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Elliott et al.

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[54] **LUBRICANT ADDITIVES**

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Related U.S. Application Data

[62] Division of Ser. No. 342,088, March 16, 1973, abandoned.

[30] **Foreign Application Priority Data**

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[58] **Field of Search**..... 252/46.6, 46.7, 400 A

[56] **References Cited**

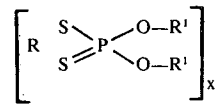
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[57] **ABSTRACT**

A compound, suitable for use as an oil-soluble, ashless, lubricant additive, has the general formula:



wherein:

i. R is the residue of a monocyclic, non-conjugated olefin containing from 8 to 12 carbon atoms and at least two ethylenically unsaturated double bonds in the ring or is the residue of the product formed by reacting at least one, but not all, of the ethylenically unsaturated double bonds in such a monocyclic, non-conjugated olefin with sulphur, phosphorus pentasulphide, a mercaptan, phenol, thiophenol, thiocyanate anion or carboxylic acid;

ii. each R^1 is the same or different and is an organic group; and

iii. x is an integer of 1, 2, or 3.

Also described are a process for preparing the compounds of the invention and lubricating compositions containing them.

14 Claims, No Drawings

LUBRICANT ADDITIVES

This is a division, of application Ser. No. 342,088, filed Mar. 16,1973, and now abandoned.

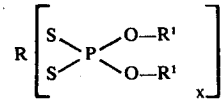
This invention relates to certain novel compounds useful as lubricant additives and more particularly to certain dithiophosphate compounds useful, inter alia, as antioxidants and as antiwear additives.

Metal salts of dithiophosphoric acids, particularly O,O-dialkyl dithiophosphoric acids, have been very widely used for many years as antioxidant and antiwear additives in lubricants. The most commonly used salts are the zinc salts, although other salts such as nickel and cadmium salts have also been proposed. The zinc dialkyl dithiophosphates have been widely used because of their very desirable combination of properties. As well as being very efficient antioxidants and useful antiwear additives, they are comparatively inexpensive due to their ready preparation from commonly available materials. In addition they have comparatively good oil-solubility and their use does not lead to excessive bearing weight loss.

Nevertheless, one important disadvantage of the foregoing additives is that the metal content forms ash as the metal salts are consumed in service. Consequently, numerous attempts have been made to prepare dithiophosphate derivatives which are ashless additives, i.e. contain no metal, yet retain the desirable combination of properties of the metal dithiophosphates. Such attempts have produced ashless additives comparable in antioxidant properties with zinc dialkyl dithiophosphates, yet corrosion of composite metal, e.g. copper-lead bearings, remains a problem.

We have now found certain dithiophosphate compounds which are useful additives. These compounds, or at least the preferred species thereof, are oil-soluble antioxidant additives, comparable in efficiency with zinc dialkyl dithiophosphates, which also inhibit excessive bearing weight loss.

Accordingly the present invention provides a compound, suitable for use as an oil-soluble, ashless, lubricant additive, which compound has the general formula:



[A]

wherein:

1. R is the residue of a monocyclic, non-conjugated olefin containing from 8 to 12 carbon atoms and at least two ethylenically unsaturated double bonds in the ring, and optionally bearing one or more alkyl, alkoxy or hydroxy groups on the ring, or is the residue of the product formed by reacting at least one, but not all, of the ethylenically unsaturated double bonds in such a monocyclic, non-conjugated olefin with sulphur, phosphorus pentasulphide, a mercaptan, phenol, thiophenol, thiocyanate anion or carboxylic acid;

11. each of R^1 is the same or different and is an organic group; and

iii. x is an integer of 1, 2 or 3, preferably 1 or 2.

The present invention further provides a process for preparing novel compounds in accordance with the present invention, which process involves reacting a di-(organo) dithiophosphoric acid and a monocylic, non-conjugated olefin containing from 8 to 12 carbon atoms and at least two ethylenically unsaturated double bonds in the ring, and optionally bearing one or more alkyl, alkoxy or hydroxy groups on the ring.

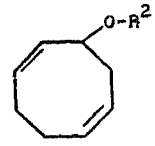
The present invention also includes the products of the foregoing process. In the process it is possible for some molecular rearrangement to occur and the resulting products are also included within the present invention. It is also possible to prepare products comprising a mixture of mono-bis- and tris-dithiophosphates within the present invention.

