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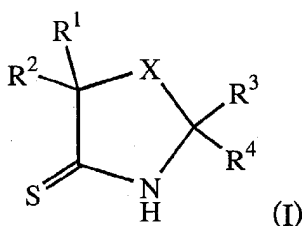
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AL LT LV MK(30) Priority: **07.08.2002 US 401542 P**(71) Applicant: **ROHM AND HAAS COMPANY****Philadelphia, Pennsylvania 19106-2399 (US)**(72) Inventor: **Mukkala, Ravindranath****Lansdale Pennsylvania 19446 (US)**(74) Representative: **Kent, Venetia Katherine****Rohm and Haas (UK) Ltd****European Operations Patent Dept.****Lennig House****2 Mason's Avenue****Croydon, CR9 3NB (GB)**(54) **Cyclic thioamides as additives for lubricating oils**

(57) A composition comprising: (a) from 0.1% to 20% of at least one cyclic thioamide of formula I:



wherein X is CR⁵R⁶, CR⁵R⁶NR⁷ or CR⁵R⁶CR⁸R⁹; R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ are independently hydrogen, alkyl, alkenyl, aryl or aralkyl; or R¹ and R², or R³ and R⁴, combine with the carbon atom to which they are attached to form an alkyl or alkenyl ring; and (b) a lubricating oil.

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DescriptionBackground

[0001] This invention relates generally to cyclic thioamides useful as additives for lubricating oils.

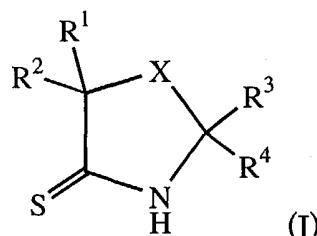
[0002] Zinc dialkyldithiophosphates (ZDDP) are widely used as lubricant additives. The principal disadvantages of these compounds are that an ash residue is produced by the zinc as the additive is consumed, and that phosphorus is known to affect the efficiency of catalytic converters in motor vehicles, thereby causing emissions problems. Cyclic compounds useful as lubricant additives are disclosed in U.S. Patent No. 6,187,722. However, the compounds disclosed therein are imidazolidinethiones which are not within the scope of the present invention.

[0003] The problem addressed by this invention is to find additional non-metallic, non-phosphorus-containing oil-soluble additives for lubricating oils.

Statement of Invention

[0004] The present invention is directed to a composition comprising:

(a) from 0.1% to 20% of at least one cyclic thioamide of formula I:



wherein X is CR^5R^6 , $\text{CR}^5\text{R}^6\text{NR}^7$ or $\text{CR}^5\text{R}^6\text{CR}^8\text{R}^9$; R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 and R^9 are independently hydrogen, alkyl, alkenyl, aryl or aralkyl; or R^1 and R^2 , or R^3 and R^4 , combine with the carbon atom to which they are attached to form an alkyl or alkenyl ring; and

(b) a lubricating oil.

[0005] The present invention is further directed to a method for improving the anti-wear characteristics of a lubricating oil by adding from 0.1% to 20% of a compound of formula I.

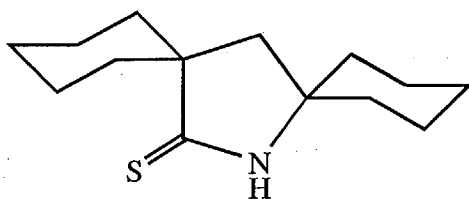
[0006] The present invention is further directed to a lubricating oil composition containing the reaction product of a compound of formula (I) with an imine; an unsaturated carboxylic acid or ester; an isocyanate or isothiocyanate; or an alkyl, alkenyl or aralkyl group bearing a leaving group; and to the aforementioned reaction products.

