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(54) Titre : HUILES DE MOTEUR RENFERMANT DES AGENTS INHIBANT LA CORROSION PAR LE PLOMB
(54) Title: ENGINE OILS COMPRISING LEAD CORROSION-INHIBITORS

(57) **Abrégé/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.



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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.

WO 2004/015043 A1

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.

- 15 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.

- 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.

- 25 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.

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.

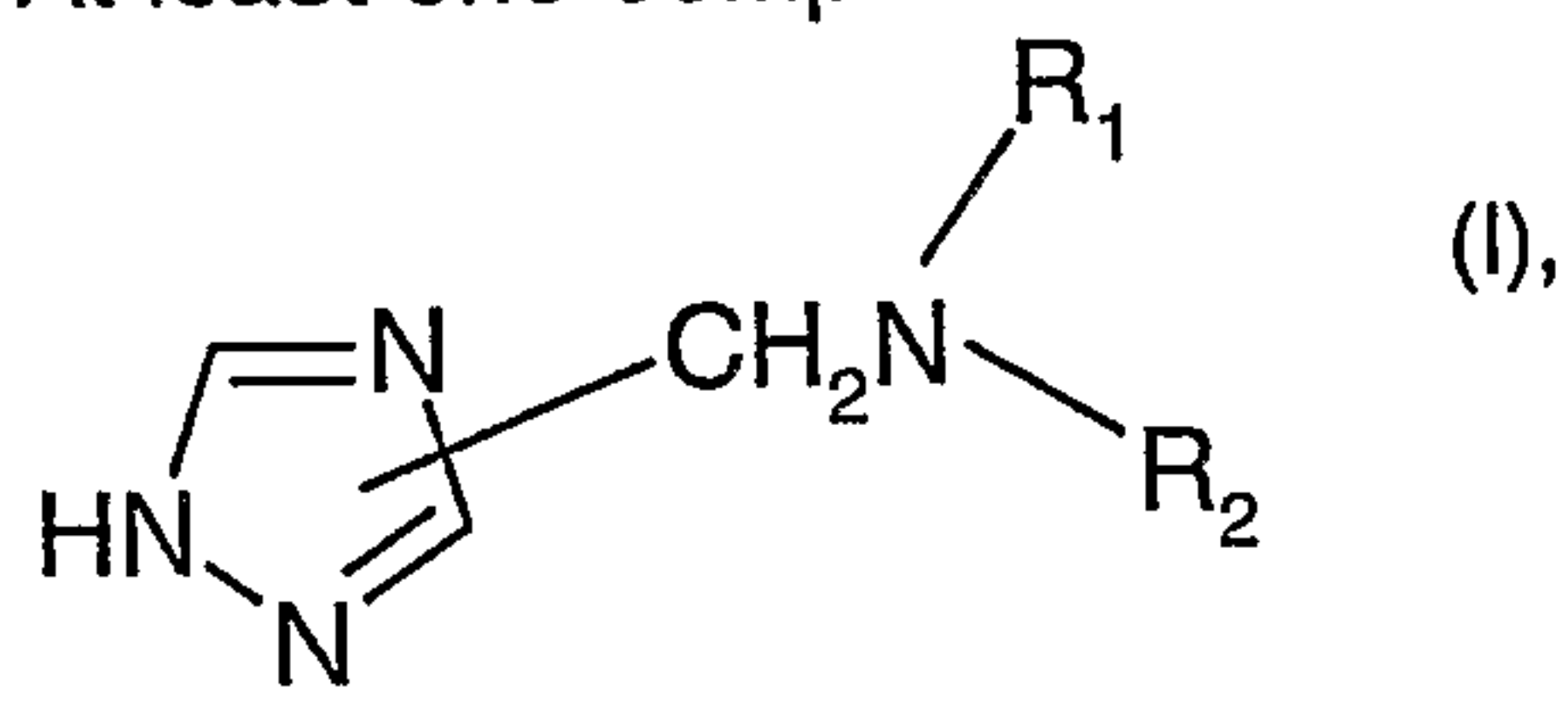
- 2 -

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 C_1 - C_{20} alkyl, C_3 - C_{20} alkenyl, C_5 - C_{12} cycloalkyl, C_7 - C_{13} aralkyl or C_6 - 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 $R_3X[(-R_4)O]_n(-R_4)-$,