The two organic moieties present in each molecule of dithiophosphoric acid, from which moieties the group R^1 of general formula [A] are derived, can be chosen in accordance with the criteria commonly adopted in dithiophosphate additives. That is to say the organic moieties should be of sufficient size and sufficiently hydrocarbon in nature to impart the desired degree of oil-solubility. However, the organic moieties desirably should not be so large that the phosphorus and sulphur content of the additive is undesirably small, in terms of weight, as this creates a need for large dosage weights to be used in lubricants in order to impart the required degree of antioxidant and antiwear properties. Within the foregoing criteria, one may select the organic moieties from among the very wide variety of organic groups known in the art as suitable for inclusion in dithiophosphoric acids. Thus the organic moieties may be alkyl, alkenyl, aryl, alkaryl or aralkyl groups, and optionally may bear one or more unreactive substituents such as alkoxy groups.

Preferably each organic moiety is an alkyl, phenyl or alkyl-substituted phenyl group. The alkyl substituted phenyl group may contain from 7 to 18 carbon atoms. Most preferably, however, each organic moiety is an alkyl group containing from 3 to 10 carbon atoms. The two organic moieties may be the same. Alternatively, a mixture of organic moieties can be employed by using a dithiophosphoric acid containing two different organic groups and/or by using a mixture of two or more different dithiophosphoric acids.

As is well known in the art dithiophosphoric acids may be prepared by reacting hydroxy-substituted organic compounds, for example alcohols, phenols, alkyl substituted phenols or mixtures thereof, with phosphorus pentasulphide in approximately 4 to 1 molar ratio.

The olefin employed in the foregoing process preferably contains two or three ethylenically unsaturated double donds in the ring. As hereinbefore described the olefin may bear an alkyl or alkoxy substitutent, as for example in the compounds described in U.K. Pat. Specification Nos. 1,248,592 and 1,248,593, having the formula:



wherein R^2 is an alkyl group. For the purposes of the present invention R^2 may contain from 1 to 20, preferably 8 to 16, carbon atoms.

Alternatively, the olefin may bear one or more hydroxy substituents on the ring. Such substituted olefins may be prepared by reacting the unsubstituted olefin in known manner using, for example, potassium perman-

ganate, hydrogen peroxide or a peracid such as performic or peracetic acid, as oxidising agent or by forming, and then hydrolysing, the epoxide of the olefin.

However, it is preferred that the olefin does not bear any alkyl, alkoxy or hydroxy substituents, the most preferred olefin being a non-conjugated cyclooctadiene or cyclododecatriene.

Reaction of the di-(organo) dithiophosphoric acid with the monocyclic, non-conjugated olefin takes place over a wide range of temperatures, for example from ambient temperature to 200°C., but a preferred reaction temperature is from 50° to 150°C. It is particularly preferred to carry out the reaction at a temperature of from 70° to 120°C.

The proportions of the reactants employed may vary from 1 to n moles of dithiophosphoric acid per mole of olefin, wherein n is the number of ethylenically unsaturated double bonds in the olefin, and, at the preferred reaction temperature, the reaction is normally completed within 2 to 50 hours, depending on temperature and the organic substituents in the dithiophosphoric acids. Completion of the reaction may conveniently be considered to have occurred when the acidity of the reaction mixture falls to a constant low level. In a preferred aspect of the invention the reaction is carried out in an inert atmosphere, for example under a nitrogen blanket.

When the proportion of dithiophosphoric acid used is less than that required to react with all ethylenically unsaturated double bonds in the olefin the resulting compounds, containing residual unsaturation, may be employed as lubricant additives. However, in an alternative aspect of the invention the residual unsaturation can be further reacted with compounds known to react with ethylenically unsaturated double bonds to produce further novel compounds in accordance with the present invention. Such compounds reacting with residual unsaturation include sulphur, phosphorus pentasulphide, mercaptans, phenols, thiocyanate anions, thiophenols and carboxylic acids. Specific examples of such compounds are mercaptans and carboxylic acids containing from 1 to 16 carbon atoms; phenol (unsubstituted) and thiophenol (unsubstituted). The foregoing compounds may be reacted with the residual unsaturation at a temperature of from 50° to 200°C and in the case of sulphur, thiocyanates and phosphorus pentasulphide no catalyst is required. In the case of the other compounds, however, it may be desirable to use a catalyst known to promote their reaction with ethylenically unsaturated double bonds, such as mineral acids or Lewis acid catalysts such as boron trifluoride or the etherate or phenolate complex thereof.