Detailed Description

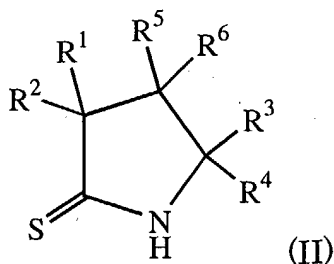
[0007] All percentages are weight percentages based on the entire composition described, unless specified otherwise. An "alkyl" group is a saturated hydrocarbyl group having from one to twenty-two carbon atoms in a linear, branched or cyclic arrangement, and having from 0 to 2 oxygen, nitrogen or sulfur atoms. Substitution on alkyl groups of one or more halo, hydroxy, alkoxy, alkanoyl or amido groups is permitted; alkoxy, alkanoyl and amido groups may in turn be substituted by one or more halo substituents. In one preferred embodiment, alkyl groups contain from two to twelve carbon atoms and from 0 to 1 oxygen, nitrogen or sulfur atoms; in another preferred embodiment, alkyl groups contain from 4 to 22 carbon atoms; in another preferred embodiment, alkyl groups contain no heteroatoms. An "alkenyl" group is an "alkyl" group in which at least one carbon-carbon single bond has been replaced with a double bond. An "aryl" group is a substituent derived from an aromatic compound, including heterocyclic aromatic compounds having heteroatoms chosen from among nitrogen, oxygen and sulfur. An aryl group has a total of from five to twenty ring atoms, and has one or more rings which are separate or fused. Substitution on aryl groups of one or more halo, alkyl, alkenyl, hydroxy, alkoxy, alkanoyl or amido groups is permitted, with substitution by one or more halo groups being possible on alkyl, alkenyl, alkoxy, alkanoyl or amido groups. An "aralkyl" group is an "alkyl" group substituted by an "aryl" group. A "lubricating oil" is a natural or synthetic oil, or a mixture thereof, having suitable viscosity for use as a lubricant, e. g., as crankcase oil in an internal combustion engine, automatic transmission fluid, turbine lubricant, gear lubricant, compressor lubricant, metal-working lubricant, hydraulic fluid, etc.

[0008] Preferably, at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 and R^9 is alkyl, alkenyl, aryl or aralkyl or R^1 and R^2 , or R^3 and R^4 , combine with the carbon atom to which they are attached to form an alkyl or alkenyl ring; more preferably at least two of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 and R^9 are alkyl, alkenyl, aryl or aralkyl. In one embodiment of the invention at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 and R^9 is aryl, aralkyl, C_4 - C_{22} alkyl or C_4 - C_{22} alkenyl; more preferably at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 and R^9 is C_4 - C_{22} alkyl or C_4 - C_{22} alkenyl; and most preferably at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 and R^9 is C_6 - C_{22} alkyl. The composition of the present invention includes at least one compound of formula (I). In one embodiment of the invention, the composition contains at least two compounds of formula (I), and more preferably contains at least three compounds of formula (I).

[0009] In one embodiment of the invention, R^1 and R^2 , or R^3 and R^4 , combine with the carbon atom to which they are attached to form an alkyl or alkenyl ring, preferably a C_5 - C_8 alkyl or alkenyl ring, most preferably a C_5 - C_6 alkyl ring. In this embodiment, either or both pairs of substituents, R^1 and R^2 , or R^3 and R^4 , become a difunctional alkyl or alkenyl group linked to the cyclic thioamide ring carbon to form an alkyl or alkenyl ring, resulting in a mono- or di-spiro- compound. For example, when X is CH_2 ; and R^1 and R^2 , and R^3 and R^4 combine with a ring carbon atom to form a C_6 alkyl ring, the following structure results:

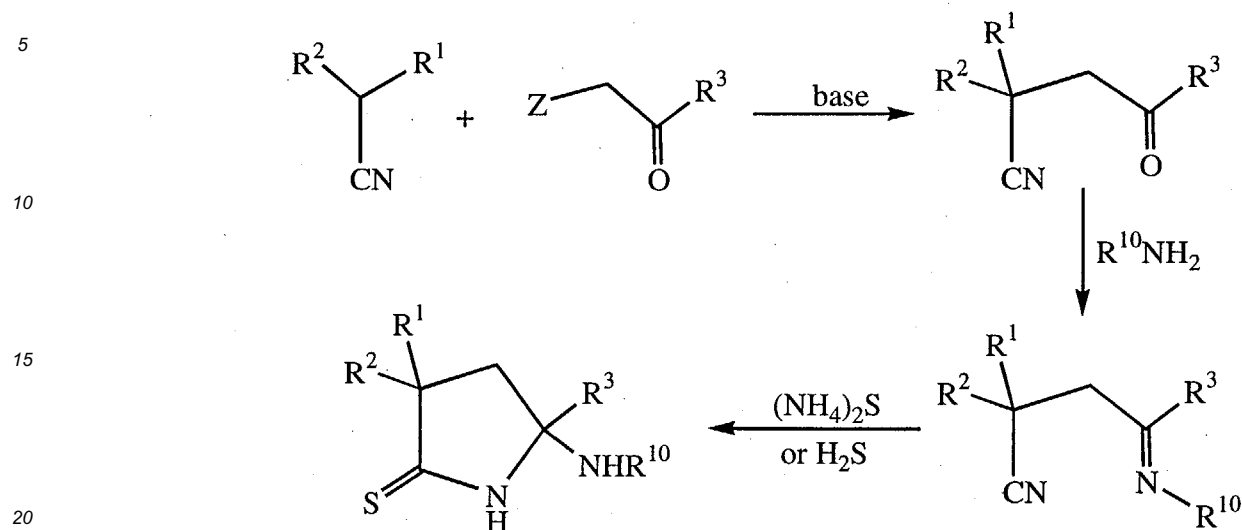


[0010] In one embodiment of the invention, X is CR^5R^6 , and the compound of formula (I) can be represented by formula (II)



Preferably, at least one of R^1 , R^2 , R^3 , R^4 , R^5 and R^6 is alkyl, alkenyl, aryl or aralkyl, or R^1 and R^2 , or R^3 and R^4 , combine with the carbon atom to which they are attached to form a C_5 - C_8 alkyl or alkenyl ring. In a preferred embodiment of the invention, R^4 is $R^{10}NH$, and R^{10} is alkyl, alkenyl, aryl or aralkyl. The compound of this embodiment can be prepared from an alkyl nitrile, a ketone bearing a leaving group at the α -position, and an amine, in a three-step process, as shown below in Scheme 1 for the embodiment in which R^5 and R^6 are hydrogen:

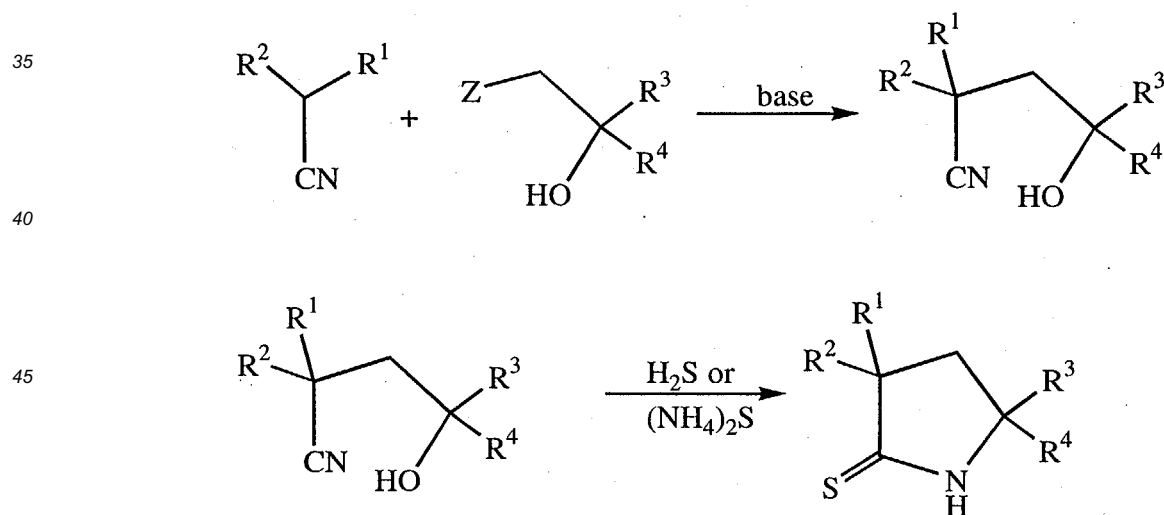
Scheme 1



wherein Z represents a suitable leaving group, including, but not limited to iodide, bromide, chloride, tosylate, mesylate or triflate. Preferably, R³ is alkyl, alkenyl, aryl or aralkyl. Preferably, R¹, R² and R³ contain no amine nitrogen atoms. Preferably, at least one of R¹, R², R³ and R¹⁰ is aryl, aralkyl, C₄-C₂₂ alkyl or C₄-C₂₂ alkenyl; more preferably C₆-C₂₂ alkyl or C₆-C₂₂ alkenyl; and most preferably C₁₀-C₂₂ alkyl. Use of a more highly substituted ketone starting material will result in a product in which one or both of R⁵ and R⁶ are not hydrogen.

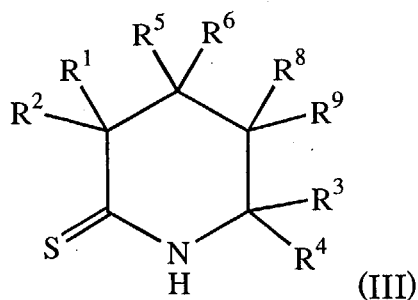
[0011] In one embodiment of the invention, a compound of formula (I) in which X is CH₂ is prepared from a 1,2-halohydrin, an alkyl nitrile and a sulfide salt, in a two-step process, as shown below in Scheme 2:

Scheme 2



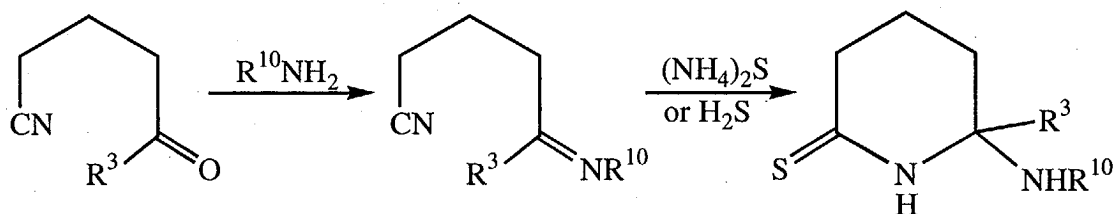
wherein Z represents a suitable leaving group, including, but not limited to iodide, bromide, chloride, tosylate, mesylate or triflate. The process can also be performed with substituted starting material to produce a compound in which X is CR⁵R⁶, and R⁵ and R⁶ are not hydrogen.

[0012] In another embodiment of the invention, X is CR⁵R⁶CR⁸R⁹ and the compound of formula (I) can be represented by formula (III)



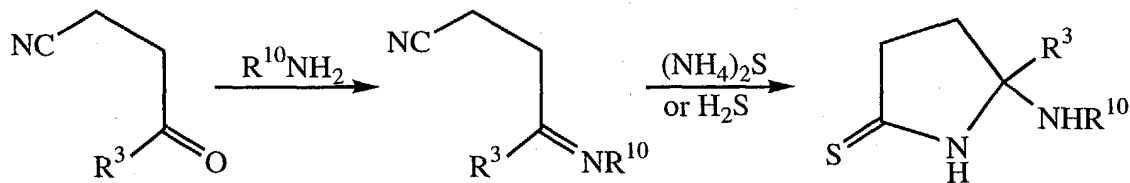
Preferably, at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^8 and R^9 is alkyl, alkenyl, aryl or aralkyl, or R^1 and R^2 , or R^3 and R^4 , combine with the carbon atom to which they are attached to form a C_5 - C_8 alkyl or alkenyl ring. In a preferred embodiment of the invention, R^4 is $R^{10}NH$, and R^{10} is alkyl, alkenyl, aryl or aralkyl. Preferably, R^3 is alkyl, alkenyl, aryl or aralkyl. Preferably, R^3 contains no amine nitrogen atoms. Preferably, at least one of R^3 and R^4 is aryl, aralkyl, C_4 - C_{22} alkyl or C_4 - C_{22} alkenyl; more preferably C_6 - C_{22} alkyl or alkenyl; and most preferably C_{10} - C_{22} alkyl. In one embodiment of the invention, R^1 , R^2 , R^5 , R^6 , R^8 and R^9 are hydrogen, and the compound of formula (III) is prepared according to the following two-step process

