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(54) Title: ENGINE OILS COMPRISING LEAD CORROSION-INHIBITORS

(57) Abstract: 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 COMPRISING LEAD CORROSION-INHIBITORS

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

U.S. Patent Specification No. 4,734,209 discloses metal deactivators for functional fluids.

5 *U.S. Patent Specification No. 4,491,527* discloses compositions useful for the inhibition of lead paint deposition in lubricants.

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.

10 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.

From 1994 onward, all diesel oils have been required to meet a lead corrosion specification 15 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.

20 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.

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 25 vegetable oil-derived friction modifiers.

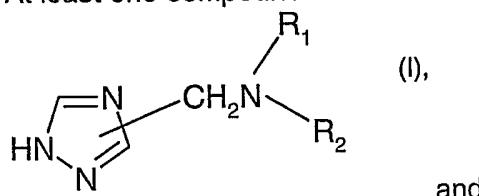
It has surprisingly been found that formulated engine oils that comprise certain 1,2,4-triazole metal deactivators are especially non-aggressive towards lead, for example lead engine parts such as bearings. The engine oils according to this invention meet corrosion protection performance requirements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

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

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.

5 Specifically, the present invention relates to an engine oil composition that is non-aggressive towards lead, which composition comprises

- (a) A base fluid,
- (b) At least one compound of the formula (I)



10 (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, pour-point depressants, demulsifiers and friction modifiers,

where

15 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

20 $\text{R}_3\text{X}[(-\text{R}_4\text{-})\text{O}]_n(-\text{R}_4\text{-})$,

where

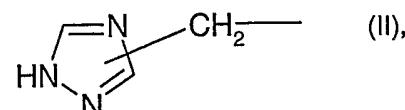
X is O, S or N,

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

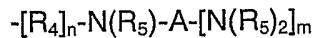
25 R_4 is $\text{C}_1\text{-C}_{12}$ alkylene,

n is 0 or an integer from 1 to 6,

or one of R_1 and R_2 is a group of formula



30 or R_2 is a group of formula (II) and R_1 is a group of formula



where

5 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-C₁₀arylene 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.

R₄ is, for example, a C₁-C₆alkylene group, for example, a C₂-C₃alkylene.

10 The number n is for example, 0, 1, 2, 3, 4, 5 or 6.

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-icosyl.

15 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.

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

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

Aryl is, for example, phenyl or naphthyl.

20 When R₁ and R₂ 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.

Alkylene includes, 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-dodecene.

25 Arylene includes, for example, phenylene and naphthylene.

Specific compounds of present formula (I) include:

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-decylaminomethyl)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;

azole; 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)-(dibutoxypropylaminomethyl)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.

10 A representative 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.

15 The present compounds of formula (I) are prepared by known methods, for example, as disclosed in *U.S. Patent Specification No. 4,734,209*, the disclosure of which is hereby incorporated by reference.

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.

20 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 example, 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 example, 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 25 from about 0.02 to about 0.3 weight percent; for example, from about 0.03 to about 1.0 or from about 0.03 to about 0.5 weight percent.

Suitable antioxidants of component (c) are selected from:

- 1) Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-butyl-4,6-di-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-iso-butylphenol, 2,6-di-cyclopentyl-4-methylphenol, 2-(a-methyl-cyclo-hexyl)-4,6-dimethylphenol, 2,6-di-octadecyl-4-methylphenol, 2,4,6-tri-cyclo-hexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, linear or side chain-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

2) Alkylthiomethylphenols, for example 2,4-di-octylthiomethyl-6-tert-butylphenol, 2,4-di-octylthiomethyl-6-methylphenol, 2,4-di-octylthiomethyl-6-ethylphenol or 2,6-di-dodecylthiomethyl-4-nonylphenol

5 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 10 bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate

4) Tocopherols, for example α -, β -, γ - or δ -tocopherol or mixtures thereof (vitamin E)

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-di-15 methyl-4-hydroxyphenyl) disulfide

15 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-(α -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'-ethylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis(6-(α -methylbenzyl)-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)-20 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-dodecylmercaptopbutane, ethylene glycol bis(3,3-bis(3'-tert-butyl-4'-25 hydroxyphenyl)butyrate), bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclo-pentadiene, 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-dodecylmercaptopbutane or 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)-pentane 30

7) O- N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxy-dibenzyl 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)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide or isoctyl 3,5-di-tert-butyl-4-hydroxy-benzylmercaptoacetate

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

5 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

10 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-hydroxyphenoxy)-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

15 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

20 12) Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide or octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate

25 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-nanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene 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 transesterifica-

30

tion products based on natural triglycerides of, for example, coconut oil, rape seed oil, sunflower oil or colza oil

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

5 15) Ascorbic acid (vitamin C)

10 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,

15 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-butylaminophenol, 4-nanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, di-(4-methoxyphenyl)-amine, 2,6-di-tert-butyl-4-dimethyl-

20 amino-methyl-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

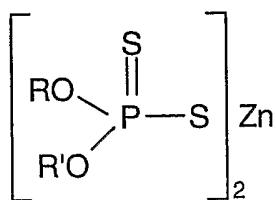
25 dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/ isohexyldiphenylamines, mixtures of mono- and dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octyl-

30 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

17) Aliphatic or aromatic phosphites, esters of thiodipropionic 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-tetra-thiahexadecane.