When residual unsaturation is further reacted in the above-described manner the resulting products have the same utility, as lubricant additives, as compounds containing residual unsaturation and compounds in which all ethylenically unsaturated double bonds have been reacted with a dithiophosphoric acid.

In yet another alternative some, but not all, of the ethylenically unsaturated double bonds in the monocyclic, non-conjugated olefin may be reacted with the compounds known to react with ethylenically unsaturated double bonds and residual unsaturation reacted with a di-(organo) dithiophosphoric acid, this sequence of reaction steps in general being preferred over the reverse sequence.

In yet another aspect of the invention there is provided a lubricating composition comprising a major amount by weight, based on the total weight of the lubricating composition, of a lubricating oil and a minor amount by weight of the additives of the present invention. In the preferred lubricating compositions the additive constitutes from 0.1 to 10%, more preferably 0.25 to 5%, by weight of the composition and the lubricating oil may be any of the well known mineral oils of appropriate viscosity characteristics.

It will be understood that the lubricating compositions of the present invention may also contain, if desired, conventional lubricant additives such as ancillary antioxidants and antiwear additives (preferably ashless), corrosion inhibitors, dispersants, particularly disperants of the succinimide type, detergents, thickeners, pour-point depressants and viscosity index improvers. Numerous examples of such conventional additives are described in U.K. Patent Specification No. 1,205,177 and the various documents referred to therein.

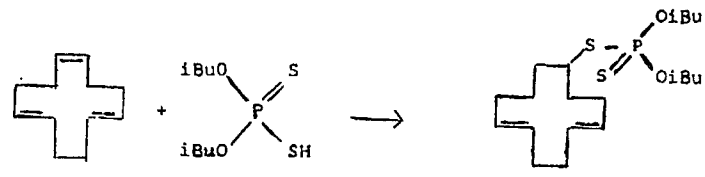
The additives of the present invention may also in certain circumstances be conveniently prepared as an additive concentrate consisting of a concentrated solution of a major amount of the additive in a minor amount of mineral oil, or as an additive package consisting of a concentrated solution in mineral oil of a major amount of a combination of the additive with one or more conventional additives. Such concentrates and packages are frequently very convenient forms in which to handle and transport additives and are diluted with further quantities of oil, and optionally blended with further additives, before use.

The present invention will now be illustrated with reference to the following examples:

EXAMPLE 1

S-Dihydro cyclododecatrienyl-O,O'-di isobutyl dithiophosphate

Reaction:



where the addition may be in the 1, 5 or 9 position.

O,O'-di-isobutyl dithiophosphoric acid (0.5 mole) was placed in a round-bottomed 3-necked flask fitted with stirrer, condenser and nitrogen cover, thermometer and dropping funnel and cyclododeca-1,5,9-triene (0.5 mole) added thereto by dropwise addition via the dropping funnel. The reaction mixture thus formed was heated on a water bath, the latter being heated to 100°C (reaction temperature about 90° to 95°C.), for a total of 10½ hours at which time the acidity of the reaction mixture had fallen to a constant low level.

The crude reaction product was worked up by the addition of petroleum ether of Boiling Point 62°–68°C.

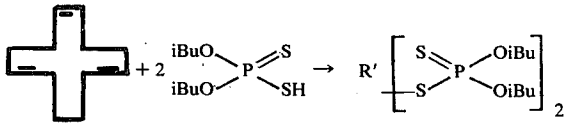
(about 200ml) and washing with two 100ml portions of 2N Na_2CO_3 solution followed by two 100ml portions of water. The reaction product was then dried over $MgSO_4$ and thereafter stripped to a base temperature of 110°C. at 0.5mm Hg to yield 175g (86.6% of S-dihydrocyclododecatrienyl-O,O'-di-isobutyl dithiophosphate as a clear greenish liquid.

