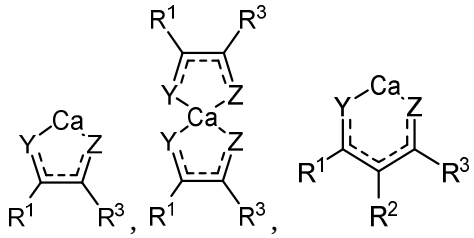
CLAIMS

1. A method of preventing or reducing low speed pre-ignition events in an internal combustion engine having a crankcase, comprising contacting the crankcase with a lubricating composition comprising a base oil and at least one cyclic calcium chelate complex.
2. The method of claim 1, wherein the internal combustion engine experiences no more than 90%, no more than 80%, no more than 70%, no more than 60%, no more than 50%, no more than 40%, no more than 30%, no more than 20%, no more than 10%, or no more than 5% of the low speed pre-ignition events experienced by an internal combustion engine lubricated with an otherwise same lubricating composition that do not include the calcium cyclic chelate complex.
3. A method of reducing or preventing corrosion in an internal combustion engine having a crankcase, comprising contacting the crankcase with a lubrication composition comprising a base oil and at least one cyclic calcium chelate complex.

4. The method according to any preceding claim, wherein the calcium chelate complex comprises a ligand comprising at least one 1,3-dicarbonyl compound, a 1,3-ketophenol, a 1,3-diimine, or ortho-ketophenol.
5. The method according to any preceding claim, wherein the calcium chelate complex comprising a complex having the formula:



wherein:

⁞ independently represents a single or double bond, provided that valence is satisfied;

Y is indepedently selected from O, S, or NR^{n1};

Z is independently selected from O, S, or NR^{n2}; and

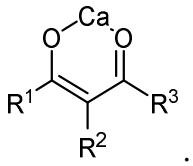
R^1, R^2, R^3, R^{n1}, and R^{n2} are independently selected from R^a, OR^b, and $N(R^b)_2$;

wherein R^a is in each case independently selected from hydrogen, C_{1-8}alkyl, C_{2-8}alkenyl, C_{2-8}alkynyl, aryl, C_{1-8}heteroaryl, C_{3-8}cycloalkyl, or C_{1-8}heterocyclyl;

R^b is in each case independently selected from C_{1-8}alkyl, C_{2-8}alkenyl, C_{2-8}alkynyl, aryl, C_{1-8}heteroaryl, C_{3-8}cycloalkyl, or C_{1-8}heterocyclyl; and

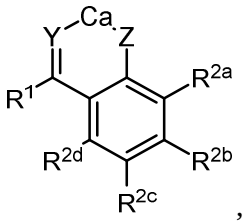
wherein any two or more of R^1, R^2, R^3, R^{n1}, and R^{n2} can together form a ring.

6. The method according to claim 5, wherein the calcium chelate complex has the formula:



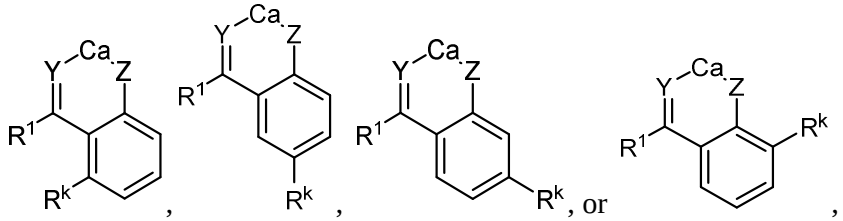
.

7. The method according to claim 5, wherein R^1 is selected from methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, tert-butoxy, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl.
8. The method according to claim 5, wherein R^3 is selected from methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, tert-butoxy, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl.
9. The method according to claim 5, wherein R^2 is selected from hydrogen, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, tert-butoxy, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl.
10. The method according to any preceding claim, wherein R^1 and R^2 together form a ring.
11. The method according to any preceding claim, wherein R^2 and R^3 together form a ring.
12. The method according to any preceding claim, wherein R^1, R^2 and R^3 together form a polycyclic ring system.
13. The method according to any preceding claim, wherein the calcium chelate complex comprises:



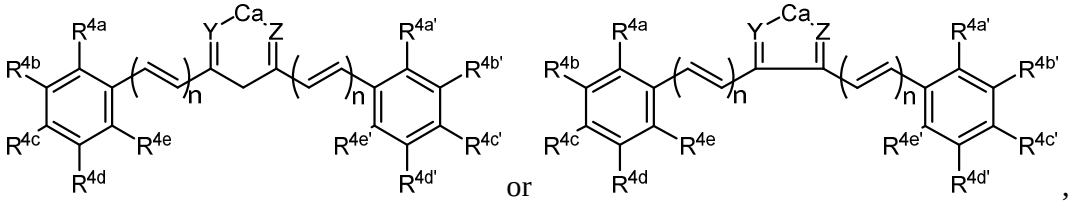
wherein R^{2a}, R^{2b}, R^{2c}, and R^{2d} are independently selected from hydrogen; hydroxy; $C_{1\text{-}22}$alkyl; and O-$C_{1\text{-}22}$alkyl; wherein any two or more of R^1, R^{2a}, R^{2b}, R^{2c}, and R^{2d} can together form a ring.

