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(54) Antioxidants in high monounsaturated vegetable oils.

(57) An antioxidant in high monounsaturated oils is described in order to prepare a composition having utility in hydraulic fluids. The composition comprises :
(A) at least one animal, vegetable or synthetic triglyeride oil,
(B) at least one alkyl phenol, and optionally
(D) a metal deactivator.
In another embodiment, the composition comprises the above (A) and (B) with
(C) at least one aromatic amine, and optionally
(D) as described above.

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Field of the Invention

The present invention relates to an anti-oxidant composition for triglyceride oils that contain at least a 60 percent monounsaturated content. Triglyceride oils containing this anti-oxidant composition have utility in hydraulic fluids, two-cycle (two-stroke) internal combustion engines, gear oils, passenger car motor oils and as a food machinery lubricant.

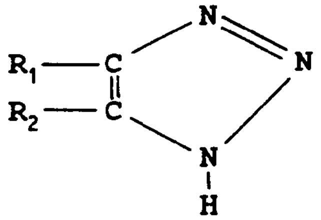
Background of the Invention

Oxidative stability is an important requirement for all lubricants regardless of their use. Auto-oxidative breakdown is strongly catalyzed by traces of metal ions (especially copper and iron) which become solubilized when the lubricant contacts a metal surface. Organic compounds, particularly those comprising relatively long hydrocarbon segments, and particularly those containing unsaturation, are subject to auto-oxidation when they are contacted with oxygen. This, in turn, results in the deterioration of the base material, often leading to increases in the total acidity, formation of gums, discoloration, loss of physical properties such as tensile strength for resins, or elasticity for elastomers, loss of potency, polymerization rancidity and/or odor.

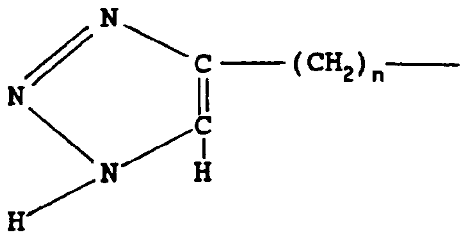
Various additives are in general added to lubricating oils, hydraulic fluids and lubricating greases in order to improve the performance characteristics of these lubricants. There is in particular, a need for additives which effectively reduce oxidation and ageing of the lubricant, and thus considerably extend the life of the lubricant.

US Patent 5,102,567 (Wolf, April 7, 1992) relates to a lubricating oil provided to lubricate parts such as bearings, gears and slide mechanism particularly in food processing equipment. The food grade lubricating oil provides oxidation, thermal and hydrolytic stability; protects against rusting and corrosion; provides wear protection, prevents foaming; and resists the formation of sludge.

US Patent 4,115,288 (Schmitt, September 19, 1978) is directed to a lubricant composition that is comprised of a major amount of a lubricating oil or grease and as an antiwear agent, a minor amount of a substituted 1,2,3-triazole characterized by the formula:



wherein R_1 and R_2 are individually selected from the group consisting of an alkyl group containing from 1 to 18 carbon atoms; an aryl group, such as phenyl; hydrogen; and



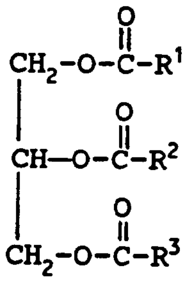
and where at least one of R_1 and R_2 is other than hydrogen and where n is an integer from 5 to 15.

US Patent 4,746,448 (Kenmochi et al, May 24, 1988) provides a cold rolling oil for steels which comprises (A) 40 to 90 wt % of a monoester of an aliphatic carboxylic acid having 12 to 22 carbon atoms and an aliphatic alcohol having 1 to 12 carbon atoms, (B) 0.5 to 10 wt % of at least one of a dimer acid and a polymerized acid of a higher aliphatic unsaturated acid having 16 to 20 carbon atoms, (C) 2 to 40 wt % of a polyester having a molecular weight of 750 to 7500 and (D) 0.1 to 10 wt % of a polymer compound having nitrogen atoms in a molecule having a molecular weight of 1000 to 100,000.

Summary of the Invention

This invention comprises an anti-oxidant composition comprising a major amount of

(A) at least one animal, vegetable or synthetic triglyceride oil of the formula



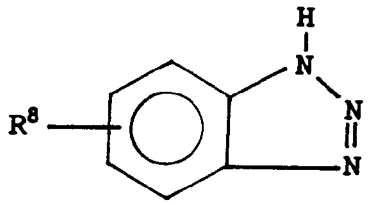
wherein R^1, R^2 and R^3 are aliphatic hydrocarbyl groups having at least 60 percent monounsaturated character and containing from about 8 to about 24 carbon atoms and a minor anti-oxidant amount of

(B) at least one alkyl phenol of the formula

wherein R^4 is an alkyl group containing from 1 up to about 24 carbon atoms and a is an integer of from 1 up to 5, and optionally

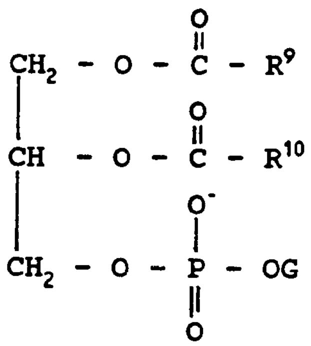
(D) a metal deactivator selected from the group consisting of

(1) a benzotriazole of the formula



wherein R^8 is hydrogen or an alkyl group of 1 up to about 24 carbon atoms,

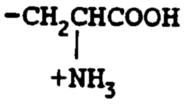
(2) a phosphatide of the formula



wherein R^9 and R^{10} are aliphatic hydrocarbyl groups containing from 8 to about 24 carbon atoms, and G is selected from the group consisting of hydrogen,

$$-CH_2CH_2\overset{+}{N}H_3,\quad -CH_2CH_2\overset{+}{N}(CH_3)_3$$

and



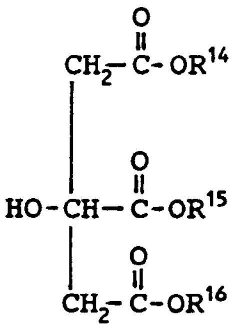
$$-CH_2\underset{\substack{|\\+NH_3}}{C}HCOOH$$

(3) a carbamate of the formula

$$R^{11}\,O\,\overset{\overset{O}{\|}}{C}\,N\,R^{12}\,R^{13}$$

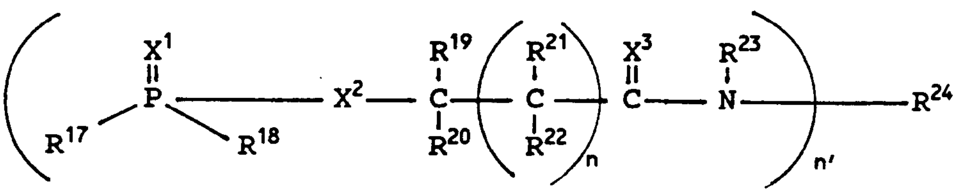
wherein R^{11} is an alkyl group containing from 1 to about 24 carbon atoms, phenyl or alkyl phenyl wherein the alkyl group contains from 1 to about 18 carbon atoms, R^{12} and R^{13} are hydrogen or an alkyl group containing from 1 to about 6 carbon atoms, with the proviso that R^{12} and R^{13} are not both hydrogen,

(4) citric acid and derivatives of citric acid of the formula



wherein R^{14}, R^{15} and R^{16} are independently hydrocarbon aliphatic hydrocarbyl groups containing from 1 to about 12 carbon atoms, with the proviso that at least one of R^{14}, R^{15} and R^{16} is an aliphatic hydrocarbyl group,

(5) a coupled phosphorus-containing amide of the formula



wherein X^1, X^2 and X^3, independently is oxygen or sulfur;

