating oil concentrate is then observed for appearance, and aliquots are stored at either 54 or 66°C for an extended period to observe the appearance and to determine the onset of haze or other indications of instability of the blends. The results thereby obtained are set forth in Table VI below:

TABLE VI

EX. NO.	ADDED BASEOIL (pts)(1)	DEMULSI- FIER(2) (pts)	COMPATIBILITY ADDITIVE(3)		MIXING METHOD	STORAGE STABILITY AT DAY No.:	
			I (pts)	II (pts)		54°C	66°C
19	2.9	0.3	0.5	1.0	A	haze at 61	haze at 47
20	2.4	0.3	1.0	1.0	A	haze at 26	haze at 19
21	1.9	0.3	1.5	1.0	A	haze at 19	haze at 12
22	2.9	0.3	0.5	1.0	B-2	OK at 96	OK at 96
23	1.9	0.3	1.5	1.0	B-2	haze at 26	haze at 26
24	1.9	0.3	1.5	1.0	B-1	haze at 26	haze at 26

NOTES:

(1) S150 N lubricating oil.

(2) As in Example 1: propoxylated adduct of polypropylene glycol and diglycidyl ether of bis-phenol A.

(3) I = glycerol monooleate; II = Diethylene glycol ester of linoleic acid dimer.

The above data illustrate the improved storage stability achieved by the premixing of the demulsifiers and compatibility additives of this invention prior to contacting the demulsifier with the remaining components of the additive package, as compared to the use of equivalent amounts of the demulsifier and compatibility additive without such premixing. The storage stability achieved by the premixing of the demulsifier with the

linoleic acid dimer glycol ester additive in Example 22 (compared to the results achieved in Example 19 without such premixing) is particularly surprising in view of the art's recognition of the instability problems heretofore observed in use of such esters as friction modifiers as discussed above. Increased storage stability also resulted from the premixing of the demulsifier with a higher concentration of the linoleic acid dimer glycol ester additive in Example 23 and by premixing the same higher concentration of the glycerol monooleate additive in Example 24 compared to the results achieved in Example 21 without any such premixing.

The principles, preferred embodiments, and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

Claims

1. An oil soluble mixture useful as an oil additive comprising:

(A) a lubricating oil ashless additive comprising at least one member selected from the group consisting of

(1) ashless dispersants comprising (i) oil soluble salts, amides, imides, oxazolines and esters, or mixtures thereof, of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; (ii) long chain aliphatic hydrocarbon having a polyamine attached directly thereto; and (iii) Mannich condensation products formed by condensing about a molar proportion of long chain hydrocarbon substituted phenol with about 1 to 2.5 moles of formaldehyde and about 0.5 to 2 moles of polyalkylene polyamine; wherein said long chain hydrocarbon group in (i), (ii) or (iii) is a polymer of a C₂ to C₁₀, e.g., C₂ to C₅, monoolefin, said polymer having a number average molecular weight of at least about 900;

(2) polymeric viscosity index improvers dispersants include: (i) polymers comprised of C₄ to C₂₄ unsaturated esters of vinyl alcohol or C₃ to C₁₀ unsaturated mono- or dicarboxylic acid with unsaturated nitrogen containing monomers having 4 to 20 carbons; (ii) polymers of C₂ to C₂₀ olefin with unsaturated C₃ to C₁₀ mono- or dicarboxylic acid neutralized with amine, hydroxy amine or alcohols; and (iii) polymers of ethylene with a C₃ to C₂₀ olefin further reacted either by grafting C₄ to C₂₀ unsaturated nitrogen containing monomers thereof or by grafting an unsaturated acid onto the polymer backbone and then reacting said carboxylic acid groups with amine, hydroxy amine or alcohol; and mixtures of (A) (1) and (A) (2); and

(B) a demulsifier additive comprising the reaction product of alkylene oxide and an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol.

2. The oil soluble mixture according to claim 1 wherein said bis-epoxide comprises diglycidyl ether of bis-phenol A.

3. The oil soluble mixture according to claim 1 or claim 2 wherein said demulsifier additive comprises a propoxylated derivative of said adduct.

4. The oil soluble mixture according to claim 3 wherein said demulsifier additive comprises from 10 to 80 weight percent of oxyalkylation units derived from said propylene oxide.

5. The oil soluble mixture according to any of claims 1 to 4 wherein said polyhydric alcohol comprises polyoxyalkylene glycol.

6. The oil soluble mixture according to claim 5 wherein said polyoxyalkylene glycol has a number average molecular weight of from 1,000 to 10,000.

7. The oil soluble mixture according to claim 6 wherein said polyoxyalkylene glycol comprises polypropylene glycol.

8. The oil soluble mixture according to claim 7 wherein said polypropylene glycol has a number average molecular weight of from 2,000 to 8,000.

9. The oil soluble mixture according to any of claims 1 to 8 wherein said ashless dispersant comprises the reaction product of (a) a hydrocarbyl substituted C₄ to C₁₀ monounsaturated dicarboxylic acid producing material formed by reacting an olefin polymer of C₂ to C₁₀ monoolefin having a number average molecular weight of at least 900 and a C₄ to C₁₀ monounsaturated acid material, said acid producing material having an average of at least 0.8 dicarboxylic acid producing moieties per molecule of said olefin polymer present in the reaction mixture used to form said acid producing material, and (b) a nucleophilic reactant selected from the group consisting of amines, alcohols, amino-alcohols and mixtures thereof.