where

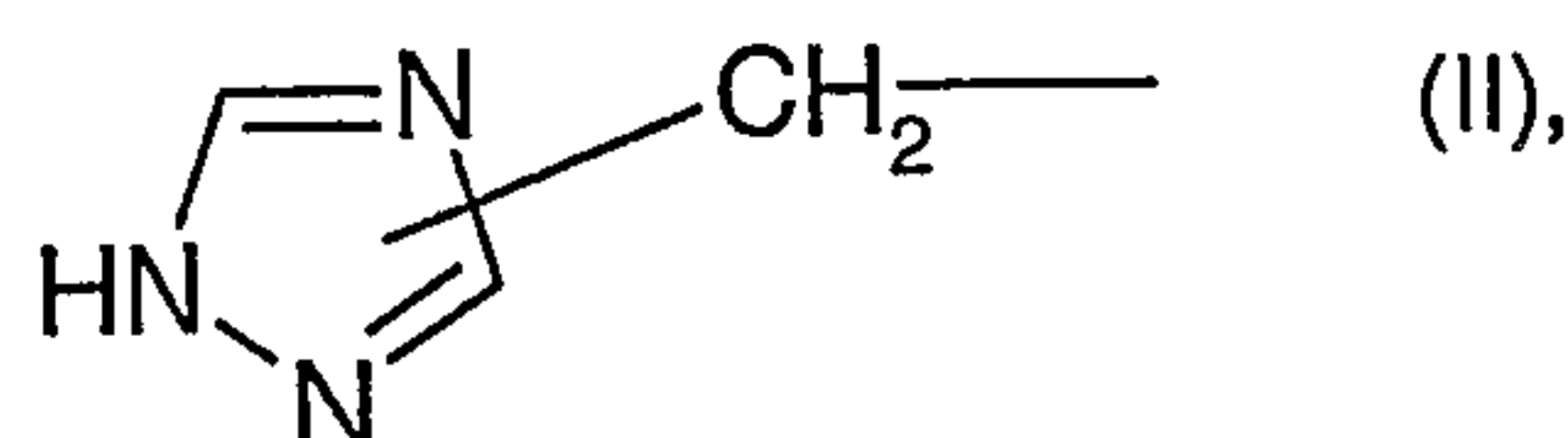
X is O, S or N,

R_3 is hydrogen or C_1 - C_{20} alkyl,

25 R_4 is C_1 - C_{12} alkylene,

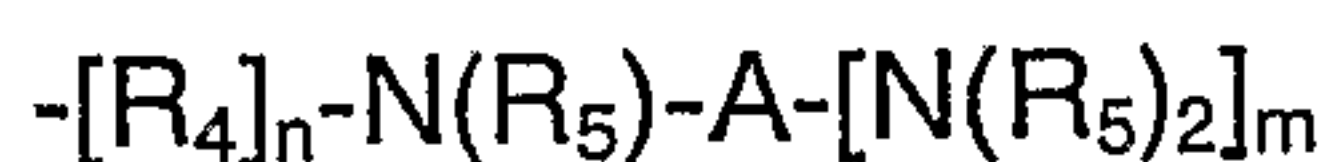
n is 0 or an integer from 1 to 6,

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

- 3 -



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-methylprop-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-dodecylene.

- 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]tri-
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- 4 -

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.

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-dimethylphenol, 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-(α -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 side chain-branched nonylphenols, for example 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methyl-undec-1'-

- 5 -

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

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

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-dimethyl-4-hydroxyphenyl) disulfide

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'-ethylenedibis(4,6-di-tert-butylphenol), 2,2'-ethylenedibis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis(6-(α -methylbenzyl)-4-nonylphenol), 2,2'-methylenebis(6-(α,α -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

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-

- 6 -

butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide or isooctyl 3,5-di-tert-butyl-4-hydroxy-benzylmercaptoacetate

- 8) Hydroxybenzylated malonates, for example dioctadecyl 2,2-bis(3,5-di-tert-butyl-4-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
- 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) Triazine compounds, for example 2,4-bisooctylmercapto-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
- 11) Benzylphosphonates, for example dimethyl 2,5-di-tert-butyl-4-hydroxybenzylphosphonate, 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
- 12) Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide or octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate
- 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, 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-phospha-2,6,7-trioxabicyclo(2.2.2)octane, glycerol or transesterifica-

