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(54) **ENGINE OILS THAT ARE
NON-AGGRESSIVE TOWARDS LEAD**

Related U.S. Application Data

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(57) ABSTRACT

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Formulated engine oils that comprise certain 1,2,4-triazole metal deactivators are especially non-aggressive towards lead engine parts such as bearings. The inclusion of certain 1,2,4-triazole compounds allows the co-use of corrosive additives such as sulfur-containing additives and vegetable oil-derived friction modifiers while at the same time meeting ASTM D 4485 specifications.

ENGINE OILS THAT ARE NON-AGGRESSIVE TOWARDS LEAD

[0001] The present invention relates to engine oil (engine fluid) compositions that are non-aggressive towards lead.

[0002] U.S. Pat. No. 4,734,209 discloses metal deactivators for functional fluids.

[0003] U.S. Pat. No. 4,491,527 teaches compositions useful for the inhibition of lead paint deposition in lubricants.

[0004] Engine oil specifications are becoming more stringent in the way of performance requirements, and new formulations are under development to meet these new specifications. Engine oil specifications are defined in ASTM D 4485.

[0005] The new engine oil formulations under development comprise certain additive chemistries. Many of these additive chemistries are corrosive to lead. It is difficult for formulators to meet the present engine oil specifications by employing certain beneficial additives while also meeting the specification for lead corrosion.

[0006] From 1994 onward, all diesel oils have been required to meet a lead corrosion specification defined in ASTM D 4485 and as measured according to either ASTM D 5968 (run at 125° C.) or ASTM D 6594 (run at 135° C.). The ASTM D 4485 Standard Specification for Performance of Engine Oils indicates a maximum allowed lead corrosion level of 60 ppm for API categories CF-4 and CG-4 by ASTM D 5968 and 120 ppm for category CH-4 by ASTM D 6594.

[0007] For example, certain components of formulated engine oils that cause lead corrosion include certain detergents, antiwear additives, friction modifiers and antioxidants. Many such desired additive chemistries are disqualified from use due to causing engine oil formulations to not meet industry specifications for limits on lead corrosion.

[0008] For example, desired additive chemistries that are aggressive towards lead and are otherwise disqualified from use in engine oils include sulfur-containing additives and certain vegetable oil-derived friction modifiers.

[0009] It has surprisingly been found that formulated engine oils that comprise certain 1,2,4-triazole metal deactivators are especially non-aggressive towards lead, for example lead engine parts such as bearings. The engine oils according to this invention meet corrosion protection performance requirements of diesel lubricant specifications defined in ASTM D 4485.

[0010] This issue of lead corrosion is generally not a problem in other types of lubricants, for example turbine and hydraulic oils.

[0011] The engine oils of this invention are diesel and universal oils. Universal oils encompass both diesel oils and passenger car oils. The engine oils are employed in internal combustion engines, for example, in motor vehicles fitted, for example, with engines of the Otto, Diesel, two-stroke, Wankel or orbital type.

[0012] Specifically, the present invention relates to an engine oil composition that is non-aggressive towards lead,

[0013] which composition comprises

[0014] (a) a base fluid,

[0015] (b) at least one compound of the formula (I)

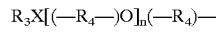


[0016] and

[0017] (c) at least one oil additive that is aggressive towards lead and which is selected from the group consisting of antioxidants, antiwear additives, dispersants, detergents, antifoam additives, viscosity index improvers, copper passivators, rust inhibitors, pourpoint depressants, demulsifiers and friction modifiers,

[0018] where

[0019] R_1 and R_2 are the same or different and are $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ alkenyl, $\text{C}_5\text{-C}_{12}$ cycloalkyl, $\text{C}_7\text{-C}_{13}$ aralkyl or $\text{C}_6\text{-C}_{10}$ aryl, or R_1 and R_2 , together with the nitrogen atom to which they are each attached may form a 5-, 6- or 7-membered heterocyclic residue, or R_1 and R_2 are a group of formula



[0020] where

[0021] X is O, S or N,

[0022] R_3 is hydrogen or $\text{C}_1\text{-C}_{20}$ alkyl,

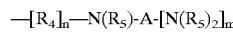
[0023] R_4 is $\text{C}_1\text{-C}_{12}$ alkylene,