10. The oil soluble mixture according to claim 9, wherein said nucleophilic reactant comprises a polyalkylenepolyamine wherein said alkylene groups contain 2 to 40 carbons and said polyalkylenepolyamine contains from 2 to about 9 nitrogen atoms per molecule.

11. The oil soluble mixture according to claim 10, wherein said olefin polymer comprises polyisobutylene having a number average molecular weight of from 1,500 to 3,000, and wherein said monounsaturated acid material comprises maleic anhydride.

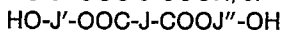
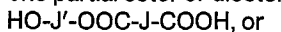
12. The oil soluble mixture according to any of claims 1 to 11, wherein said oil soluble mixture additionally contains at least one metal detergent additive comprising at least one magnesium or calcium salt of a

material selected from the group consisting of sulfonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates and naphthenates.

13. The oil soluble mixture according to any of claims 1 to 12 which additionally contains a compatibilizing effective amount of at least one compatibility additive comprising a glycol ester or hydroxyamide derivative of a mono- or polycarboxylic acid having a total of from 24 to 90 carbon atoms and at least about 1 carboxylic acid group per molecule.

14. The oil soluble mixture according to claim 13 wherein said polycarboxylic acid glycol ester has from 2 to 3 carboxylic acid groups per molecule.

15. The oil soluble mixture according to claim 14 wherein said compatibility additive comprises at least one partial ester or diester of the formulas:



wherein J is the hydrocarbon radical of an aliphatic saturated or unsaturated polycarboxylic acid having a total of from 24 to 90 carbon atoms and from 2 to 3 carboxylic acid groups per molecule with at least 9 carbon atoms between the carboxylic acid groups, J' and J'' are the same or different and each comprises the hydrocarbon radical of an alkane diol or an oxy-alkylene radical.

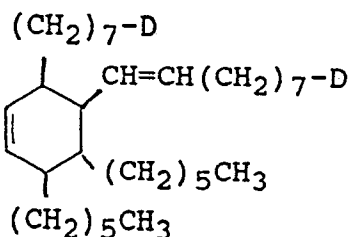
16. The oil soluble mixture according to any of claims 13 to 15 wherein said compatibility additive is employed in an amount of from 0.1 to 5 parts by weight based upon the overall weight of said demulsifier additive in said oil soluble mixture.

17. The oil soluble mixture according to claim 13 wherein said compatibility additive comprises at least one dimer acid ester friction reducing ester.

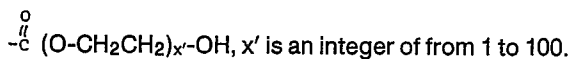
18. The oil soluble mixture according to claim 13 wherein said compatibility additive comprises at least one ester of a substituted cyclohexane dicarboxylic acid formed by a Diels-Alder thermal condensation of C₁₈-C₂₂ unsaturated fatty acids.

19. The oil soluble mixture according to claim 18 wherein said unsaturated fatty acid comprises oleic acid, linoleic acid, or a mixture thereof.

20. The oil soluble mixture according to claim 19 wherein said compatibility additive comprises an ester of the formula:



wherein D is



21. A process for forming a concentrate of improved storage stability useful as an oil additive which comprises: (1) providing a first additive mixture comprising at least one ashless dispersant lubricating oil additive and at least one metal detergent additive; (2) providing a second additive mixture comprising at least one demulsifier additive and at least one compatibility additive; and (3) admixing said first and second additive mixtures to form said concentrate of improved storage stability, wherein:

(A) said ashless dispersant lubricating oil additive comprises at least one member selected from the group consisting of (i) oil soluble salts, amides, imides, oxazolines and esters, or mixtures thereof, of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; (ii) long chain aliphatic hydrocarbon having a polyamide attached directly thereto; and (iii) Mannich condensation products formed by condensing about a molar proportion of long chain hydrocarbon substituted phenol with from 1 to 2.5 moles of formaldehyde and from 0.5 to 2 moles of polyalkylene polyamine; wherein said long chain hydrocarbon group in (i), (ii) or (iii) is a polymer of a C₂ to C₁₀, monoolefin, said polymer having a number average molecular weight of at least 900, said dispersant additive being employed in an amount sufficient to provide a concentration of said dispersant additive of from 3 to 45 wt % in said concentrate;

(B) said demulsifier additive comprises the reaction product of alkylene oxide and an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol, said demulsifier additive being employed in an amount sufficient to provide a concentration of said demulsifier additive of from 0.01 to 3 wt % of in said concentrate;

(C) said compatibility additive comprises a glycol ester or hydroxyamide derivative of a mono- or polycarboxylic acid having a total of from 24 to 90 carbon atoms and at least about 1 carboxylic acid

group per molecule; said compatibility additive being employed in an amount sufficient to provide a concentration of said compatibility additive of from 0.0005 to 2 wt % in said concentrate; and

(D) said metal detergent additive material comprises at least one magnesium or calcium salt of a material selected from the group consisting of sulfonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates and naphthenates, said detergent additive being employed in an amount sufficient to provide a concentration of said detergent additive of from 2 to 45 wt % in said concentrate.

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