5 Suitable antiwear additives of component (c) are selected from:

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



10 where R and R' are independently represent C₁-C₂₀alkyl, C₃-C₂₀alkenyl, C₅-C₁₂cyclo-alkyl, C₇-C₁₃aralkyl or C₆-C₁₀aryl, for example R and R' are independently C₁-C₁₂alkyl and

15 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(isopropoxyphosphinothioyl)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)amino-methyl)-2-mercaptop-1H-1,3-benzothiazole or ethoxycarbonyl 5-octyldithiocarbamate.

20 25 Suitable dispersants of component (c) are selected from:

- 1) Mannich bases that are condensation reaction products of a high molecular weight phenol, an alkylene polyamine and an aldehyde such as formaldehyde
- 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 and

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).

Ashless (metal-free) polymeric materials that usually contain an oil soluble high molecular

5 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

10 backbone via a bridge.

Suitable detergents of component (c) are selected from: 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 carbon-

15

Suitable antifoam additives of component (c) are selected from: silicone oils, polysiloxanes and polyethylene glycol ethers.

Suitable viscosity index improvers of component (c) are selected from: polyisobutylene, co-

20 polymers 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.

Suitable copper passivators of component (c) are selected from:

25 1) Benzotriazoles and their derivatives, for example 4- or 5-alkylbenzotriazoles (e.g. tolutriazole) and derivatives thereof, 4,5,6,7-tetrahydrobenzotriazole, 5,5'-methylene-bisbenzotriazole; Mannich bases of benzotriazole or tolutriazole, such as 1-(di(2-ethylhexyl)aminomethyl)tolutriazole and 1-(di-(2-ethylhexyl)aminomethyl)-benzotriazole; alkoxyalkylbenzotriazoles, such as 1-(nonyloxymethyl)-benzotriazole, 1-(1-butoxyethyl)-benzotriazole or 1-(1-cyclohexyloxybutyl)-tolutriazole

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

- 10 -

- 3) Sulfur-containing heterocyclic compounds, for example 2-mercaptobenzothiazole, 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, and
- 4) Amino compounds, for example salicylidenepropylenediamine, salicylaminoguanidine or salts thereof.

5 Suitable rust inhibitors of component (c) are selected from:

- 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 hydroxycarboxylic 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-oleoylsarcosine, sorbitan monooleate, lead naphthenate and alkenylsuccinic anhydrides, for example dodecylsuccinic anhydride, 2-(2-carboxyethyl)-1-dodecyl-3-methylglycerol and its salts, for example, sodium and triethanolamine salts
- 2) Nitrogen-containing compounds selected from:
 - 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, or
 - ii) Heterocyclic compounds, for example: substituted imidazolines or oxazolines, for example, 2-heptadecenyl-1-(2-hydroxyethyl)-imidazoline
- 3) Phosphorus-containing compounds, for example amine salts of phosphoric acid, phosphoric acid partial esters or phosphonic acid partial esters or zinc dialkyldithiophosphates
- 25 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, and
- 5) Glycerol derivatives, for example glycerol monooleate, 1-(alkylphenoxy)-3-(2-hydroxyethyl)glycerols, 1-(alkylphenoxy)-3-(2,3-dihydroxypropyl)glycerols or 2-carboxyalkyl-1,3-dialkylglycerols.

30 Suitable pour point depressants of component (c) are selected from polymethacrylates and alkylated naphthalene derivatives.

Suitable demulsifiers of component (c) are selected from polyetherpolyols and dinonylnaphthalenesulfonates.

Suitable friction modifiers of component (c) are selected from fatty acids and their derivatives, e.g. natural esters of fatty acids such as glycerol monooleate, amides, imides and

5 amines, e.g. 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.

10 Additives that are aggressive towards lead are antioxidants, antiwear additives, detergents, copper passivators or friction modifiers, such as sulfur-containing antioxidants, sulfur-containing antiwear additives, sulfur-containing copper passivators or vegetable oil-derived friction modifiers. For example, the sulfur-containing antioxidants aggressive towards lead are phenothiazine antioxidants.

15 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.

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 master batch (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.

20 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.

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

The following Example illustrates the invention in more detail. They are not to be construed as limiting the instant invention in any manner whatsoever.

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

In this test four metal specimen 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

10 50 ppm lead in the stressed oil is desirable.

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, diteriarytrisulfide (TPS® 27), are added sepa-

15 rately 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:

- 13 -

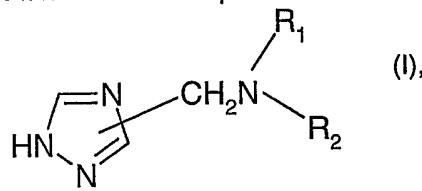
	No IRGAMET 30	With IRGAMET 30
1) Base formulation	75 ppm	-----
2) (1) plus 1.0% GMO	358 ppm	29 ppm
3) (1) plus 0.5% TPS 27	117 ppm	43 ppm

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.