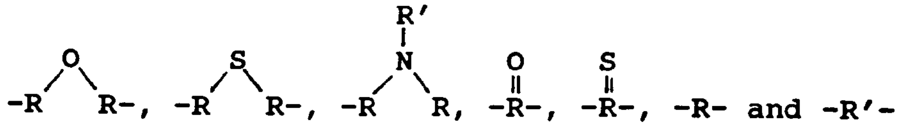
wherein R^{17} and R^{18}, independently is a hydrocarbyl, a hydrocarbyl-based oxy, the hydrocarbyl portions of which contain 6 to about 22 carbon atoms, or a hydrocarbyl-based thio, having from 4 to about 34 carbon atoms;

wherein R^{19} R^{20} R^{21} and R^{22}, independently is hydrogen, or an alkyl having from 1 to about 22 carbon atoms, or an aromatic, an alkyl-substituted aromatic or an aromatic-substituted alkyl having from 6 to about 34 atoms;

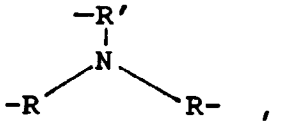
wherein n is zero or 1;

wherein n' is 2 or 3

wherein R^{23} is hydrogen; and when n' is 2, R^{24} is selected from the group consisting of

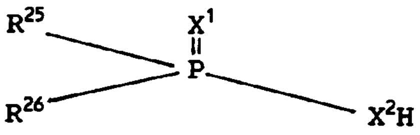


wherein R is an alkyl moiety, in the form of alkylene or alkylidene containing from 1 to 12 carbon atoms and R' is an alkyl moiety, alkylene, alkylidene or carboxyl containing 1 to 60 carbon atoms and when n' is 3, R^{24} is



or

(6) a methylacrylate derivative formed by the reaction of equal molar amounts of a phosphorus acid of the formula



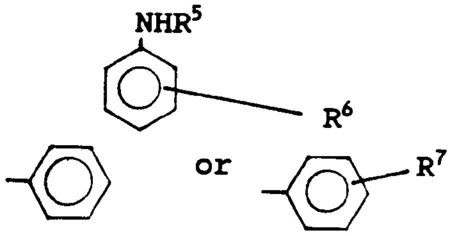
with methylacrylate wherein X^1 and X^2 are as defined above in (D) (5) and R^{25} and R^{26} are each independently a hydrocarbyl, a hydrocarbyl-based thio or preferably a hydrocarbyl-based oxy group wherein the hydrocarbyl portion contains from 1 to about 30 carbon atoms.

In another embodiment, the invention comprises an anti-oxidant composition comprising a major amount of:

(A) The triglyceride oil as described above with a minor anti-oxidant amount of

(B) at least one alkyl phenol as described above,

(C) at least one aromatic amine of the formula wherein R^5 is



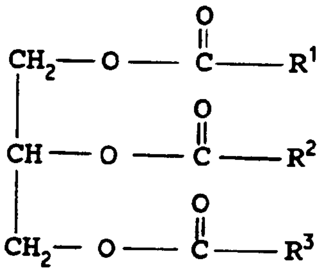
and R^6 and R^7 are independently a hydrogen or an alkyl group containing from 1 up to about 24 carbon atoms and optionally

(D) The metal deactivator as described above.

Various preferred features and embodiments of the present invention will now be described by way of non-limiting example.

(A) The Trialyceride Oil

In practicing this invention a triglyceride oil is employed which is a natural or synthetic oil of the formula



Within the triglyceride formula are aliphatic hydrocarbyl groups having at least 60 percent monounsaturated character and containing from about 8 to about 24 carbon atoms. The term "hydrocarbyl group" as used herein denotes a radical having a carbon atom directly attached to the remainder of the molecule. The aliphatic hydrocarbyl groups include the following:

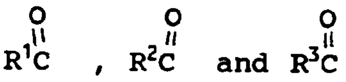
(1) Aliphatic hydrocarbon groups; that is, alkyl groups such as heptyl, nonyl, undecyl, tridecyl, heptadecyl; alkenyl groups containing a single double bond such as heptenyl, nonenyl, undecenyl, tridecenyl, heptadecenyl, heneicosenyl; alkenyl groups containing 2 or 3 double bonds such as 8,11-heptadecadienyl and 8,11,14-heptadecatrienyl. All isomers of these are included, but straight chain groups are preferred.

(2) Substituted aliphatic hydrocarbon groups; that is groups containing non-hydrocarbon substituents which, in the context of this invention, do not alter the predominantly hydrocarbon character of the group. Those skilled in the art will be aware of suitable substituents; examples are hydroxy, carbalkoxy, (especially lower carbalkoxy) and alkoxy (especially lower alkoxy), the term, "lower" denoting groups containing not more than 7 carbon atoms.

(3) Hetero groups; that is, groups which, while having predominantly aliphatic hydrocarbon character within the context of this invention, contain atoms other than carbon present in a chain or ring otherwise composed of aliphatic carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, oxygen and sulfur.

Naturally occurring triglycerides are either vegetable oil triglycerides or animal oil triglycerides. The synthetic triglycerides are those formed by the reaction of one mole of glycerol with three moles of a fatty acid or mixture of fatty acids. Preferred are vegetable oil triglycerides.

Regardless of the source of the triglyceride oil, the fatty acid moieties are such that the triglyceride has a monounsaturated character of at least 60 percent, preferably at least 70 percent and most preferably at least 80 percent. For example, a triglyceride comprised exclusively of an oleic acid moiety has an oleic acid content of 100% and consequently a monounsaturated content of 100%. Where the triglyceride is made up of acid moieties that are 70% oleic acid, 10% stearic acid, 5% palmitic acid, 7% linoleic and 8% hexadecanoic acid, the monounsaturated content is 78%. It is also preferred that the monounsaturated character be derived from an oleyl radical, i.e.,

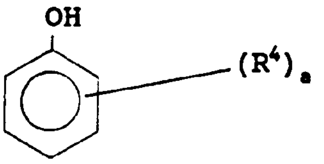


$$R^1\overset{O}{\overset{\|}{C}} \quad , \quad R^2\overset{O}{\overset{\|}{C}} \quad \text{and} \quad R^3\overset{O}{\overset{\|}{C}}$$

is the residue of oleic acid. The preferred triglyceride oils are high oleic (at least 60 percent) acid triglyceride oils. Typical high oleic vegetable oils employed within the instant invention are high oleic safflower oil, high oleic corn oil, high oleic rapeseed oil, high oleic sunflower oil, high oleic soybean oil, high oleic cottonseed oil and high oleic palm olein. A preferred high oleic vegetable oil is high oleic sunflower oil obtained from Helianthus SP available from SVO Enterprises Eastlake, Ohio as Sunyl^R high oleic sunflower oil.

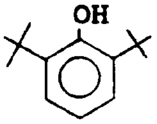
(B) The Alkyl Phenol

Component (B) is at least one alkyl phenol of the formula



wherein R^4 is an alkyl group containing from 1 up to about 24 carbon atoms and a is an integer of from 1 up to 5. Preferably R^4 contains from 4 to 18 carbon atoms and most preferably from 4 to 12 carbon atoms. R^4 may be either straight chained or branched chained and branched chained is preferred. The preferred value for a is an integer of from 1 to 4 and most preferred is from 1 to 3. An especially preferred value for a is 2. When a is not 5, it is preferred that the position para to the OH group be open.

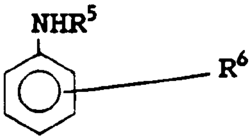
The (B) component is an alkyl phenol, however, mixtures of alkyl phenols may be employed. Preferably the phenol is a butyl substituted phenol containing 2 or 3 t-butyl groups. When a is 2, the t-butyl groups occupy the 2,6-position, that is, the phenol is sterically hindered:



When a is 3, the t-butyl groups occupy the 2,4,6-position.