[0024] n is 0 or an integer from 1 to 6,

[0025] or one of R_1 and R_2 is a group of formula



[0026] or R_2 is a group of formula (II) and R_1 is a group of formula



[0027] where

[0028] m is 0 or 1 and, when m is zero, A is a group of formula (II) and, when m is 1, A is alkylene or $\text{C}_6\text{-C}_{10}$ arylene and R_5 is a group of formula (II), and

[0029] where in the absence of component (b), the engine oil composition exceeds about 100 ppm lead as measured according to test ASTM D 6594.

[0030] R_4 is for example a C_1 - C_6 alkylene group, for instance a C_2 - C_3 alkylene.

[0031] n is for instance 0, 1, 2, 3, 4, 5 or 6.

[0032] Alkyl is straight or branched chain and is for example methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl or n-eicosyl.

[0033] Alkenyl is straight or branched chain and is for example prop-2-enyl, but-2-enyl, 2-methyl-prop-2-enyl, pent-2-enyl, hexa-2,4-dienyl, dec-10-enyl or eicos-2-enyl.

[0034] Cycloalkyl is for example cyclopentyl, cyclohexyl, cyclooctyl, cyclodecyl, adamantyl or cyclododecyl.

[0035] Aralkyl is for example benzyl, 2-phenylethyl, benzhydryl or naphthylmethyl.

[0036] Aryl is for example phenyl or naphthyl.

[0037] When R_1 and R_2 together with the nitrogen atom to which they are attached form a heterocyclic group, the heterocyclic group is for example a morpholine, pyrrolidine, piperidine or a perhydroazepine ring.

[0038] Alkylene moieties include for example methylene, ethylene, 1:2- or 1:3-propylene, 1:4-butylene, 1:6-hexylene, 1:8-octylene, 1:10-decylene and 1:12-dodecylene.

[0039] Arylene moieties include for example phenylene and naphthylene.

[0040] Specific compounds of present formula (I) include:

- [0041] 1-(or 4)-(dimethylaminomethyl) triazole
- [0042] 1-(or 4)-(diethylaminomethyl) triazole
- [0043] 1-(or 4)-(di-isopropylaminomethyl) triazole
- [0044] 1-(or 4)-(di-n-butylaminomethyl) triazole
- [0045] 1-(or 4)-(di-n-hexylaminomethyl) triazole
- [0046] 1-(or 4)-(di-isooctylaminomethyl) triazole
- [0047] 1-(or 4)-(di-(2-ethylhexyl)aminomethyl) triazole
- [0048] 1-(or 4)-(di-n-octylaminomethyl) triazole
- [0049] 1-(or 4)-(di-n-decylaminomethyl) triazole
- [0050] 1-(or 4)-(di-n-dodecylaminomethyl) triazole
- [0051] 1-(or 4)-(di-n-octadecylaminomethyl) triazole
- [0052] 1-(or 4)-(di-n-eicosylaminomethyl) triazole
- [0053] 1-(or 4)-[di-(prop-2'-enyl)aminomethyl] triazole
- [0054] 1-(or 4)-[di-(but-2'-enyl)aminomethyl] triazole
- [0055] 1-(or 4)-[di-(eicos-2'-enyl)aminomethyl] triazole
- [0056] 1-(or 4)-(di-cyclohexylaminomethyl) triazole
- [0057] 1-(or 4)-(di-benzylaminomethyl) triazole
- [0058] 1-(or 4)-(di-phenylaminomethyl) triazole
- [0059] 1-(or 4)-(4'-morpholinomethyl) triazole
- [0060] 1-(or 4)-(1'-pyrrolidinomethyl) triazole
- [0061] 1-(or 4)-(1'-piperidinomethyl) triazole
- [0062] 1-(or 4)-(1'-perhydroazepinomethyl) triazole
- [0063] 1-(or 4)-(2',2"-dihydroxyethyl)aminomethyl] triazole
- [0064] 1-(or 4)-(dibutoxypropyl-aminomethyl) triazole
- [0065] 1-(or 4)-(dibutylthiopropyl-aminomethyl) triazole
- [0066] 1-(or 4)-(di-butylaminopropyl-aminomethyl) triazole
- [0067] N,N-bis-(1- or 4-triazolylmethyl) laurylamine
- [0068] N,N-bis-(1- or 4-triazolylmethyl) oleylamine
- [0069] N,N-bis-(1- or 4-triazolylmethyl) ethanolamine and
- [0070] N,N,N',N'-tetra(1- or 4-triazolylmethyl) ethylene diamine.