Claims

1. An engine oil composition that is non-aggressive towards lead, which composition comprises

5 a) A base fluid,
b) At least one compound of the formula (I)



and

10 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

15 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



20

where

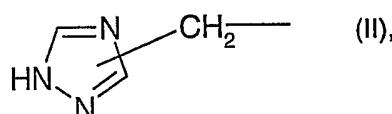
X is O, S or N,

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

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

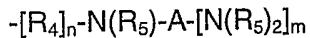
25 n is 0 or an integer from 1 to 6,

or one of R_1 and R_2 is a group of formula



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

30



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 C_6-C_{10} arylene and R_5 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.

- 10 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-isoctylaminomethyl)triazole, 1-(or 4)-(di-(2-ethylhexyl)aminomethyl)triazole, 1-(or 4)-(di-n-octylaminomethyl)triazole, 1-(or 4)-(di-n-decylaminomethyl)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.
- 25 3. A composition according to claim 1 in which the compound of formula (I) is 1-(di-isoctylaminomethyl)-1,2,4-triazole or 1-(di-(2-ethylhexyl)aminomethyl)-1,2,4-triazole. 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.
- 30 4. 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.
5. 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.

6. 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.
7. A composition according to claim 1 in which the additives of component (c) are selected from the group consisting of sulfur-containing antioxidants, sulfur-containing antiwear additives sulfur-containing copper passivators and vegetable oil-derived friction modifiers.
8. 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.
- 10 9. 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.
- 15

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10M141/08 C10M133/44

//(C10M141/08,133:44,135:02,135:04,135:06,135:22),C10N30:10,40:25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 721 979 A (CIBA GEIGY AG) 17 July 1996 (1996-07-17) claims 1,11,18; examples 1,14,17 page 7, line 3 - page 10, line 50 -----	1-8
X	US 6 410 490 B1 (ROHRBACH PETER ET AL) 25 June 2002 (2002-06-25) column 2, line 53 - line 65 column 4, line 22 - line 40 column 7, line 34 - line 43 claims 1-5; examples -----	1-9
A	GB 1 111 680 A (SHELL INT RESEARCH) 1 May 1968 (1968-05-01) the whole document ----- -/-	1-9

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the International filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the International search report

22 January 2004

10 2 03 03

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 734 209 A (PHILLIPS EMYR ET AL) 29 March 1988 (1988-03-29) cited in the application the whole document -----	1-9

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: -

Present claims 1-9 relate to a product or method defined by references to desirable characteristics or properties, namely:

- "(non-)aggressive towards lead".
- "in the absence of compound (b), the engine oil exceeds about 100 ppm lead as measured according to test ASTM D6594".

The claims cover all compositions and compositions comprising a compound having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT for only a very limited number of such compositions. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the composition by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible.

Furthermore, present claims 1-9 also relate to an extremely large number of possible compositions and contain so many possible permutations that a lack of clarity and conciseness within the meaning of Article 6 PCT and a lack of disclosure within the meaning of Article 5 PCT arises to such an extent as to render a meaningful search of the claims impossible.

Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the compositions comprising a base oil, an aminomethyl triazole according to formula (1) and, as compound (c), a partial glycerol fatty acid ester or a sulfurised alkane, as disclosed in the examples, (p. 12).

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/08352

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple Inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

International Application No

PCT/EP 03/08352

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0721979	A	17-07-1996	US	5580482 A	03-12-1996
			AT	216422 T	15-05-2002
			BR	9600084 A	27-01-1998
			CA	2167017 A1	14-07-1996
			DE	69620657 D1	23-05-2002
			DE	69620657 T2	17-10-2002
			EP	0721979 A2	17-07-1996
			ES	2174045 T3	01-11-2002
			FI	960120 A	14-07-1996
			JP	8231976 A	10-09-1996
			ZA	9600242 A	15-07-1996
US 6410490	B1	25-06-2002	CN	1274743 A	29-11-2000
			EP	1054052 A2	22-11-2000
			JP	2000351984 A	19-12-2000
GB 1111680	A	01-05-1968	DE	1594621 A1	01-10-1970
			FR	1502381 A	18-11-1967
			NL	6616840 A	02-06-1967
US 4734209	A	29-03-1988	AU	578274 B2	20-10-1988
			AU	4039985 A	10-10-1985
			BR	8501583 A	03-12-1985
			CA	1249280 A1	24-01-1989
			DE	3572974 D1	19-10-1989
			EP	0160620 A2	06-11-1985
			GB	2156813 A ,B	16-10-1985
			HK	48490 A	29-06-1990
			JP	2594031 B2	26-03-1997
			JP	60237077 A	25-11-1985
			SU	1349699 A3	30-10-1987
			ZA	8502515 A	27-11-1985