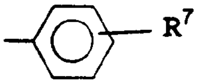
<u>(C) The Aromatic Amine</u>

Component (C) is at least one aromatic amine of the formula

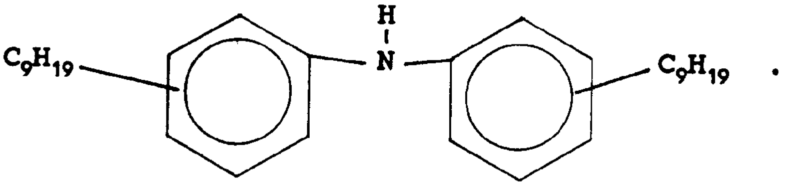


wherein R^5 is

and R^6 and R^7 are independently a hydrogen or an alkyl group containing from 1 up to 24 carbon atoms. Preferably R^5 is



and R^6 and R^7 are alkyl groups containing from 4 up to about 20 carbon atoms. In a particularly advantageous embodiment, component (C) comprises an alkylated diphenylamine such as nonylateddiphenylamine of the formula



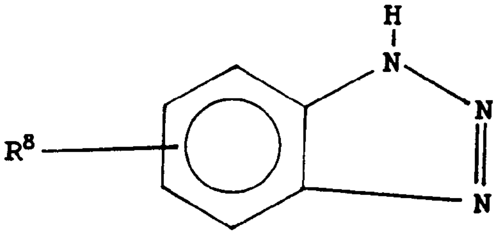
<u>(D) The Optional Metal Deactivator</u>

An optional metal deactivator may be employed wherein the metal deactivator is selected from the group consisting of:

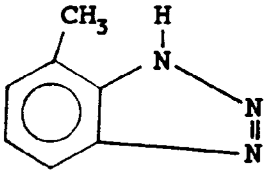
(1) a benzotriazole,
(2) a phosphatide,
(3) a carbamate,
(4) citric acid or its derivatives, or
(5) a coupled phosphorus-containing amide.

(D) (1) The Benzotriazole

A useful metal deactivator is benzotriazole compound of the formula



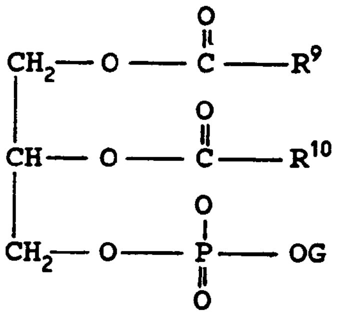
wherein R^8 is hydrogen a straight or branched-chain alkyl group containing from 1 up to about 24 carbon atoms, preferably 1 to 12 carbon atoms and most preferably 1 carbon atom. When R is 1 carbon atom the benzotriazole compound is tolyltriazole of the formula



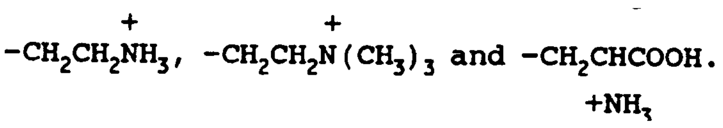
Tolyltriazole is available under the trade name Cobratec TT-100 from Sherwin-Williams Chemical.

(D) (2) The Phosphatide

Another metal deactivator are the phosphatides of the formula



wherein R^9 and R^{10} are aliphatic hydrocarbyl groups containing from 8 to about 24 carbon atoms and G is selected from the group consisting of hydrogen,



$$-CH_2CH_2\overset{+}{N}H_3,\ -CH_2CH_2\overset{+}{N}(CH_3)_3 \text{ and } -CH_2\underset{+NH_3}{CH}CO\overset{-}{O}H.$$

Preferably G is

$$-CH_2CH_2\overset{+}{N}(CH_3)_3$$

such that the phosphatide is lecithin. Particularly effective phosphatides are soybean lecithin, corn lecithin, peanut lecithin, sunflower lecithin, safflower lecithin and rapeseed lecithin.

(D) (3) The Carbamate

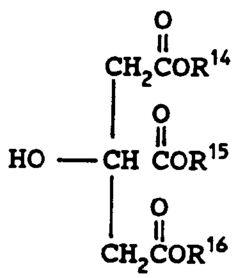
A third useful metal deactivator are the carbamates of the formula

$$R^{11}\ O\ \overset{\overset{\displaystyle O}{\|}}{C}\ N\ R^{12}\ R^{13}$$

wherein R^{11} is an alkyl group containing from 1 to about 24 carbon atoms, phenyl or alkyl phenyl wherein the alkyl group contains from 1 to about 18 carbon atoms. Preferably R^{11} is an alkyl group containing from 1 to 6 carbon atoms. The groups R^{12} and R^{13} are hydrogen or an alkyl group containing from 1 to about 6 carbon atoms, with the proviso that R^{12} and R^{13} are not both hydrogen.

(D) (4) The Citric Acid and its Derivatives

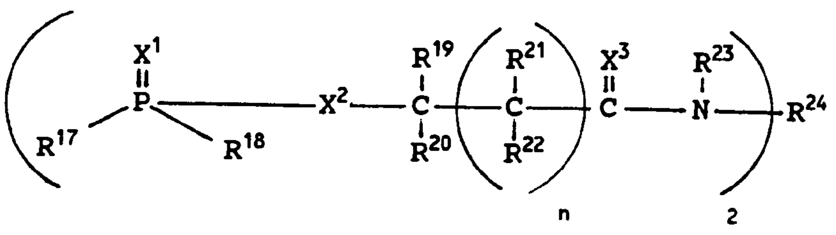
A fourth useful metal deactivator is citric acid or derivatives of citric acid of the formula



wherein R^{14}, R^{15} and R^{16} are independently hydrogen or aliphatic hydrocarbyl groups containing from 1 to about 12 carbon atoms, with the proviso that at least one of R^{14}, R^{15} and R^{16} is an aliphatic hydrocarbyl group and preferably contains from 1 to about 6 carbon atoms.

(D) (5) The Coupled Phosphorus-Containing Amide

The fifth useful metal deactivator is a coupled phosphorus-containing amide that is a statisticalmixture of compounds having the following formula



Considering X^1 and X^2, it independently is oxygen or sulfur and preferably is sulfur whereas X^3 is oxygen or sulfur and preferably oxygen. R^{17} and R^{18} each independently is a hydrocarbyl, a hydrocarbyl-based thio or preferably a hydrocarbyl-based oxy group wherein the hydrocarbyl portion contains 6 to 22 carbon atoms. The hydrocarbyl portion of R^{17} and R^{18} generally contains from 1 to about 34 carbon atoms. When R^{13} is hydrogen and R^{24} is methylene, R^{17} and R^{18} will contain 6 to 12 carbon atoms in order to provide for sufficient oil solubility. The hydrocarbyl portion of R^{17} and R^{18} independently can be alkyl or aromatic. Although the hydrocarbyl portion of both R^{17} and R^{18} can be the same type of hydrocarbyl group, that is both alkyl or both aromatic, often one such group can be alkyl and the remaining group can be aromatic. Different coupled phosphorus-containing amide compounds which are made by reacting a mixture of two or more different reactants each containing an alkyl hydrocarbyl group as well as an aromatic hydrocarbyl (R^{17} and R^{18}) group therein. The same or different compounds are coupled via different coupling groups R^{24} to form a statistical mixture of coupled compounds or are reacted with different compounds to provide different functional groups R^{24} thereon.