[0071] The present compound of formula (I) is for example 1-(di-isooctylaminomethyl) triazole, that is 1-(di-isooctylaminomethyl)-1,2,4-triazole, or is 1-(di-(2-ethylhexyl)aminomethyl)1,2,4-triazole.

[0072] The present compounds of formula (I) are prepared by known methods, for example as taught in U.S. Pat. No. 4,734,209, the disclosure of which is hereby incorporated by reference.

[0073] The base fluids in accordance with the invention utilize mineral oil based fluids (API Group I, II and III), poly- α -olefins—PAOs (API Group IV), esters (API Group V), other synthetic fluids, natural oils that are animal or vegetable in origin, and mixtures thereof. The base fluids are of suitable viscosity for utilization in engine oil applications.

[0074] The present compounds of formula (I) are employed at concentrations of about 0.01 to about 1.0% by weight, based on the weight of the formulated engine oil. For instance, the compounds of formula (I) are present from about 0.02 to about 0.5 weight percent. For example, from about 0.03 to about 0.3 weight percent. For instance from about 0.01 to about 0.5 or from about 0.01 to about 0.3 weight percent. For example from about 0.02 to about 1.0 or from about 0.02 to about 0.3 weight percent. For instance, from about 0.03 to about 1.0 or from about 0.03 to about 0.5 weight percent.

[0075] The antioxidants of component (c) are selected from:

- [0076] 1) alkylated monophenols, for example 2,6-di-*tert*-butyl-4-methylphenol, 2-butyl-4,6-dimethylphenol, 2,6-di-*tert*-butyl-4-ethylphenol, 2,6-di-*tert*-butyl-4-n-butylphenol, 2,6-di-*tert*-butyl-4-isobutylphenol, 2,6-di-cyclopentyl-4-methylphenol, 2-(a-methyl-cyclohexyl)-4,6-dimethylphenol, 2,6-di-octadecyl-4-methylphenol, 2,4,6-tri-cyclo-hexylphenol, 2,6-di-*tert*-butyl-4-methoxymethylphenol, linear or sidechain-branched nonylphenols, for example 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methyl-undec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol or mixtures thereof,
- [0077] 2) alkylthiomethylphenols, for example 2,4-di-octylthiomethyl-6-*tert*-butylphenol, 2,4-di-oc-

tylthiomethyl-6-methylphenol, 2,4-di-octylthiomethyl-6-ethylphenol or 2,6-di-dodecylthiomethyl-4-nonylphenol,

[0078] 3) hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butyl-hydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate or bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate,

[0079] 4) tocopherols, for example α -, β -, γ - or δ -tocopherol or mixtures thereof (vitamin E),

[0080] 5) hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec.-amylphenol) or 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulfide,

[0081] 6) alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis(4-methyl-6-(alpha-methylcyclohexyl)-phenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis(6-(alpha-methylbenzyl)-4-nonylphenol), 2,2'-methylenebis(6-(alpha,alpha-dimethylbenzyl)-4-nonylphenol), 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis(3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate), bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis(2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl)terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane or 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)-pentane,

[0082] 7) O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl 4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl 4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiobenzoate, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide or isoctyl 3,5-di-tert-butyl-4-hydroxy-benzylmercaptoacetate,

[0083] 8) hydroxybenzylated malonates, for example dioctadecyl 2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, dioctadecyl 2-(3-tert-butyl-

4-hydroxy-5-methylbenzyl)-malonate, di-dodecyl mercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-malonate or di(4-(1,1,3,3-tetramethylbutyl)phenyl)2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate,