Scheme 3

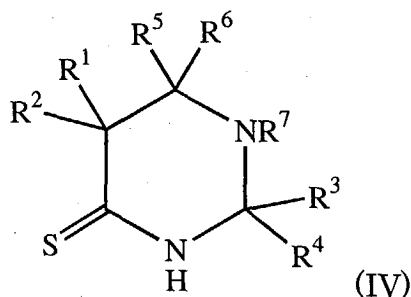


This process also may be performed with various R groups on the starting material to give substituted versions of the product in which some or all of R^1 , R^2 , R^5 , R^6 , R^8 and R^9 are not hydrogen. The process also is capable of producing the five-membered analog of the product, i.e., X is CR^5R^6 , with or without substituents on the ring carbons. This is illustrated below in Scheme 4 for the embodiment in which R^1 , R^2 , R^5 and R^6 are hydrogen:

Scheme 4

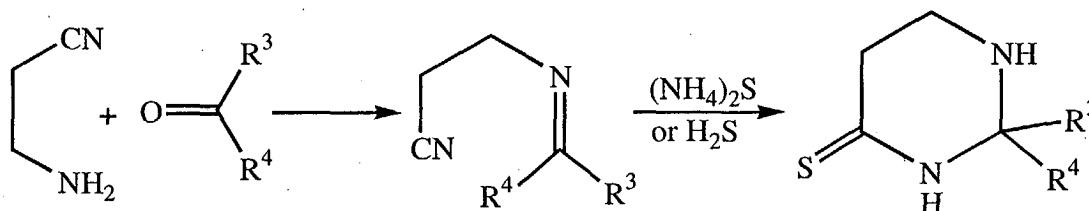


[0013] In another embodiment of the invention, X is $CR^5R^6NR^7$ and the compound of formula (I) can be represented by formula (IV)



Preferably, at least one of R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ is alkyl, alkenyl, aryl or aralkyl, or R¹ and R², or R³ and R⁴, combine with the carbon atom to which they are attached to form a C₅-C₈ alkyl or alkenyl ring. In a preferred embodiment, R¹, R², R⁵, R⁶ and R⁷ are hydrogen, and the compound of formula (IV) is prepared according to the following two-step process

Scheme 5



This process also may be performed with various R groups on the starting material, or with subsequent alkylation on the amine nitrogen, to give substituted versions of the product in which some or all of R¹, R², R⁵, R⁶ and R⁷ are not hydrogen. Preferably, at least one of R³ and R⁴ is alkyl, alkenyl, aryl or aralkyl; more preferably at least one of R³ and R⁴ is aryl, aralkyl, C₄-C₂₂ alkyl or C₄-C₂₂ alkenyl; more preferably C₆-C₂₂ alkyl or C₆-C₂₂ alkenyl; and most preferably C₁₀-C₂₂ alkyl. Preferably, R³ and R⁴ contain no amine nitrogen atoms.