The hydrocarbyl group of R^{17} and R^{18} is preferably an alkyl containing from 6 to 22 (more preferably 8-12) carbon atoms. Examples of such groups include hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, octadecyl, behenyl, and the like, including all isomers thereof. Should the R^{17} or R^{18} hydrocarbyl be an aromatic, it can be phenyl or naphthyl. Often times it will have an alkyl substituent thereon. Thus, the alkyl-substituted aromatic can have an alkyl substituent containing from zero, that is phenyl, to about 28 carbon atoms, and preferably from about 7 to about 12 carbon atoms. Whenever a blend of the compounds of coupled phosphorus-containing amide is utilized containing significant or effective amounts of alkyl type R^{17} or R^{18} substituents, the aromatic substituent can contain preferably from about 6 to about 12 carbon atoms in the alkyl group thereof, that is, the alkyl-substituted aromatic. This is because although the solubility of phenyl or low alkyl-substituted aromatics may be somewhat low, the overall solubility in a lubricant composition is generally increased to a desirable level through the utilization of the R^{17} and R^{18} hydrocarbyl portions which are alkyl and/or through the use of R^{23} and/or R^{24} groups which have a large number of carbon atoms therein. The use of lower alkyls, e.g., less than 6 carbon atoms at R^{17} and R^{18} above with a methylene at R^{24} is undesirable with respect to oil solubility.

Considering now the alkyl-substituted aromatic group, the aromatic preferably is phenyl while the alkyl can be the same as set forth hereinabove. Specific examples of such alkyl groups on the aromatic nucleus include methyl, ethyl, propyl, butyl, pentyl, heptyl, octyl, decyl, behenyl, and the like including isomers thereof.

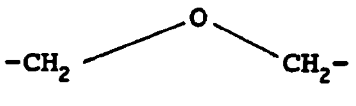
Accordingly, specific examples of mixed hydrocarbyl (R^{17} and R^{18}) portions of substituents include tolyl and octyl, tolyl and hexyl, isobutylphenyl and amyl, phenyl and isooctyl, and the like. Mixed hydrocarbyl (R^{17} and R^{18}) substituents are also assured when cresylic acids are utilized to form the phosphorus portion of the coupled phosphorus-containing amide compound. The sources, type and variety of cresylic acids are known to those skilled in the art. The number of different molecular entities in the mixture is further increased by the different coupling groups, R^{24} as defined above for coupled phosphorus-containing amide when n' is 2 or 3.

When X^1 and X^2 is sulfur and especially when X^2 is sulfur, the alkyl hydrocarbyl substituent (R^{17} or R^{18}) contains 6 or more carbon atoms. However, when X^1 or X^2 is oxygen and especially when X^2 is oxygen, the alkyl hydrocarbyl substituent (R^{17} or R^{18}) is 6 to 12 carbon atoms.

Considering R^{19}, R^{20}, R^{21} and R^{22}, each independently can be hydrogen or a saturated hydrocarbyl having up to 22 carbon atoms. The saturated hydrocarbyl group can be an alkyl having from 1 to 22 carbon atoms, a cycloalkyl having from 4 to 22 carbon atoms, or an aromatic, an aromatic-substituted alkyl or an alkyl-substituted aromatic having from 6 to about 34 carbon atoms. Preferably, R^{19}, R^{20}, R^{21} and R^{22} is hydrogen or methyl with hydrogen being highly preferred. Examples of specific R^{19}, R^{20}, R^{21} and R^{22} alkyl groups include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, etc., as well as isomers thereof whereas examples of specific aromatic groups include phenyl, tolyl, naphthyl, heptylphenyl, nonylphenyl, dodecylphenyl, wax-substituted phenyl, and the like. With regard to the R^{21}-C-R^{22} group, n can be zero or 1. Preferably n is 1.

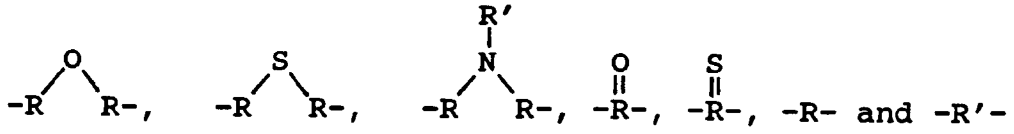
Considering now the amide portion of the molecule, R^{23} is hydrogen or an alkyl having from 1 to 22 carbon atoms with hydrogen being highly preferred. Examples os specific alkyl groups include methyl, ethyl, propyl, butyl, and so forth including the various isomers thereof.

A particularly preferred embodiment of (D) (5) includes a statistical mixture (i.e., coupled and uncoupled compounds each with different substituent groups providing a variety of different compounds) of different phosphorus containing amide compounds bonded to or couple by different R^{24} groups with the proviso that in general coupled phosphorus-containing amide the mixture includes some compounds wherein n' is 1 and R^{24} is -CH_2OH and also where n' is 2, $R2^4$ is

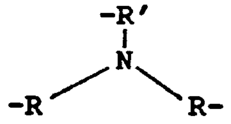


$$-CH_2-O-CH_2-$$

Any such statistical mixture is likely to include some coupled amide compounds of coupled phosphorus-containing amide wherein R^{24} is methylene. When R^{24} is methylene, R^{17} and R^{18} generally must contain more than 6 carbon atoms in order to maintain good oil solubility. When n' is 1, R^{24} is selected from the group consisting of H, -ROH, - ROR, -RSR and $RN(R)_2$ and when n' is 2 or 3, R^{24} is selected from the group consisting of



and when n' is 3, R^{24} is



wherein R is independently hydrogen or an alkyl moiety, alkylene or alkylidene of 1 to 12 carbon atoms and R' is hydrogen or an alkyl or carboxy alkyl moiety, alkylene or alkylidene of containing 1 to 60 carbon atoms, R is preferably methylene and R' is preferably an alkyl moiety of 1 to 28 carbons. When R and R' are linking groups, they may be alkylene and/or alkylidene, i.e., the linkage may be vicinal and/or geminal.

The following illustrate the preparation of the coupled phosphorus-containing compounds. All parts and percentages are by weight unless otherwise indicated.

Example (D)(5)-1

To a mixture of 1775 parts (4.26 equivalents) of O,O-di-isooctyl phosphorodithioic acid and 980 parts of toluene under a nitrogen atmosphere are added 302 parts (4.26 equivalents) of acrylamide. The reaction mixture exotherms to about 56°C and 77 parts (2.33 equivalents) of paraformaldehyde and 215 parts (0.11 equivalent) of p-toluenesulfonic acid hydrate are added. Heating is continued at reflux (92-127°C) while removing 48 parts of water. Upon cooling the mixture to 100°C, 9.2 parts (0.11 equivalent) of sodium bicarbonate is added and cooling continued to about 30°C. A vacuum is applied (15 mm. Hg) and toluene solvent removed while raising the temperature to 110°C. The residue is filtered through a filter aid and the filtrate is the desired product. The product contains 6.86% P (6.74% theory).

Example (D)(5)-2

To a mixture of 1494 parts (3.79 equivalents) of O,O-di-isooctyl phosphorodithioic acid and 800 parts of toluene under a nitrogen atmosphere are added 537 parts (3.79 equivalents) of 50% aqueous acrylamide solution over a period of one hour. The reaction mixture exotherms to about 53°C and 64 parts (1.93 equivalents) of paraformaldehyde and 18 parts (0.095 equivalent) of p-toluenesulfonic acid hydrate are added. Heating is continued at reflux (91-126°C) for 4 hours while collecting 305 parts of water. The mixture is cooled to about 90°C and 7.6 parts (0.095 equivalent) of 50% aqueous sodium hydroxide solution are added. Cooling is continued to about 30°C and a vacuum is applied (15 mm. Hg). Toluene solvent is removed while raising the temperature to 110°C. The residue is filtered through a filter aid and the filtrate is the desired product. The product contains 6.90% P (6.75% theory) and 2.92% N (2.97% theory).