[0084] 9) aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene or 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol,

[0085] 10) triazine compounds, for example 2,4-bisoctylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxo)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexahydro-1,3,5-triazine or 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)-isocyanurate,

[0086] 11) benzylphosphonates, for example dimethyl 2,5-di-tert-butyl-4-hydroxybenzyl-phosphonate, diethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate or the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid,

[0087] 12) acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide or octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate,

[0088] 13) esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid, β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid, 3,5-di-tert-butyl-4-hydroxyphenylacetic acid or β -(5-tert-butyl-4-hydroxyphenyl)-3-thiabutyric acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiobutylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethyl-hexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospho-2,6,7-trioxabicyclo(2.2.2)octane, glycerol or transesterification products based on natural triglycerides of, for example, coconut oil, rape seed oil, sunflower oil or colza oil,

[0089] 14) amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine or N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine,

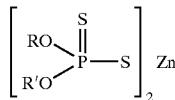
[0090] 15) ascorbic acid (vitamin C),

[0091] 16) amine-type antioxidants, for example N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methyl-pentyl)-p-phenylenediamine, N,N'-bis(1-methyl-heptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di-(naphth-2-yl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfonamido)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxy-diphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, e.g. p,p'-di-tert-octyldiphenyl-amine, 4-n-butylaminophenol, 4-butylamino-phenol, 4-nanoylamino-phenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, di-(4-methoxyphenyl)-amine, 2,6-di-tert-butyl-4-dimethylaminomethyl-phenol, 2,4'-diamino-diphenylmethane, 4,4'-diamino-diphenylmethane, N,N,N',N'-tetramethyl-4,4'-diamino-diphenylmethane, 1,2-di-((2-methyl-phenyl)-amino)-ethane, 1,2-di-(phenylamino)propane, (o-tolyl)biguanide, di-(4(1',3'-dimethyl-butyl)-phenyl)amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyl-diphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isoxyldiphenylamines, mixtures of mono- and dialkylated tert-butylidiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octyl-phenothiazines, a mixture of mono- and dialkylated tert-octyl-phenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis-(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine, bis-(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 2,2,6,6-tetramethylpiperidin-4-one or 2,2,6,6-tetramethylpiperidin-4-ol, and

[0092] 17) aliphatic or aromatic phosphites, esters of thiadipropionic acid or of thiodiacetic acid, or salts of dithiocarbamic or dithiophosphoric acid, 2,2,12,12-tetramethyl-5,9-dihydroxy-3,7,1-trithiatridecane or 2,2,15,15-tetramethyl-5,12-dihydroxy-3,7,10,14-tetrathiahexadecane.

[0093] The antiwear additives of component (c) are selected from:

[0094] 1) dihydrocarbyl dithiophosphate metal salts where the metal is aluminum, lead, tin manganese, cobalt, nickel, zinc or copper, but most often zinc. The zinc salt (zinc dialkyl dithiophosphate) is represented as



[0095] where R and R' are independently C₁-C₂₀ alkyl, C₃-C₂₀ alkenyl, C₅-C₁₂ cycloalkyl, C₇-C₁₃ aralkyl or C₆-C₁₀ aryl, for example R and R' are independently C₁-C₁₂ alkyl,

[0096] and

[0097] 2) sulfur- and/or phosphorus- and/or halogen-containing compounds, such as sulfurized olefins and vegetable oils, tritolyl phosphate, tricresyl phosphate, chlorinated paraffins, alkyl and aryl di- and trisulfides, amine salts of mono- and dialkyl phosphates, amine salts of methylphosphonic acid, diethanolaminomethyltolyltriazole, di(2-ethylhexyl)-aminomethyltolyltriazole, derivatives of 2,5-dimercapto-1,3,4-thiadiazole, ethyl ((bis(isopropyl)oxyphosphinothioyl)thio)propionate, triphenyl thiophosphate (triphenyl phosphorothioate), tris(alkylphenyl) phosphorothioates and mixtures thereof (for example tris(isononylphenyl) phosphorothioate), diphenylmonononylphenyl phosphorothioate, isobutylphenyl diphenyl phosphorothioate, the dodecylamine salt of 3-hydroxy-1,3-thiaphosphetan 3-oxide, trithiophosphoric acid 5,5,5-tris(isooctyl 2-acetate), derivatives of 2-mercaptopbenzothiazole, such as 1-(N,N-bis(2-ethylhexyl)aminomethyl)-2-mercaptop-1H-1,3-benzothiazole or ethoxycarbonyl 5-octyldithiocarbamate.