- 7 -

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

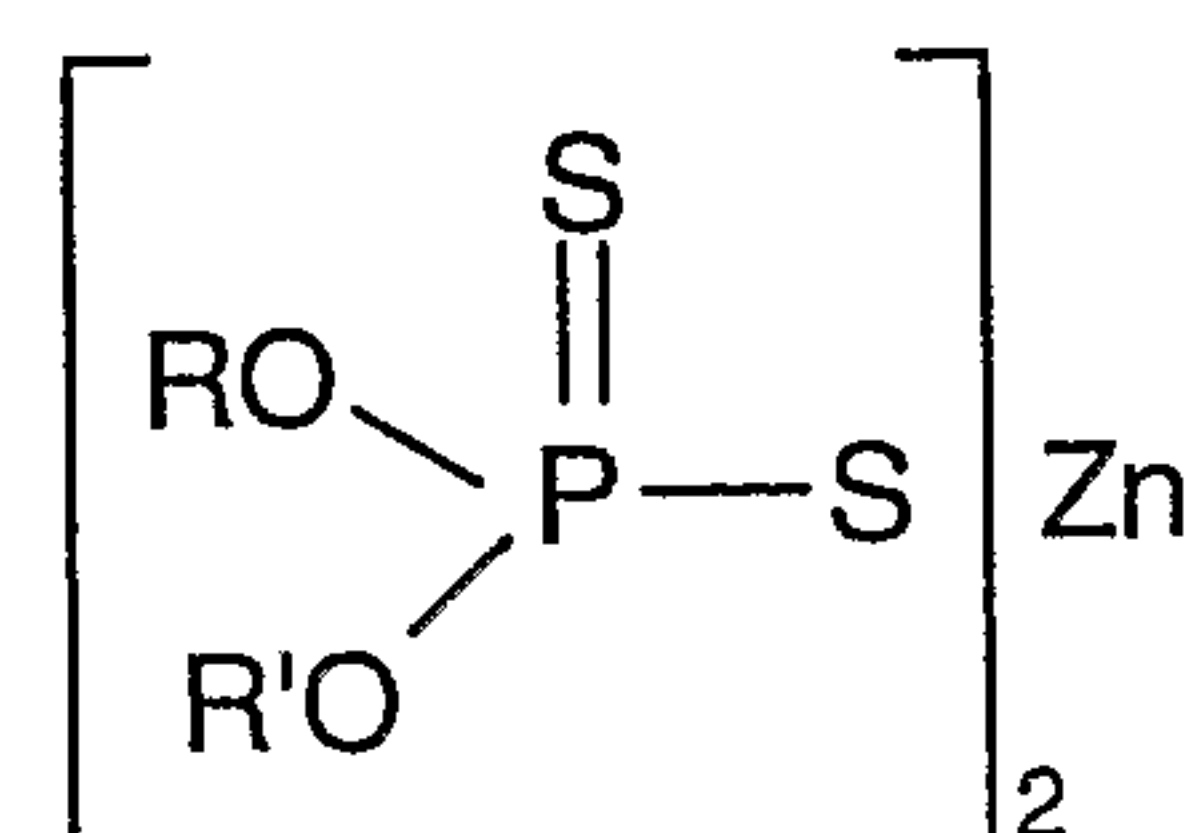
15) Ascorbic acid (vitamin C)

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-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, di-(4-methoxyphenyl)-amine, 2,6-di-tert-butyl-4-dimethyl-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 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-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-C₁₂cycloalkyl, C₇-C₁₃aralkyl or C₆-C₁₀aryl, for example R and R' are independently C₁-C₁₂alkyl and

- 2) Sulfur- and/or phosphorus- and/or halogen-containing compounds, such as sulfurized olefins and vegetable oils, tritoyl phosphate, tricresyl phosphate, chlorinated paraf-
fins, alkyl and aryl di- and trisulfides, amine salts of mono- and dialkyl phosphates,
amine salts of methylphosphonic acid, diethanolaminomethyltolyltriazole, di(2-ethyl-
hexyl)-aminomethyltolyltriazole, derivatives of 2,5-dimercapto-1,3,4-thiadiazole, ethyl
((bisisopropoxyphosphinothioyl)thio)propionate, triphenyl thiophosphate (triphenyl
phosphorothioate), tris(alkylphenyl) phosphorothioates and mixtures thereof (for ex-
ample tris(isononylphenyl) phosphorothioate), diphenylmonononylphenyl phosphoro-
thioate, isobutylphenyl diphenyl phosphorothioate, the dodecylamine salt of 3-hydro-
xy-1,3-thiaphosphetan 3-oxide, trithiophosphoric acid 5,5,5-tris(isooctyl 2-acetate),
derivatives of 2-mercaptobenzothiazole, such as 1-(N,N-bis(2-ethylhexyl)amino-
methyl)-2-mercapto-1H-1,3-benzothiazole or ethoxycarbonyl 5-octyldithiocarbamate.