Example (D) (5)-3

To a mixture of 984 parts (1.30 equivalents) of O,O-p-di-dodecylphenyl phosphorodithioic acid and 575 parts of toluene under a nitrogen atmosphere are added 100 parts (0.65 equivalent) of methylenebisacrylamide. The reaction mixture exotherms to about 40°C and is heated at 80-85°C for 2 hours. After cooling the mixture to 30°C, a vacuum (15 mm. Hg) is applied and toluene solvent is removed while raising the temperature to 100°C. The residue is filtered through a filter aid and the filtrate is the desired product. The product contains 4.09% P (4.31% theory).

Example (D) (5)-4

A reaction vessel is charged with 820 parts of toluene and 930 parts (2.32 equivalents) of a O,O-dialkyl phosphorodithioic acid prepared from a mixture of 20 mole percent isobutyl alcohol and 80 mole percent 2-ethylhexyl alcohol. To this mixture under a nitrogen atmosphere are added 178.6 parts (1.16 equivalents) of methylenebisacrylamide. The mixture exotherms to about 65°C and is heated at about 80-85° for 2 hours. Upon cooling to 50°C, a vacuum (30 mm. Hg) is applied. Toluene solvent is removed while raising the temperature to 115°C. The residue is filtered through a filter aid and the filtrate is the desired product. The product contains 7.30% P (7.28% theory).

Example (D)(5)-5

To a mixture of 305 parts of toluene and 611 parts (1.82 equivalents) of a O,O-di-alkyl-substituted phosphorodithioic acid prepared from a mixture of 20 mole percent phenol and 80 mole percent i-octyl alcohol, are added 258 parts (1.82 equivalents) of a 50% aqueous acrylamide solution over a 20-minute period under a nitrogen atmosphere. After an initial exotherm to 60°C, 32.1 parts (0.97 equivalent) of paraformaldehyde and 7.3 parts (0.038 equivalent) of p-toluenesulfonic acid hydrate are added. The mixture is heated at reflux (91-127°C) for 2 hours while removing 131 parts of water. The mixture is cooled to 80°C and 3.1 parts (0.038 equivalent) of 50% aqueous sodium hydroxide solution is added. Cooling is continued to 50°C and a vacuum (30 mm. Hg) is applied. Toluene solvent is removed while raising the temperature to 110°C. The residue is filtered through a filter aid and the filtrate is the desired product. The product contains 7.09% P (7.42% theory).

Example (D) (5)-6

To 1017 parts (3.0 equivalents) of O,O-di-4-methyl-2-pentyl phosphorodithioic acid under nitrogen is added 213 parts (3.0 equivalents) of acrylamide. The reaction exotherms to 65°C and held for one to three hours at 65-75°C. The product is filtered through a filter aid and the filtrate is the desired product. The product contains 7.65% P (7.82% theory), 3.51% N (3.50% theory), and 16.05% S (16.06% theory).

Example (D) (5)-7

To 614 parts (1.5 equivalents) of O,O-di-iso-octyl phosphorodithioic acid under nitrogen is added 213 parts (1.5 equivalents) of a 50% aqueous acrylamide solution. The reaction exotherms to 65°C and held for two hours at 70°C. A vacuum is applied (20 mm. Hg) while raising temperature to 90°C. The residue is filtered through a filter aid and the filtrate is the desired product. The product contains 6.67% P (6.60% theory), 2.94% N (2.97% theory), and 14.50% S (13.60% theory).

Example (D) (5)-8

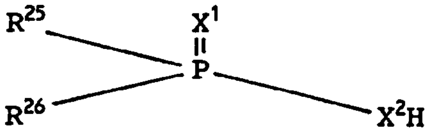
To 1340 parts (3.41 equivalents) of O,O-di-isooctyl phosphorodithioc acid under nitrogen is added 242 parts (3.41 equivalents) of acrylamide. The reaction exotherms to 60°C and is held at 65-70°C for one hour. To this mixture are added 400 parts of toluene, 14 parts of potassium carbonate, and 307 parts (3.58 equivalents) of 35% aqueous formaldehyde. The mixture is heated under a nitrogen atmosphere at 35-40°C for 16 hours. To this mixture is added 18.2 parts of glacial acetic acid.

Example (D)(5)-9

From the product of Example (D) (5)-8, water is removed using a Dean Stark trap at reflux for 6 hours. After 234 parts of water is collected (temperature is 120°C), the mixture is cooled to 30°C. A vacuum is applied (30 mm. Hg) while raising temperature to 115°C. The mixture is filtered through a filter aid and the filtrate is the desired product. The product contains 6.71% phosphorus.

(D) (6) The Methylacrylate Derivative

The last remaining metal deactivator is a methylacrylate derivative formed by the reaction of equal molar amounts of a phosphorus acid of the formula



with methylacrylate wherein X^1 and X^2 are as defined above in (D) (5) and R^{25} and R^{26} are each independently a hydrocarbyl, a hydrocarbyl-based thio or preferably a hydrocarbyl-based oxy group wherein the hydrocarbyl portion contains from 1 to about 30 carbon atoms. Preferably R^{25} and R^{26} are hydrocarbyl-based oxy groups wherein the hydrocarbyl group contains from 1 to 12 carbon atoms and X^1 and X^2 are sulfur. Since the reaction does not go to completion, the remaining acidity is neutralized with propylene oxide.

In preparing (D) (6), methylacrylate is added to the phosphorus acid and at the end of this addition, propylene oxide is added. Generally one mole of propylene oxide is employed for every 20-25 moles of phosphorus acid.

The following illustrates the preparation of the methylacrylate derivative. All parts and percentages are by weight unless otherwise indicated.

Example (D) (6)-1

To 2652 parts (9.04 equivalents) of a O,O-di-alkylphosphorodithioic acid prepared from a mixture of 65 mole percent iso-butyl alcohol and 35 mole percent iso-amyl alcohol is added 776 parts (9.04 equivalents) of methyl acrylate. The methyl acrylate addition is done dropwise and the temperature increases from 60° to 93°C. The contents are held at this temperature for 6 hours and then cooled to 35°C at which 23 parts (0.04 equivalents) propylene oxide is added dropwise. The contents are filtered to give a product having a % phosphorus of 7.54 (8.12% theory).

RBOT Test

The rotary bomb oxidation test (RBOT) is a relatively short term test method for the oxidation stability of oils.

The RBOT test is a rapid means of estimating the oxidation stability of lubricating oils. In the test, the oil sample, water and a copper catalyst coil are placed in a covered glass container, and placed in a bomb equipped with a pressure gauge. The bomb is charged with oxygen to a pressure of 90 psi (620 Kpa) and placed in a constant temperature oil bath maintained at 150°C and rotated at 100 rpm. The pressure in the bomb is monitored continuously. At first the pressure increases sharply, typically to about 190-200 psi, because of the increase in temperature. The pressure remains relatively stable, until the oil breaks down. The bomb "life" of the sample is the time in minutes from the start of the test to a 25 psi drop from the established plateau pressure. Usually the test uses a 3m length of 14 Awg of copper wire which has been cleaned. The longer the "life", the more stable the oil formulation (i.e., the more effective the anti-oxidant).

The composition of the present invention comprising components (A) and (B) and optionally (D) or (A), (B) and (C) and optionally (D) have utility in hydraulic fluids, two-cycle (two-stroke) internal combustion engines, gear oils, passenger car motor oils and as a food machinery lubricant. The composition of this invention comprises a major amount of (A) and a minor amount (B) and optionally (D) or a major amount of (A) and a minor amount of (B) and (C) and optionally (D). By a major amount is meant more than 50%. Thus 51%, 75% and 99% are major amounts. A minor amount is less than 50%. Examples of minor amounts are 1%, 25% and 49%. The following states the ranges of components (A), (B), (C) and (D) in parts by weight.