Analysis: Calculated: 7.67% P; 15.8%S. Found: 8.1%P; 17.6%S.

EXAMPLE 2

S-tetrahydro cyclododecatrienyl bis (O,O'-di-isobutyl dithiophosphate)

Reaction:



R' = tetrahydrocyclododecatrienyl

A 2:1 addition product was prepared using the same technique as in Example 1 except in that 1.0 mole of the dithiophosphoric acid was used and heating on the water bath was continued for a total of 35 hours.

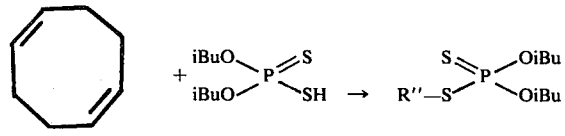
The crude reaction product was worked up in the same manner as Example 1 to yield 281.9g (87.2%) of S-tetrahydrocyclododecatrienyl-bis (O,O'-di-isobutyl dithiophosphate).

Analysis: Calculated: 9.6%P; 19.8%S. Found: 9.2%P; 20.3%S.

EXAMPLE 3

1,2-Dihydro-cyclooctadienyl-5-O,O'-di-isobutyl dithiophosphate

Reaction:



R'' = dihydrocyclooctadienyl

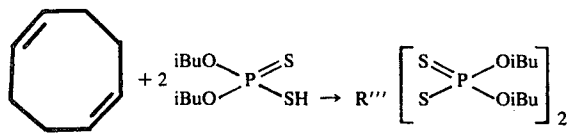
Using the same technique as in Example 1, 0.5 mole of O,O'-di-isobutyl dithiophosphoric acid and 0.5 mole of cycloocta-1,5-diene were heated together for a total of 21 hours and worked up to yield 150g (85.7%) of S-dihydrocyclooctadienyl-O,O'-di-isobutyl dithiophosphate.

Analysis: Calculated: 8.86%P; 18.3%S. Found: 9.9%P; 20.0%S.

EXAMPLE 4

S-Tetrahydro cyclooctadienyl bis (O,O'-di-isobutyl dithiophosphate)

Reaction:



R''' = tetrahydrocyclooctadienyl

O,O'-di-isobutyl dithiophosphoric acid (1.0 mole) and cycloocta-1,5-diene (0.5 mole) were placed in a round-bottomed three-necked flask fitted as in Example 1 and 15g of the diethyl etherate of boron trifluoride added dropwise thereto over a period of 5 minutes. The reactants were stirred for 15 minutes and then heated on a water bath (temperature 100°C.) for a total of 24 hours. A further 4g of the boron trifluoride etherate were added and heating continued for a further 6 hours but no significant further reduction of the acidity of the reaction mixture was obtained thereby.

The crude reaction product was placed in a separatory funnel with petroleum ether of Boiling Point 62°–68°C. and washed with four 100ml portions of water, followed by three 100ml portions of 2N Na_2CO_3 (giving considerable evolution of CO_2) and finally with a further three portions of water before being dried over $MgSO_4$ overnight. The following day the product was rewashed with two 100ml portions of water, dried over $MgSO_4$ and stripped to a base temperature of 100°C. at 0.1mm Hg to yield 230g (77.7%) of S-tetrahydrocyclooctadienyl-bis-(O,O'-di-isobutyl dithiophosphate) as a slightly cloudy golden liquid.

Analysis: Calculated: 10.5%P; 21.6%S. Found: 10.1%P; 21.9%S.

EXAMPLE 5

A further quantity of the product of Example 3 was prepared by adding 15g of the diethyl etherate of boron trifluoride dropwise over a period of about 5 minutes, to a mixture of the dithiophosphoric acid (0.5 mole) and the olefin (0.5 mole) in the round-bottomed flask. The reaction mixture was then heated on a water bath, the temperature of which was gradually raised to 100°C. over a period of 3 hours, whereafter heating at that temperature was continued for 6 hours.