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 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.

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 carbonates.

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, 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.

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

- 1) Benzotriazoles and their derivatives, for example 4- or 5-alkylbenzotriazoles (e.g. tolutriazole) and derivatives thereof, 4,5,6,7-tetrahydrobenzotriazole, 5,5'-methylenebisbenzotriazole; 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
- 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.

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 dodecenylsuccinic 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
- 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.

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

- 11 -

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 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.

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.

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)

- 12 -

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, dithionyltrisulfide (TPS[®] 27), are added separately to the base formulation. These are both tested per ASTM D 6594 with and without 0.2
15 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 |

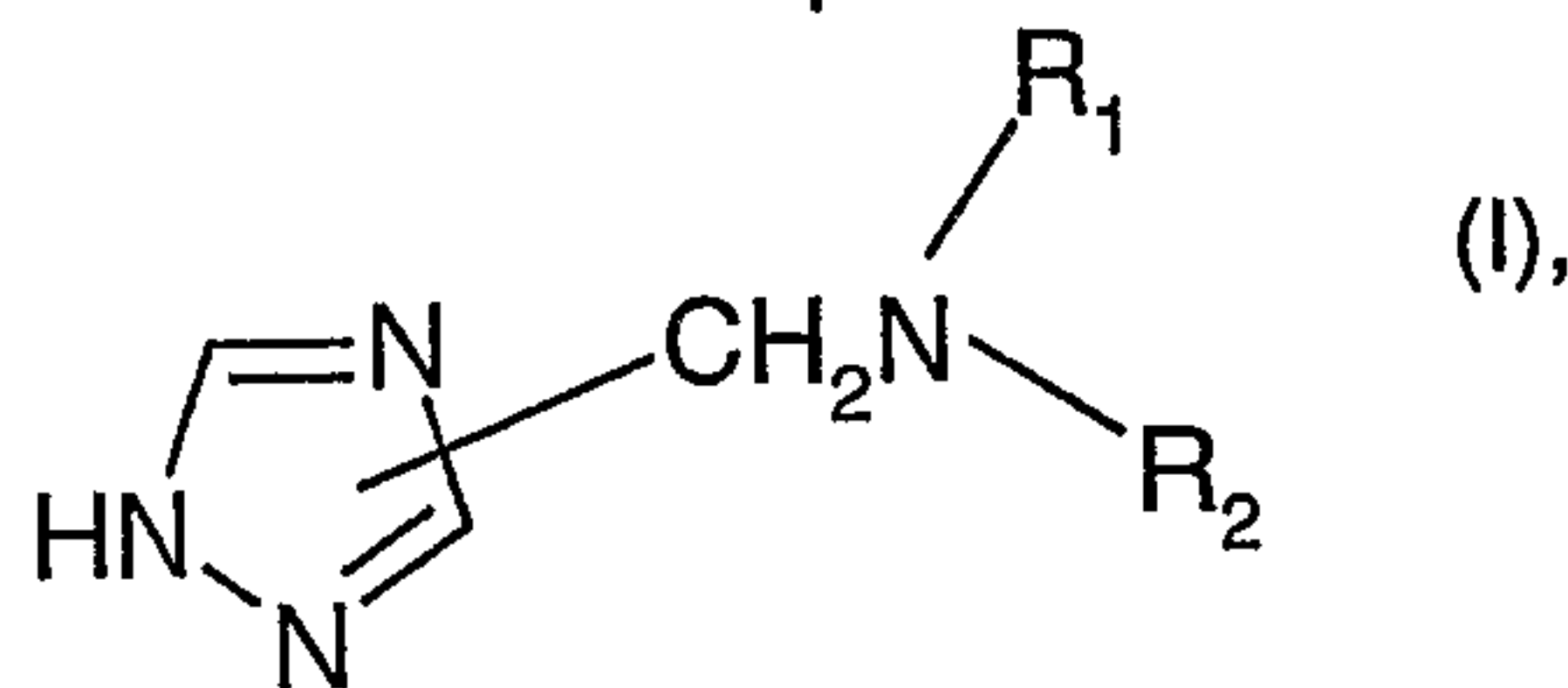
Both the GMO and TPS 27 add to the corrosion of the base formulation making it unsuitable for use. In each case, IRGAMET 30 reduces the corrosion significantly to very acceptable levels.