Component	Generally	Preferred	Most Preferred
(A)	75 - 99	85 - 99	95 - 99
(B)	0.1 - 10	0.3 - 8	0.5 - 5
(C)	0.1 - 10	0.3 - 8	0.5 - 5
(D)	0 - 2	0 - 0.5	0 - 0.25

It is understood that other components besides (A), (B), (C) and (D) may be present within this composition.

The components of this invention are blended together according to the above ranges to effect solutions. The below Table I outlines examples so as to provide those of ordinary skill in the art with a complete disclosure and description on how to make the composition of this invention and it is not intended to limit the scope of what the inventors regard as their invention. All parts are by weight. Where the triglyceride oil, component (A), is identified with a number such as Sunyl^R 80 High Oleic Sunflower oil, it means that the oleic acid residue of the triglyceride is 80 percent. In some instances, more than one triglyceride oil is utilized. For example, 80 parts of Sunyl^R 90 is blended with normal sunflower oil that contains 20% oleic acid residue to give a sunflower oil blend containing 76% oleic acid residue.

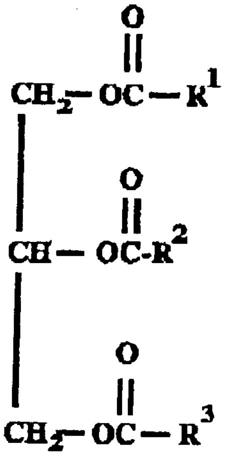
TABLE I

EXAMPLE NUMBERS

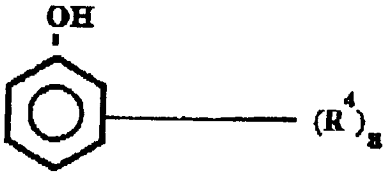
COMPONENTS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SUNYL^{R} 90 HIGH OLEIC SUNFLOWER OIL	100	97	80	77.6												
NORMAL SUNFLOWER OIL			20	19.4												
SUNYL^{R} 80 HIGH OLEIC SUNFLOWER OIL					99	98	100	97.8	97.3	97.4	100	100	97.3	97.7	97.4	97.8
2,6-DI-T-BUTYLPHENOL		3		3		1	2	1.5	1.5	1.5	0.75	1.0	0.75	0.75	0.75	0.75
NONYLATED-DIPHENYLAMINE											0.75	1.0	0.75	0.75	0.75	0.75
TOLYLTRIAZOLE								0.004	0.05	0.004			0.05	0.05	0.004	0.004
PRODUCT OF EXAMPLE (D)(6)-1								0.6	1.0	1.0			1.0	0.6	1.0	0.6
RBOT	21	266	16	154	15	149	189	188	224	180	127	131	272	274	214	211

Claims

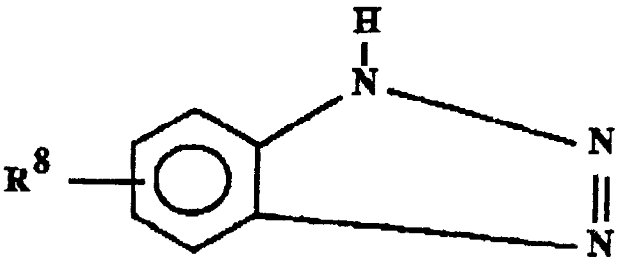
1. An anti-oxidant composition for triglyceride oils comprising a major amount of
   (A) at least one vegetable triglyceride oil of the formula



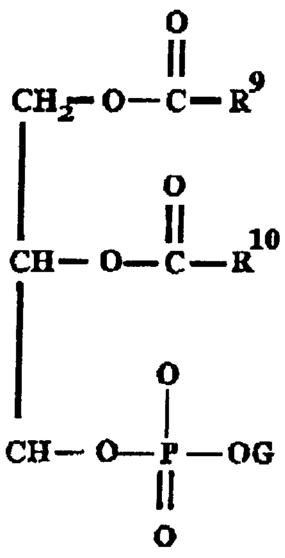
wherein R^1 R^2 and R^3 are aliphatic hydrocarbyl groups having at least 60 percent monounsaturated character and containing from about 8 to about 24 carbon atoms and a minor anti-oxidant amount of
(B) at least one alkyl phenol of the formula



wherein R^4 is an alkyl group containing from 1 up to about 24 carbon atoms, a is 2 and the position para to the OH group is open, and optionally
(D) a metal deactivator selected from
(1) a benzotriazole of the formula



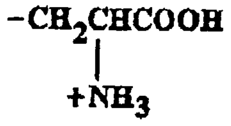
wherein R^8 is hydrogen or an alkyl group of 1 up to about 24 carbon atoms,
(2) a phosphatide of the formula



wherein R^9 and R^{10} are aliphatic hydrocarbyl groups containing from 8 to about 24 carbon atoms, and G is selected from

$$-CH_2CH_2\overset{+}{N}H_3, -CH_2CH_2\overset{+}{N}(CH_3)_3$$

and

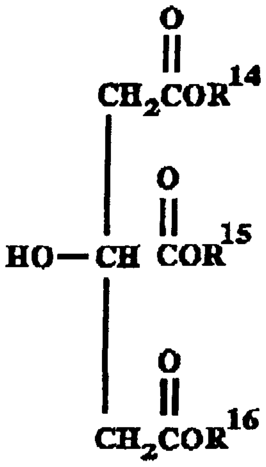


$$-CH_2\underset{\underset{+NH_3}{|}}{C}HCOOH$$

(3) a carbamate of the formula

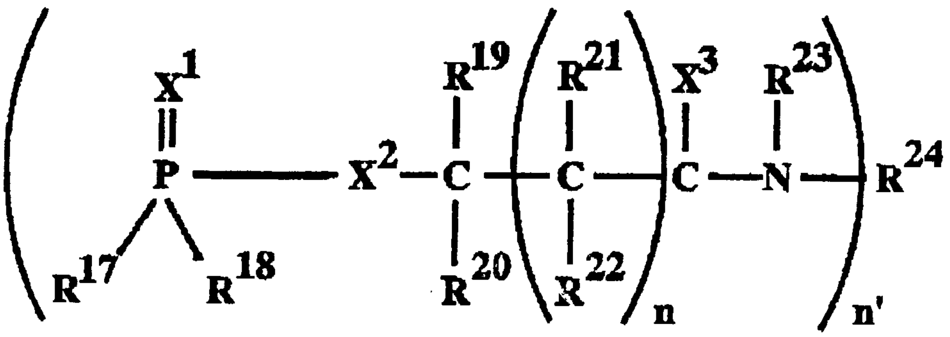
$$R^{11}O\overset{\overset{O}{\|}}{C}NR^{12}R^{13}$$

wherein R^{11} is an alkyl group containing from 1 to about 24 carbon atoms, phenyl or alkyl phenyl wherein the alkyl group contains from 1 to about 18 carbon atoms, R^{12} and R^{13} are hydrogen or an alkyl group containing from 1 to about 6 carbon atoms, with the proviso and that R^{12} and R^{13} are not both hydrogen, (4) citric acid and derivatives of citric acid of the formula



wherein R^{14}, R^{15} and R^{16} are independently hydrocarbon or aliphatic hydrocarbyl groups containing form 1 to about 12 carbon atoms, with the proviso that at least one of R^{14}, R^{15} and R^{16} is an aliphatic hydrocarbyl group,

(5) a coupled phosphorus-containing amide of the formula



wherein X^1, X^2 and X^3, independently is oxygen or sulfur;