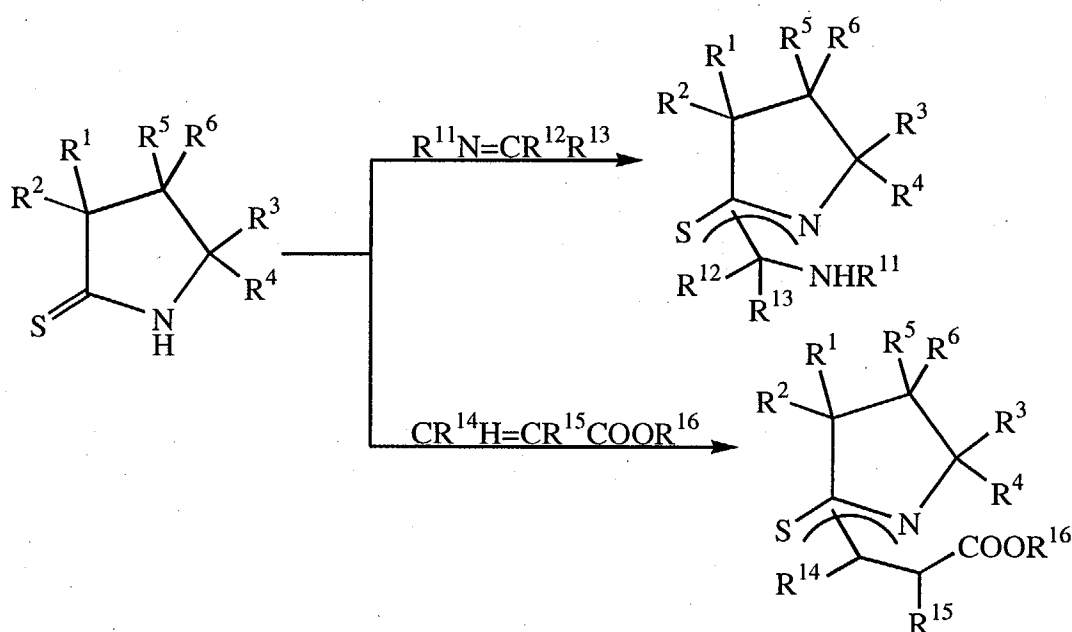
[0014] In a preferred embodiment of the invention, the thioamide group or an amine group of the compound of formula (I) is further functionalized by reaction with imines of formula R¹¹N=CR¹²R¹³; unsaturated carboxylic esters of formula CHR¹⁴=CR¹⁵COOR¹⁶; isocyanates, R¹⁸NCO, or isothiocyanates, R¹⁸NCS; or R¹⁷Y; wherein R¹², R¹³ and R¹⁶ independently are hydrogen, alkyl, alkenyl, aryl or aralkyl; R¹⁷ is alkyl, alkenyl or aralkyl; R¹⁴ and R¹⁵ independently are hydrogen or C₁-C₄ alkyl; R¹¹ and R¹⁸ independently are alkyl, alkenyl, aryl or aralkyl; and Y is a suitable leaving group capable of being displaced by the nitrogen or the sulfur of a thioamide group, or by a primary or secondary amine nitrogen. Suitable leaving groups include, e.g., iodide, bromide, chloride, tosylate, mesylate or triflate. Functionalization of the thioamide group can occur on the thioamide nitrogen or the thioamide sulfur, provided of course that the thioamide nitrogen bears at least one hydrogen. The product also can be a mixture of the compound functionalized on the nitrogen and the one functionalized on the sulfur. In compounds also having a primary or secondary amino group, functionalization also may occur solely or partially on the amino group.