Claims

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

a) A base fluid,

b) At least one compound of the formula (I)



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

R_1 and R_2 are the same or different and are C_1 - C_{20} alkyl, C_3 - C_{20} alkenyl, C_5 - C_{12} cycloalkyl, C_7 - C_{13} aralkyl or C_6 - 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



where

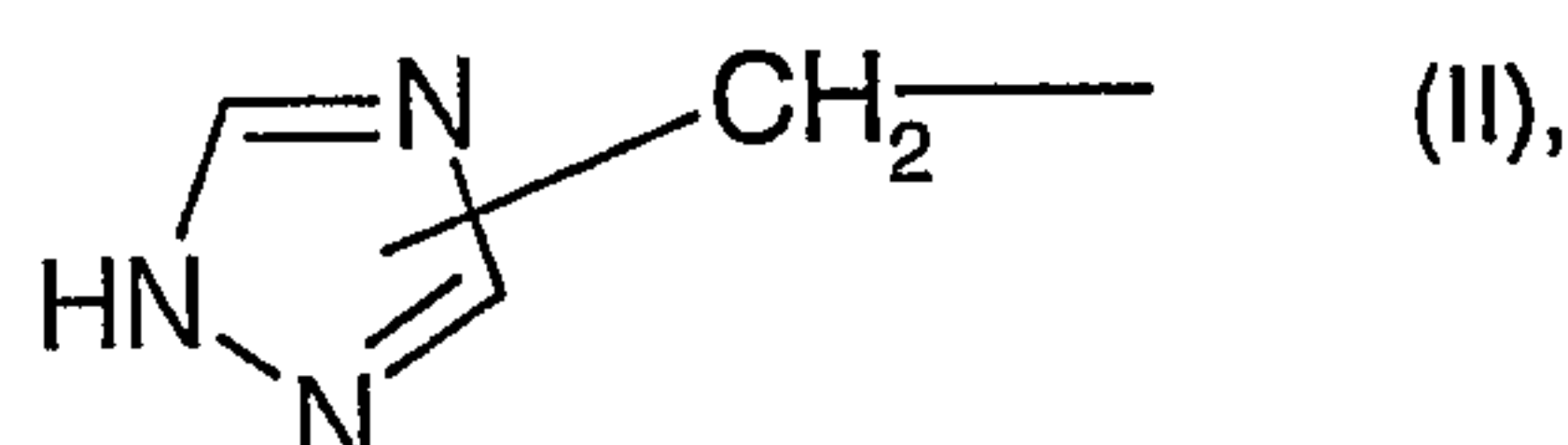
X is O, S or N,

R_3 is hydrogen or C_1 - C_{20} alkyl,

R_4 is C_1 - C_{12} alkylene,

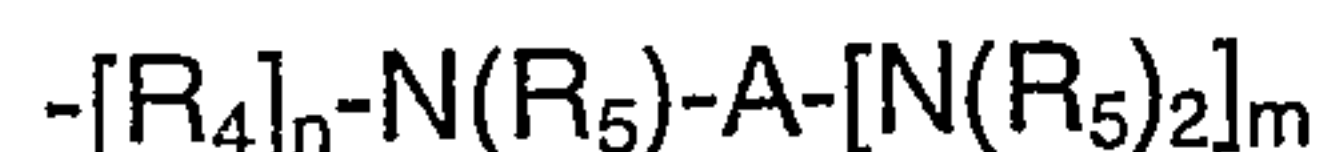
n is 0 or an integer from 1 to 6,

or one of R_1 and R_2 is a group of formula



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

- 15 -



where

m is 0 or 1 and, when m is zero, A is a group of formula (II) and,

5 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.

- 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)-(diisopropylaminomethyl)triazole, 1-(or 4)-(di-n-butylaminomethyl)triazole, 1-(or 4)-(di-n-hexylaminomethyl)triazole, 1-(or 4)-(diisooctylaminomethyl)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)-(dicyclohexylaminomethyl)triazole, 1-(or 4)-(dibenzylaminomethyl)triazole, 1-(or 4)-(diphenylaminomethyl)triazole, 1-(or 4)-(4'-morpholinomethyl)triazole, 1-(or 4)-(1'-pyrrolidinomethyl)triazole, 1-(or 4)-(1'-piperidinomethyl)triazole, 1-(or 4)-(1'-perhydrazepinomethyl)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.
- 15
- 20
- 25
- 30 3. A composition according to claim 1 in which the compound of formula (I) is 1-(diisooctylaminomethyl)-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.
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.

- 16 -

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.
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.