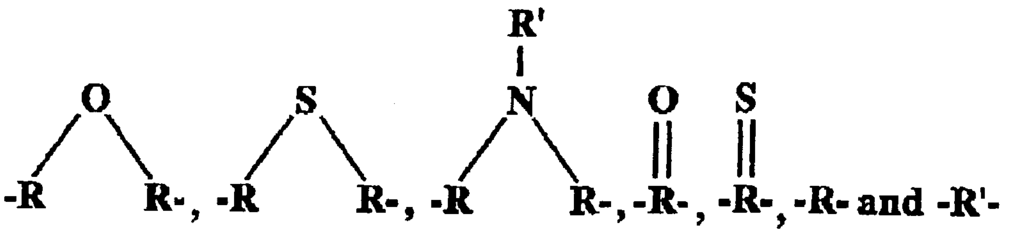
wherein R^{17} and R^{18}, independently is a hydrocarbyl, a hydrocarbyl-based oxy, the hydrocarbyl portions of which contain 6 to about 22 carbon atoms, or a hydrocarbyl-based thio, having from 4 to about 34 carbon atoms;

wherein R^{19}, R^{20}, R^{21} and R^{22}, independently is hydrogen, or an alkyl having from 1 to about 22 carbon atoms, or an aromatic, an alkyl-substituted aromatic or an aromatic-substituted alkyl having from 6 to about 34 atoms;

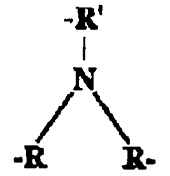
wherein n is zero or 1;

wherein n' is 2 or 3

wherein R^{23} is hydrogen; and when n' is 2, R^{24} is selected from



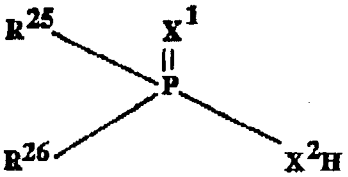
wherein R is an alkyl moiety, in the form of alkylene or alkylidene containing form 1 to 12 carbon atoms and R' is an alkyl moiety, alkylene, alkylidene or carboxyl containing 1 to 60 carbon atoms and when n' is 3, R^{24} is



;

or

(6) a methylacrylate derivative prepared by reacting equal molar amounts of a phosphorus acid of the formula



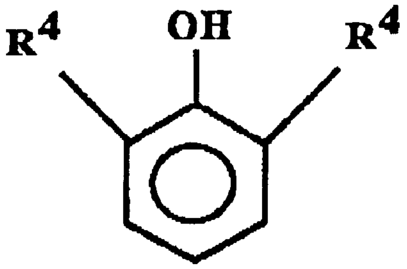
with methylacrylate wherein X^1 and X^2 are oxygen or sulfur and R^{25} and R^{26} are each independently a hydrocarbyl, a hydrocarbyl-based thio or a hydrocarbyl-based oxy group wherein the hydrocarbyl portion contains from 1 to about 30 carbon atoms and remaining acidity is neutralized with 1 mole propylene oxide for each 20-25 moles of phosphorus acid.

2. The composition of claim 1 wherein the vegetable oil triglyceride is an ester of at least one straight chain fatty acid and glycerol wherein the fatty acid contains from about 8 to about 22 carbon atoms.

3. The composition of claim 1 or claim 2 wherein the mono-unsaturated fatty acid is oleic acid.

4. The composition of any preceding claim wherein a is 2 and R^4 contains from 1 up to about 8 carbon atoms.

5. The composition of claim 4 wherein the alkyl phenol is of the formula



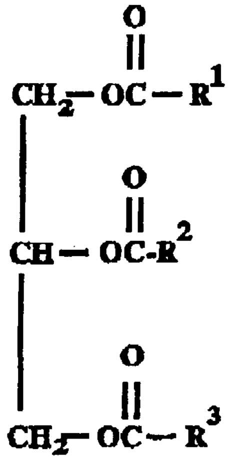
wherein R^4 is t-butyl.

6. The composition of any preceding claim wherein R^8 is a methyl group.

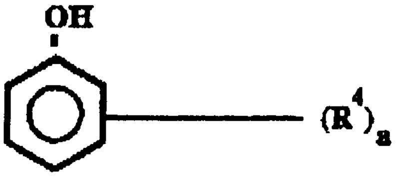
7. The composition of any preceding claim wherein X^1 and X^2 are sulfur and R^{25} and R^{26} are hydrocarbyl-based oxy groups wherein the hydrocarbyl group contains from 1 to 12 carbon atoms.

8. The composition of any preceding claim containing from about 75 - 99 parts by weight (A), 0.1-10 parts by weight (B) and optionally from 0-2 parts by weight (D).

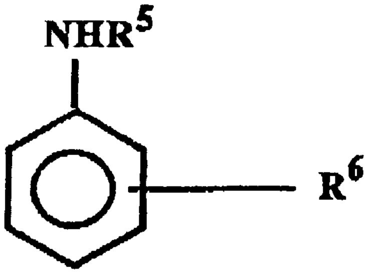
9. An anti-oxidant composition for triglyceride oils comprising a major amount of
(A) at least one animal, vegetable or synthetic triglyceride oil of the formula



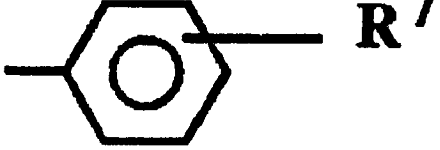
wherein R^1, R^2 and R^3 are aliphatic hydrocarbyl groups having at least 60 percent monounsaturated character and containing from about 8 to about 24 carbon atoms and a minor anti-oxidant amount of (B) at least one alkyl phenol of the formula



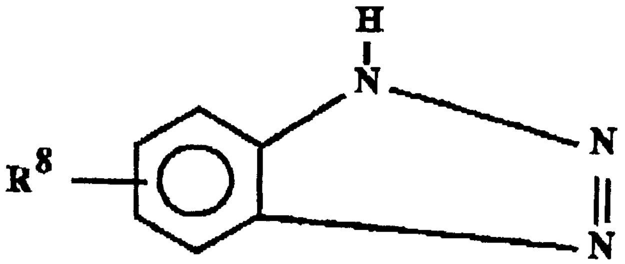
wherein R^4 is an alkyl group containing from 1 up to about 24 carbon atoms, a is 2, and the position para to the OH group is open,
(C) at least one aromatic amine of the formula



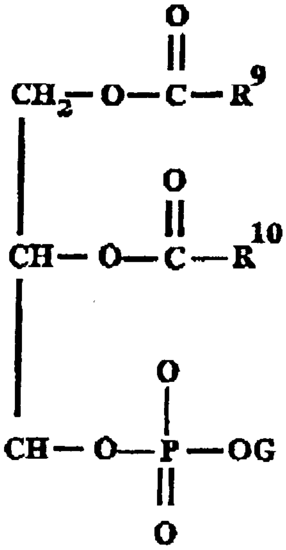
wherein R^5 is



and R^6 and R^7 are alkyl groups containing from 4 up to about 18 carbon atoms and optionally
(D) a metal deactivator selected from



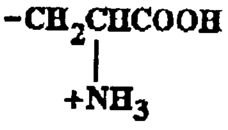
(1) a benzotriazole of the formula
wherein R^8 is hydrogen or an alkyl group of 1 up to about 24 carbon atoms,
(2) a phosphatide of the formula



wherein R^9 and R^{10} are aliphatic hydrocarbyl groups containing from 8 to about 24 carbon atoms, and G is selected from

$$-CH_2CH_2\overset{+}{N}H_3, -CH_2CH_2\overset{+}{N}(CH_3)_3$$

and



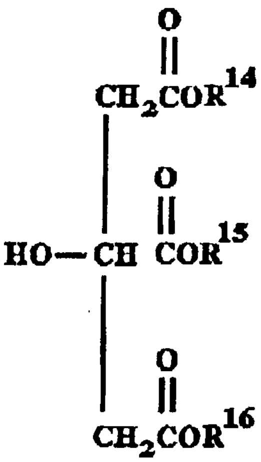
$$-CH_2\underset{\substack{| \\ +NH_3}}{CH}COOH$$