[0098] The dispersants of component (c) are selected from:

[0099] 1) Mannich bases that are condensation reaction products of a high molecular weight phenol, an alkyne polyamine and an aldehyde such as formaldehyde,

[0100] 2) succinic-based dispersants that are reaction products of a olefin polymer and succinic acylating agent (acid, anhydride, ester or halide) further reacted with an organic hydroxy compound and/or an amine,

[0101] and

[0102] 3) high molecular weight amides and esters such as reaction products of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol (such as glycerol, pentaerythritol or sorbitol).

[0103] Ashless (metal-free) polymeric materials that usually contain an oil soluble high molecular weight backbone linked to a polar functional group that associates with particles to be dispersed are typically used as dispersants. Commonly used hydrocarbon backbone materials are olefin polymers and copolymers, i.e.—ethylene, propylene, butylene, isobutylene, styrene; there may or may not be further functional groups incorporated into the backbone of the

polymer. Polar materials such as amines, alcohols, amides or esters are attached to the backbone via a bridge.

[0104] The detergents of component (c) are selected from:

[0105] Calcium, magnesium, barium, sodium or lithium salts of organic acids, for example sulphonates, alkylphenates, sulfurised alkyl phenates, carboxylates, salicylates, phosphonates, thiophosphonates and phosphinates. The salts may be neutral or may be overbased by for example metal hydroxides or carbonates.

[0106] The antifoam additives of component (c) are selected from:

[0107] Silicone oils, polysiloxanes and polyethylene glycol ethers.

[0108] The viscosity index improvers of component (c) are selected from:

[0109] Polyisobutylene, copolymers of ethylene and propylene, polyacrylates, polymethacrylates, vinylpyrrolidone/methacrylate copolymers, polyvinylpyrrolidones, polybutenes, olefin copolymers, styrene/acrylate copolymers, styrene/isoprene copolymers, styrene/isobutadiene copolymers, isoprene/butadiene copolymers and polyethers.

[0110] The copper passivators of component (c) are selected from:

[0111] 1) benzotriazoles and their derivatives, for example 4- or 5-alkylbenzotriazoles (e.g. toltriazole) and derivatives thereof, 4,5,6,7-tetrahydrobenzotriazole, 5,5'-methylenebisbenzotriazole; Mannich bases of benzotriazole or toltriazole, such as 1-(di(2-ethylhexyl)aminomethyl)toltriazole and 1-(di(2-ethylhexyl)aminomethyl)-benzotriazole; alkoxyalkylbenzotriazoles, such as 1-(nonyloxymethyl)-benzotriazole, 1-(1-butoxyethyl)-benzotriazole or 1-(1-cyclohexoxybutyl)-toltriazole,

[0112] 2) imidazole derivatives, for example 4,4'-methylenebis(2-undecyl-5-methyl-imidazole), bis((N-methyl)imidazol-2-yl)carbinol octyl ether,

[0113] 3) sulfur-containing heterocyclic compounds, for example 2-mercaptopbenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2,5-dimercaptobenzothiadiazole and derivatives thereof or 3,5-bis(di(2-ethylhexyl)aminomethyl)-1,3,4-thiadiazolin-2-one,

[0114] and

[0115] 4) amino compounds, for example salicylidenepropylenediamine, salicylaminoguanidine or salts thereof.