[0015] Preferably, R¹⁴ and R¹⁵ independently are hydrogen or methyl. Preferably, the compound of formula CHR¹⁴=CR¹⁵COOR¹⁶ is an alkyl or aralkyl acrylate having R¹⁴=R¹⁵=H and R¹⁶=alkyl or aralkyl; or a methacrylate ester having R¹⁴=H and R¹⁵=CH₃; or a crotonate ester having R¹⁵=H and R¹⁴=CH₃. Preferably, R¹⁴ is hydrogen. Preferably, R¹⁶ is alkyl or aralkyl, most preferably C₄-C₂₂ alkyl. Preferably, R¹⁸ is aryl, alkyl or aralkyl, most preferably C₈-C₂₂ alkyl. Preferably, R¹¹ is C₁₂-C₂₂ alkyl. In one embodiment, R¹¹ is derived from an unsubstituted C₁₆-C₂₂ alkyl amine, R¹¹NH₂, preferably one which is an oil-soluble amine. In one embodiment, the alkyl amine is a tertiary alkyl primary amine, i.e., a primary amine in which the alkyl group is attached to the amino group through a tertiary carbon. Examples of commercially available tertiary alkyl primary amines are the Primene™ amines available from Rohm and Haas Company, Philadelphia, PA. Preferably, R¹² and R¹³ independently are alkyl or hydrogen. In a preferred embodiment of the invention, R¹¹N=CR¹²R¹³ is a formaldehyde imine, R¹¹N=CH₂. Preferably, R¹⁷ is C₄-C₂₂ alkyl, C₄-C₂₂ alkenyl or aralkyl; more preferably C₆-C₂₂ alkyl or C₆-C₂₂ alkenyl; and most preferably C₈-C₂₂ alkyl.

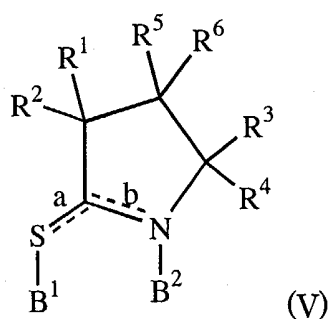
[0016] As an example, the reaction of the compound of formula (II) with an imine and an acrylate is illustrated below

in Scheme 6.

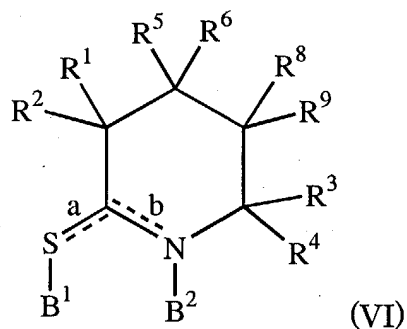
Scheme 6



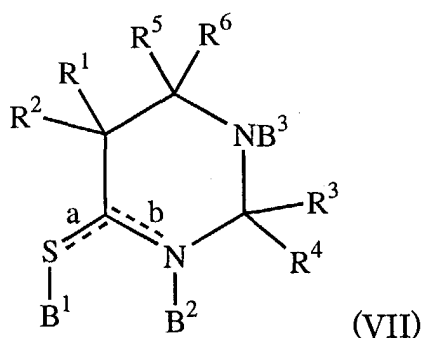
[0017] The compound resulting from functionalization of the thioamide group in the compound of formula (II) can be represented by formula (V).



wherein bonds a and b are single or double bonds, provided that one of a and b is a single bond and the other is a double bond; one of B¹ and B² is $-CR^{14}H-CR^{15}H-COOR^{16}$, $-CR^{12}R^{13}NHR^{11}$, $-C(O)NHR^{18}$, $-C(S)NHR^{18}$ or R¹⁷, and the other is absent. When B¹ is present, bond "b" is a double bond; and when B² is present, bond "a" is a double bond. An analogous structure exists for the compound resulting from functionalization of the compound of formula (III), in which functionalization also occurs on the thioamide nitrogen or sulfur, as shown in formula (VI).



The compound resulting from functionalization of the thioamide group and/or a secondary amino group in the compound of formula (IV) can be represented by formula (VII).



wherein B³ represents R⁷, -CR¹⁴H-CR¹⁵H-COOR¹⁶, -CR¹²R¹³NHR¹¹, -C(O)NHR¹⁸, -C(S)NHR¹⁸ or R¹⁷. If R⁷ in formula (IV) is not hydrogen, then functionalization at the NR⁷ amino group would not occur, and B³ would simply be R⁷. Other primary or secondary amino groups in formulas (II), (III) or (IV) can be functionalized in this way, e.g., when R⁴ is R¹⁰NH, the R¹⁰NH amino group can be functionalized.