(3) a carbamate of the formula

$$R^{11}O\overset{\substack{O \\ \|}}{C}NR^{12}R^{13}$$

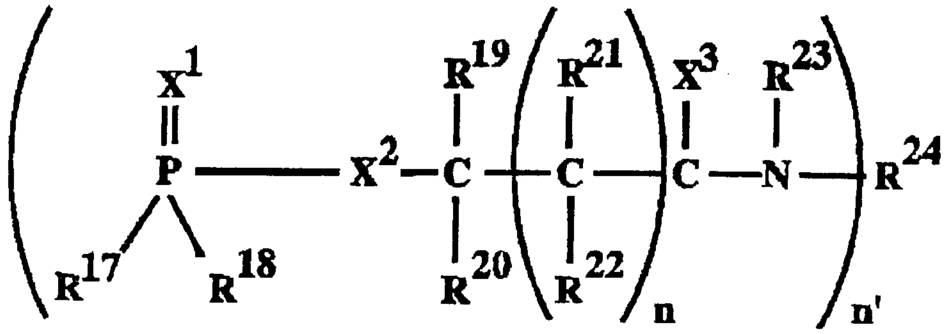
wherein R^{11} is an alkyl group containing from 1 to about 24 carbon atoms, phenyl or alkyl phenyl wherein the alkyl group contains from 1 to about 18 carbon atoms, R^{12} and R^{13} are hydrogen or an alkyl group containing from 1 to about 6 carbon atoms, with the proviso and that $R^{12}$and R^{13} are not both hydrogen,

(4) citric acid and derivatives of citric acid of the formula



wherein R^{14}, R^{15} and R^{16} are independently hydrocarbon or aliphatic hydrocarbyl groups containing form 1 to about 12 carbon atoms, with the proviso that at least one of R^{14}, R^{15} and R^{16} is an aliphatic hydrocarbyl group,

(5) a coupled phosphorus-containing amide of the formula



wherein X^1, X^2 and X^3, independently is oxygen or sulfur;

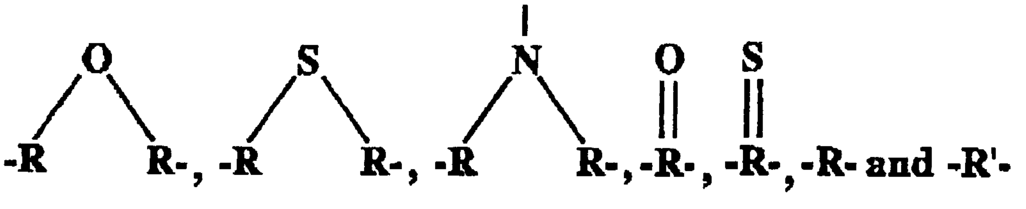
wherein $R^{17}$and R^{18}, independently is a hydrocarbyl, a bydrocarbyl-based oxy, the hydrocarbyl portions of which contain 6 to about 22 carbon atoms, or a hydrocarbyl-based thio, having from 4 to about 34 carbon atoms;

wherein R^{19}, R^{20}, R^{21} and R^{22}, independently is hydrogen, or an alkyl having from 1 to about 22 carbon atoms, or an aromatic, an alkyl-substituted aromatic or an aromatic-substituted alkyl having from 6 to about 34 atoms;

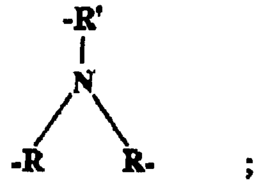
wherein n is zero or 1;

wherein n' is 2 or 3

wherein R^{23} is hydrogen; and when n' is 2, R^{24} is selected from

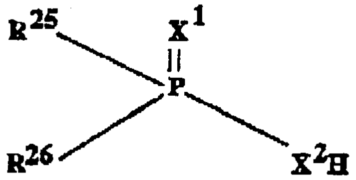


wherein R is an alkyl moiety, in the form of alkylene or alkylidene containing form 1 to 12 carbon atoms and R' is an alkyl moiety, alkylene, alkylidene or carboxyl containing 1 to 60 carbon atoms and when n' is 3, R^{24} is



or

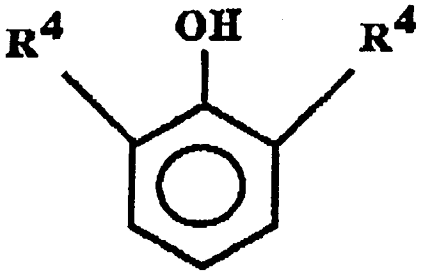
(6) a methylacrylate derivative prepared by reacting equal molar amounts of a phosphorus acid of the formula



with methylacrylate wherein X^1 and X^2 are oxygen or sulfur and R^{25} and R^{26} are each independently a hydrocarbyl, a hydrocarbyl-based thio or a hydrocarbyl-based oxy group wherein the hydrocarbyl portion contains from 1 to about 30 carbon atoms and remaining acidity is neutralized with 1 mole propylene oxide for each 20-25 moles of phosphorus acid.

10. The composition of claim 9 wherein a is 2 and R^4contains from 1 up to about 8 carbon atoms.

11. The composition of claim 10 wherein the alkyl phenol is of the formula



wherein R^4 is t-butyl.

12. The composition of any one of claims 9 to 11 wherein R^8 is hydrogen or an alkyl group containing from 1 up to about 8 carbon atoms.

13. The composition of claim 12 wherein R^8 is a methyl group.

14. The composition of any one of claims 9 to 13 wherein R^6 and R^7 are nonyl groups.

15. The composition of any one of claims 9 to 14 wherein X^1 and X^2 are sulfur and R^{25} and R^{26} are hydrocarbyl-based oxy groups wherein the hydrocarbyl group contains from 1 to 12 carbon atoms.

16. The composition of any one of claims 9 to 15 containing from about 75 - 99 parts by weight (A), 0.1-10 parts by weight (B), from 0.1-10 parts by weight (C) and optionally from 0-2 parts by weight (D).

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 30 6775

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y	WO-A-88 05808 (RAISION TEHTAAT OY AB) * page 2, line 17 - page 3, line 2 * * page 3, line 6 - line 11 * * claim 1 * * page 10; examples 3,10 * * page 11, line 2 - line 4 * * page 11, line 6 - line 7 * * page 11, line 10 * ---	1-5, 8-11,14, 16	C10M129/10 C10M141/00 C10M141/06 C10M169/04 //C10N30/10, C10N40/02, C10N40/08, C10N40/25, C10N40/26, (C10M169/04, 101:04,129:10, 129:76,133:12, 133:18,133:44, 137:04,137:10, 137:12,137:14, 159:12)
Y	EP-A-0 456 925 (ETHYL PETROLEUM ADDITIVES) * page 6, line 51 - page 7, line 3 * * page 15, line 33 * * page 15, line 47 * ---	1-5, 8-11,14, 16	
A	GB-A-2 134 923 (OY KASVIOLJY-VAXTOLJE AB) * page 5, line 27 * ---	1	
P,A	WO-A-93 03123 (THE LUBRIZOL CORPORATION) * page 51, paragraph 2 * * claims 1-7,44 * ---	1,6,9, 12,13	**TECHNICAL FIELDS SEARCHED (Int.Cl.5)** C10M
A	EP-A-0 239 536 (CIBA-GEIGY) * page 2, line 47 - page 3, line 23 * * page 4, line 19 * * page 4, line 30 * * page 4, line 43 * ---	1,4-6, 8-13,16	
D,A	US-A-5 102 567 (L.R.WOLF) * column 3, line 18 * * column 4, line 47 * * column 5, line 47 - line 56 * -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 November 1993	Hilgenga, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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