14. The method according to any preceding claim, wherein the calcium chelate complex comprises:



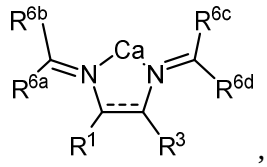
wherein R^k is selected from hydroxyl, amino, $C_{1\text{-}22}$alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl; and O- $C_{1\text{-}22}$alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy.

15. The method according to any preceding claim, wherein the calcium chelate complex has the formula:



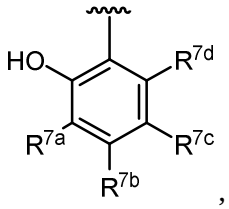
wherein n is 0, 1 or 2; and R^{4a}, $R^{4a'}$, R^{4b}, $R^{4b'}$, R^{4c}, $R^{4c'}$, R^{4d}, $R^{4d'}$, R^{4e}, and $R^{4e'}$ are independently selected from hydrogen; hydroxy; $C_{1\text{-}22}$alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl; $C_{1\text{-}22}$O-alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy; wherein any two or more of R^{4a}, $R^{4a'}$, R^{4b}, $R^{4b'}$, R^{4c}, $R^{4c'}$, R^{4d}, $R^{4d'}$, R^{4e}, and $R^{4e'}$ can together form a ring, preferably R^{4c} and $R^{4c'}$ are either hydroxyl or amino, preferably R^{4b} and $R^{4b'}$ are each methoxy.

16. The method according to any preceding claim, wherein Y is NR^{n1}, and R^{n1} is C_{1-8}alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl; C_{1-8}O-alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy.
17. The method according to any preceding claim, wherein Z is NR^{n2}, and R^{n2} is C_{1-8}alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl; C_{1-8}O-alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy.
18. The method according to any preceding claim, wherein Y is NR^{n1}, Z is NR^{n2}, and R^{n1} is C_{1-8}alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl, R^{n2} is C_{1-8}alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl, and R^2 is hydrogen or methyl.
19. The method according to any preceding claim, wherein the calcium complex has the formula:



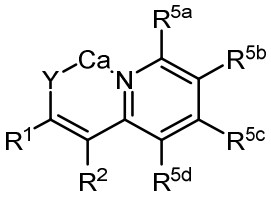
,

wherein R^{6a} and R^{6d} are independently selected from hydrogen or C_{1-8}alkyl, and R^{6b} and R^{6c} are each



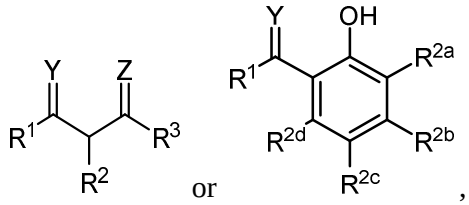
,

in which R^{7a}, R^{7b}, R^{7c}, and R^{7d} are independently selected from hydrogen, hydroxyl, C_{1-8}alkyl, and O-C_{1-8}alkyl; wherein any two or more of R^{7a}, R^{7b}, R^{7c}, and R^{7d} can together form a ring.
20. The method according to any preceding claim, wherein the calcium chelate complex has the formula:



wherein R^{5a}, R^{5b}, R^{5c}, and R^{5d} are independently selected from hydrogen; hydroxy; $C_{1\text{-}22}$alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl; $C_{1\text{-}22}$O-alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy; wherein any two or more of R^2, R^{5a}, R^{5b}, R^{5c}, and R^{5d} can together form a ring.

21. The method according to any preceding claim, wherein the cyclic calcium chelate complex is the reaction product a calcium compound and a ligand having the formula:



wherein

Y is selected from O, S, NR^{n1};

Z is selected from O, S, NR^{n2};

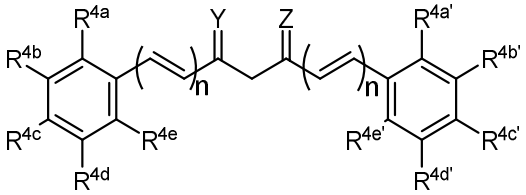
R^1, R^2, R^3, R^{n1}, and R^{n2} are independently selected from R^a, OR^b, and $N(R^b)_2$;

wherein R^a is in each case independently selected from hydrogen, $C_{1\text{-}8}$alkyl, $C_{2\text{-}8}$alkenyl, $C_{2\text{-}8}$alkynyl, aryl, $C_{1\text{-}8}$heteroaryl, $C_{3\text{-}8}$cycloalkyl, or $C_{1\text{-}8}$heterocyclyl;