[0116] The rust inhibitors of component (c) are selected from:

[0117] 1) nonionic polyoxyalkylene polyols and their esters, polyoxyalkylene phenols, organic acids, their esters, metal salts, amine salts and anhydrides, for example alkyl- and alkenylsuccinic acids and the partial esters thereof with alcohols, diols or hydroxy-carboxylic acids, partial amides of alkyl- and alkenylsuccinic acids, 4-nonylphenoxyacetic acid, alkoxy- and alkoxyethoxycarboxylic acids, such as dodecyloxyacetic acid, dodecyloxy(ethoxy)acetic acid and the amine salts thereof, or N-oleylsar-

cosine, sorbitan monooleate, lead naphthenate and alkenylsuccinic anhydrides, for example dodecylsuccinic anhydride, 2-(2-carboxyethyl)-1-dodecyl-3-methylglycerine and its salts, for instance sodium and triethanolamine salts,

[0118] 2) nitrogen-containing compounds selected from:

[0119] i.) primary, secondary or tertiary aliphatic or cycloaliphatic amines and amine salts of organic and inorganic acids, for example oil-soluble alkylammonium carboxylates, and also 1-(N,N-bis(2-hydroxyethyl)amino)-3-(4-nonylphenoxy)propan-2-ol,

[0120] ii.) heterocyclic compounds, for example substituted imidazolines or oxazolines, for instance 2-heptadecenyl-1-(2-hydroxyethyl)-imidazoline,

[0121] 3) phosphorus-containing compounds, for example amine salts of phosphoric acid, phosphoric acid partial esters or phosphonic acid partial esters or zinc dialkyldithiophosphates,

[0122] 4) sulfur-containing compounds, for example barium dinonylnaphthalene-sulfonates, calcium petroleum sulfonates, alkylthio-substituted aliphatic carboxylic acids, esters of aliphatic 2-sulfocarboxylic acids or salts thereof,

[0123] and

[0124] 5) glycerine derivatives, for example glycerine monooleate, 1-(alkylphenoxy)-3-(2-hydroxyethyl)glycerines, 1-(alkylphenoxy)-3-(2,3-dihydroxypropyl)glycerines or 2-carboxyalkyl-1,3-dialkylglycerines.

[0125] The pour point depressants of component (c) are selected from:

[0126] polymethacrylates and alkylated naphthalene derivatives.

[0127] The demulsifiers of component (c) are selected from:

[0128] polyetherpolyols and dinonylnaphthalene-sulfonates.

[0129] The friction modifiers of component (c) are selected from:

[0130] Fatty acids and their derivatives (i.e. natural esters of fatty acids such as glycerol monooleate), amides, imides and amines (i.e. oleylamine), sulfur containing organomolybdenum dithiocarbamates, sulfur-phosphorus containing organomolybdenum dithiophosphates, sulfur-nitrogen containing organomolybdenum compounds based on dispersants, molybdenum carboxylate salts, molybdenum-amine complexes, molybdenum amine/alcohol/amid complexes and molybdenum cluster compounds, Teflon™ and molybdenum disulfide.

[0131] For example, certain additives that are aggressive towards lead are antioxidants, antiwear additives, detergents, copper passivators and friction modifiers.

[0132] For example, certain additives that are aggressive towards lead are sulfur-containing antioxidants, sulfur-con-

taining antiwear additives and sulfur-containing copper passivators; and vegetable oil-derived friction modifiers.

[0133] For example, the sulfur-containing antioxidants aggressive towards lead are phenothiazine antioxidants.

[0134] The additives of component (c) are added in the customary amounts in each case in the range from about 0.01 to about 10.0% by weight, based on the engine oil composition.

[0135] The compounds of the formula (I) can be introduced into the engine oil in manners known per se. The compounds are readily soluble in oils. It is also possible to prepare a so-called additive masterbatch (package) that can be diluted with the corresponding fluid to use concentrations at the rate at which they are required. The compounds of formula (I) may be introduced as part of an additive package.

[0136] In the absence of the present compounds of formula (I), the engine oils comprising components (a) and (c) do not meet or only come close to meeting the lead corrosion specification defined in ASTM D 4485 as measured by ASTM D 6594. That is, the engine oils comprising components (a) and (c), in the absence of the present compounds of formula (I), have in excess of about 100 ppm, about 120 ppm, about 150 ppm, about 180 ppm, or about 210 ppm as measured by ASTM D 6594.