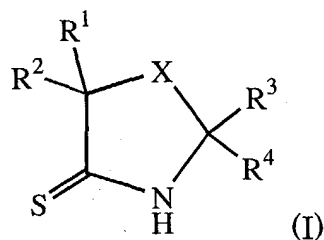
[0018] Preferably, the compound(s) of formula (I) is present in a lubricating oil in a total amount of at least 0.2%, more preferably at least 0.3%, and most preferably at least 0.4%. Preferably, the compound(s) of formula (I) is present in a lubricating oil in a total amount no greater than 10%, more preferably no greater than 5%, and most preferably no greater than 2%. Preferably, the compounds are soluble at the aforementioned levels.

[0019] Optionally, other additives typically used in lubricating oils are present in the composition. Such additives include, but are not limited to, other anti-wear additives, anti-corrosion additives, dispersants, detergents, antioxidants, antifoamants, friction modifiers, seal swell agents, demulsifiers, viscosity index improvers and pour point depressants. Other anti-wear additives that can be used in combination with the compound of formula (I) include the commercial products known as ZDDP, which are zinc dialkyldithiophosphates. In addition to improving the anti-wear characteristics of lubricating oils, the compound of formula (I) typically also improves anti-corrosion characteristics and functions as an anti-oxidant.

Claims

1. A composition comprising:

(a) from 0.1% to 20% of at least one cyclic thioamide of formula I:



wherein X is CR⁵R⁶, CR⁵R⁶NR⁷ or CR⁵R⁶CR⁸R⁹; R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ are independently hydrogen, alkyl, alkenyl, aryl or aralkyl; or R¹ and R², or R³ and R⁴, combine with the carbon atom to which they are attached to form an alkyl or alkenyl ring; and
(b) a lubricating oil.

2. The composition of claim 1 in which X is CR⁵R⁶, and at least one of R¹, R², R³, R⁴, R⁵ and R⁶ is alkyl, alkenyl, aryl or aralkyl, or R¹ and R², or R³ and R⁴, combine with the carbon atom to which they are attached to form a C₅-C₈ alkyl or alkenyl ring.
3. The composition of claim 2 in which R⁴ is R¹⁰NH, and R¹⁰ is alkyl, alkenyl, aryl or aralkyl.
4. The composition of claim 1 in which X is CR⁵R⁶CR⁸R⁹, and at least one of R¹, R², R³, R⁴, R⁵, R⁶, R⁸ and R⁹ is alkyl, alkenyl, aryl or aralkyl, or R¹ and R², or R³ and R⁴, combine with the carbon atom to which they are attached to form a C₅-C₈ alkyl or alkenyl ring.
5. The composition of claim 4 in which R⁴ is R¹⁰NH, and R¹⁰ is alkyl, alkenyl, aryl or aralkyl.
6. The composition of claim 1 in which X is CR⁵R⁶NR⁷, and at least one of R¹, R², R³, R⁴, R⁵ and R⁶ is alkyl, alkenyl, aryl or aralkyl, or R¹ and R², or R³ and R⁴, combine with the carbon atom to which they are attached to form a C₅-C₈ alkyl or alkenyl ring.
7. The composition of claim 6 in which R⁷ is hydrogen, and at least one of R³ and R⁴ is alkyl, alkenyl, aryl or aralkyl.
8. The composition of claim 1 in which at least one of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ is aryl, aralkyl, C₄-C₂₂ alkyl or C₄-C₂₂ alkenyl.
9. The composition of claim 1 which comprises at least two cyclic thioamide compounds of formula (I).
10. The method of claim 9 in which said at least two cyclic thioamide compounds are present in a total amount from 0.2% to 5%.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 03 25 4690

DOCUMENTS CONSIDERED TO BE RELEVANT			
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The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 20 November 2003	Examiner Steendijk, M
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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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