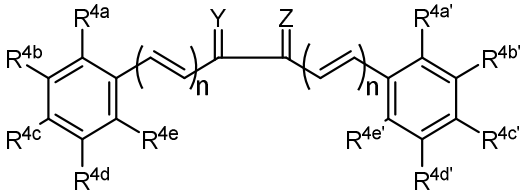
R^b is in each case independently selected from $C_{1\text{-}8}$alkyl, $C_{2\text{-}8}$alkenyl, $C_{2\text{-}8}$alkynyl, aryl, $C_{1\text{-}8}$heteroaryl, $C_{3\text{-}8}$cycloalkyl, or $C_{1\text{-}8}$heterocyclyl;

wherein R^{2a}, R^{2b}, R^{2c}, and R^{2d} are independently selected from hydrogen; hydroxy; $C_{1\text{-}22}$alkyl; and O-$C_{1\text{-}22}$alkyl; wherein any two or more R groups can together form a ring.

22. The method according to any preceding claim, wherein the calcium chelate complex is the reaction product of a calcium compound and a ligand compound having the formula:



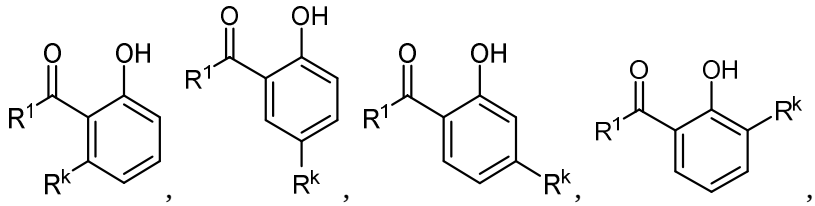
or



,

wherein n is 0, 1 or 2; and R^{4a}, $R^{4a'}$, R^{4b}, $R^{4b'}$, R^{4c}, $R^{4c'}$, R^{4d}, $R^{4d'}$, R^{4e}, and $R^{4e'}$ are independently selected from hydrogen; hydroxy; C_{1-22}alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl; C_{1-22}O-alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy; wherein any two or more of R^{4a}, $R^{4a'}$, R^{4b}, $R^{4b'}$, R^{4c}, $R^{4c'}$, R^{4d}, $R^{4d'}$, R^{4e}, and $R^{4e'}$ can together form a ring, preferably R^{4c} and $R^{4c'}$ are either hydroxyl or amino, preferably R^{4b} and $R^{4b'}$ are each methoxy.

23. The method according to any preceding claim, wherein the calcium chelate complex is the reaction product of a calcium compound and a ligand compound having the formula:



,

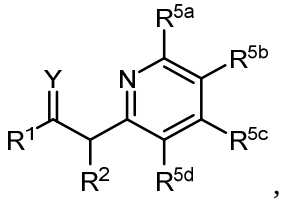
,

,

,

wherein R^k is selected from hydroxyl, amino, C_{1-22}alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl; and O- C_{1-22}alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy.

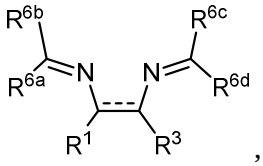
24. The method according to any preceding claim, wherein the calcium chelate complex is the reaction product of a calcium compound and a ligand compound having the formula:



,

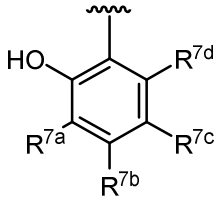
wherein R^{5a}, R^{5b}, R^{5c}, and R^{5d} are independently selected from hydrogen; hydroxy; $C_{1\text{-}22}$alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl; $C_{1\text{-}22}$O-alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy; wherein any two or more of R^2, R^{5a}, R^{5b}, R^{5c}, and R^{5d} can together form a ring.

25. The method according to any preceding claim, wherein the calcium chelate complex is the reaction product of a calcium compound and a ligand compound having the formula:



,

wherein R^{6a} and R^{6d} are independently selected from hydrogen or $C_{1\text{-}8}$alkyl, and R^{6b} and R^{6c} are each



,

in which R^{7a}, R^{7b}, R^{7c}, and R^{7d} are independently selected from hydrogen, hydroxyl, $C_{1\text{-}8}$alkyl, and O-$C_{1\text{-}8}$alkyl; wherein any two or more of R^{7a}, R^{7b}, R^{7c}, and R^{7d} can together form a ring.

26. The method according to claim 21, wherein the calcium compound comprises a calcium base.

27. The l method according to claim 21, wherein the calcium compound comprises a calcium salt.