[0137] The invention also relates to a method of preventing corrosion of lead parts that are in the presence of an engine oil composition comprising

[0138] (a) a base fluid and

[0139] (c) at least one oil additive that is aggressive towards lead and which is selected from the group consisting of antioxidants, antiwear additives, dispersants, detergents, antifoam additives, viscosity index improvers, copper passivators, rust inhibitors, pourpoint depressants, demulsifiers and friction modifiers,

[0140] which method comprises incorporating into said engine oil composition

[0141] (b) at least one compound of the formula (I),

[0142] where in the absence of component (b), the engine oil composition exceeds about 100 ppm lead as measured according to test ASTM D 6594.

[0143] The following Examples illustrate the invention in more detail. They are not to be construed as limiting the instant invention in any manner whatsoever.

EXAMPLE 1

ASTM D 6594 Evaluation of Corrosiveness of Diesel Engine Oil at 135° C

[0144] In this test four metal specimens of copper, lead, tin and phosphor bronze are immersed in a measured amount of engine oil. The oil, at 135° C. is blown with air for 168 hours. When the test is completed, the stressed oil is examined to detect corrosion and corrosion products. The presence of copper, lead and tin in the used oil is measured by ICP. A result of less than 50 ppm lead in the stressed oil is desirable.

[0145] A fully formulated, non-corrosive engine oil is used as the base formulation for this example. To demonstrate the effectiveness of the invention, 1.0 weight percent of a friction modifier/corrosion inhibitor, glycerol monooleate (GMO) and 0.5 weight percent of a sulfur-containing anti wear/extreme pressure additive, diterinaryl-trisulfide (TPS® 27), are added separately to the base formulation. These are both tested per ASTM D 6594 with and without 0.2 weight percent of a compound of formula (1): 1-(di-(2-ethylhexyl)aminomethyl)1,2,4-triazole (Irgamet® 30, Ciba Specialty Chem.). The results for lead corrosion generated during the test are shown in the following table:

	No Irgamet 30	With Irgamet 30
1) Base formulation	75 ppm	—
2) (1) plus 1.0% GMO	358 ppm	29 ppm
3) (1) plus 0.5% TPS 27	117 ppm	43 ppm

[0146] Both the GMO and TPS 27 add to the corrosion of the base formulation making it unsuitable for use. In each case, Irgamet 30 reduces the corrosion significantly to very acceptable levels.

What is claimed is:

1. An engine oil composition that is non-aggressive towards lead, which composition comprises
 - a base fluid,
 - (b) at least one compound of the formula (I)

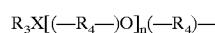


and

(c) at least one oil additive that is aggressive towards lead and which is selected from the group consisting of antioxidants, antiwear additives, dispersants, detergents, antifoam additives, viscosity index improvers, copper passivators, rust inhibitors, pourpoint depressants, demulsifiers and friction modifiers,

where

R₁ and R₂ are the same or different and are C₁-C₂₀ alkyl, C₃-C₂₀ alkenyl, C₅-C₁₂ cycloalkyl, C₇-C₁₃ aralkyl or C₆-C₁₀ aryl, or R₁ and R₂, together with the nitrogen atom to which they are each attached may form a 5-, 6- or 7-membered heterocyclic residue, or R₁ and R₂ are a group of formula



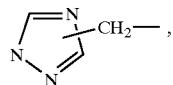
where

X is O, S or N,

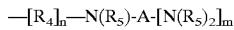
R₃ is hydrogen or C₁-C₂₀ alkyl,

R₄ is C₁-C₁₂ alkylene,

n is 0 or an integer from 1 to 6,
or one of R₁ and R₂ is a group of formula



or R₂ is a group of formula (II) and R₁ is a group of formula



where

m is 0 or 1 and, when m is zero, A is a group of formula (II) and, when m is 1, A is alkylene or C₆-C₁₀ arylene and R₅ is a group of formula (II), and

where in the absence of component (b), the engine oil composition exceeds about 100 ppm lead as measured according to test ASTM D 6594.

2. A composition according to claim 1 in which the compounds of formula (I) are selected from the group consisting of

1-(or 4)-(dimethylaminomethyl) triazole
1-(or 4)-(diethylaminomethyl) triazole
1-(or 4)-(di-isopropylaminomethyl) triazole
1-(or 4)-(di-n-butylaminomethyl) triazole
1-(or 4)-(di-n-hexylaminomethyl) triazole
1-(or 4)-(di-isooctylaminomethyl) triazole
1-(or 4)-(di-(2-ethylhexyl)aminomethyl) triazole
1-(or 4)-(di-n-octylaminomethyl) triazole
1-(or 4)-(di-n-decyldiaminomethyl) triazole
1-(or 4)-(di-n-dodecylaminomethyl) triazole
1-(or 4)-(di-n-octadecylaminomethyl) triazole
1-(or 4)-(di-n-eicosylaminomethyl) triazole
1-(or 4)-[di-(prop-2'-enyl)aminomethyl] triazole
1-(or 4)-[di-(but-2'-enyl)aminomethyl] triazole
1-(or 4)-[di-(eicos-2'-enyl)aminomethyl] triazole
1-(or 4)-(di-cyclohexylaminomethyl) triazole
1-(or 4)-(di-benzylaminomethyl) triazole
1-(or 4)-(di-phenylaminomethyl) triazole
1-(or 4)-(4'-morpholinomethyl) triazole
1-(or 4)-(1'-pyrrolidinomethyl) triazole
1-(or 4)-(1'-piperidinomethyl) triazole
1-(or 4)-(1'-perhydoroazepinomethyl) triazole
1-(or 4)-(2',2"-dihydroxyethyl)aminomethyl] triazole
1-(or 4)-(dibutoxypropyl-aminomethyl) triazole
1-(or 4)-(dibutylthiopropyl-aminomethyl) triazole
1-(or 4)-(di-butylaminopropyl-aminomethyl) triazole

N,N-bis-(1- or 4-triazolylmethyl) laurylamine

N,N-bis-(1- or 4-triazolylmethyl) oleylamine

N,N-bis-(1- or 4-triazolylmethyl) ethanolamine and

N,N,N',N'-tetra(1- or 4-triazolylmethyl) ethylene diamine.

3. A composition according to claim 1 in which the compound of formula (I) is 1-(di-isooctylaminomethyl)-1,2,4-triazole or 1-(di-(2-ethylhexyl)aminomethyl)-1,2,4-triazole.

4. A composition according to claim 1 where in the absence of component (b), the engine oil composition exceeds about 150 ppm lead as measured according to test ASTM D 6594.

5. A composition according to claim 4 where in the absence of component (b), the engine oil composition exceeds about 210 ppm lead as measured according to test ASTM D 6594.

6. A composition according to claim 1 in which component (b) is present from about 0.01 to about 1.0% by weight, based on the weight of the engine oil.

7. A composition according to claim 1 in which component (b) is present from about 0.02 to about 0.5 weight percent, based on the weight of the engine oil.

8. A composition according to claim 1 in which component (b) is present from about 0.03 to about 0.3 weight percent, based on the weight of the engine oil.

9. A composition according to claim 1 in which the additives of component (c) are selected from the group consisting of antioxidants, antiwear additives, detergents, copper passivators and friction modifiers.

10. A composition according to claim 1 in which the additives of component (c) are selected from the group consisting of

the sulfur-containing antioxidants, sulfur-containing antiwear additives and sulfur-containing copper passivators; and

the vegetable oil-derived friction modifiers.

11. A composition according to claim 1 in which the additives of component (c) are selected from the group consisting of phenothiazine antioxidants and vegetable oil-derived friction modifiers.

12. A method of preventing corrosion of lead parts that are in the presence of an engine oil composition comprising

(a) a base fluid and

(c) at least one oil additive that is aggressive towards lead and which is selected from the group consisting of antioxidants, antiwear additives, dispersants, detergents, antifoam additives, viscosity index improvers, copper passivators, rust inhibitors, pourpoint depressants, demulsifiers and friction modifiers,

which method comprises incorporating into said engine oil composition

(b) at least one compound of the formula (I) according to claim 1,

where in the absence of component (b), the engine oil composition exceeds about 100 ppm lead as measured according to test ASTM D 6594.