The crude reaction product so obtained was placed in a separatory funnel with about 300ml petroleum ether (Boiling Point 62°–68°C.) and washed with water to remove the boron trifluoride etherate "catalyst". The product was then washed with three 200ml portions of 2N Na_2CO_3, washed again with water and dried over $MgSO_4$; whereafter it was filtered, stripped to a base temperature of 160°C. at 0.1mm Hg and refiltered after cooling to yield 106.7g (61.0%) of the S-dihydrocyclooctadienyl-O,O-di-isobutyl dithiophosphate as a brown viscous liquid.

Analysis: Calculated: 8.86%P; 18.3%S. Found: 8.2%P; 21.0%S.

It should be noted that the boron trifluoride etherate catalyst employed in the preparations of Examples 4 and 5 did not appear, in the event, materially to affect the reaction.

EXAMPLE 6

S-(Benzylthiocyclododecenyl)-O,O'-di-isobutyl dithiophosphate

a. O,O'-di-isobutyl dithiophosphoric acid

Isobutanol (1480g., 20m) was placed in a 5-liter round-bottomed flask fitted with a stirrer, condenser, nitrogen inlet, NaOH traps, thermometer and side-arm

addition assembly. The alcohol was heated, with stirring, on an isomantle to a temperature of 80°C., whereafter phosphorus pentasulphide (1120g., 5m) was added via the side-arm addition assembly over a period of 1¼ hours while maintaining the temperature in the range of 82°–86°C. After addition of the phosphorus pentasulphide, the equivalent weight of the resulting dithiophosphoric acid was 285. Stirring of the reaction mixture was continued for 40 minutes, with the temperature raised to 88°C. and the product cooled to about 50°C. in an air stream for 15 minutes to yield a dark green liquid of equivalent weight 264 after filtration.

b. Benzylthiocyclododecadiene.

Cyclododeca-1,5,9-triene (162g., 1.0m) and benzyl mercaptan (124g., 1.0m) were placed in a 500ml, round-bottomed, three-necked flask fitted with thermometer stirrer, condenser and N_2cover. To the resulting reaction mixture was added 2ml of the diethyl etherate of boron trifluoride and the mixture heated to 180°C. The reaction mixture was maintained at this temperature for a total of 46 hours with addition of further 1 ml portions of the boron trifluoride etherate after 16, 23½ and 38½ hours. To the crude product was added an equal volume of petroleum ether (Boiling Point range 62°–68°C.) and the product washed with 102 ml water, 100ml 2N Na_2CO_3 solution (no CO_2 evolved and finally with two 50ml portions of water before being dried over anhydrous magnesium sulphate and stripped to yield 183g of a dark brown liquid product containing 12.1%S (theory 11.2%) and 90g of a clear liquid distillate consisting essentially 1 of unreacted cyclododeca-1,5,9-triene.

c. S-(Benzylthiocyclododecenyl)-O,O'-di-isobutyl dithiophosphate.

The product of (b) (85.8g, 0.3m) was placed in a 250ml round-bottomed, three-necked flask fitted with stirrer, dropping funnel, thermometer, condenser and N_2 cover. The contents of the flask were stirred on a cold water bath at 17°C. and the product of (a) (79.2g, 0.3m) added over a period of 15 minutes (no exotherm). The reaction mixture was heated gradually, with stirring, on the water bath over 1 hour to a temperature of 90°–100°C. The reaction temperature was maintained at 95°–100°C. for a total of 19 hours. The resulting crude product was then placed in a separatory funnel and an approximately equal volume of petroleum ether (Boiling Point range 62°–68°C) added thereto, whereafter the product was washed with 150ml aqueous 2N Na_2CO_3 (no CO_2 evolved) followed by a further 100 ml aqueous 2N Na_2 CO_3 (no CO_2 evolved) and finally two 100 ml portions of water. The product was dried over anhydrous magnesium sulphate and stripped to yield 111.5g of a very dark brown liquid containing 18.9%S and 3.75%P (theory 18.2%S and 5.86%P).

EXAMPLE 7

Cyclododecene-1,2-diol-O,O'-di-isobutyl dithiophosphate

a. Cis-5-trans-9-cyclododecadiene-trans-1,2-diol.

A sample of cis-5-trans-9-cyclododecadiene-trans-1,2-diol was prepared from cyclododeca-1,5,9-triene by oxidation with permanganate according to the method of Ohno, Okamoto and Torimitsu as outlined in Bull. Chem. Soc. Japan 39(2)316 (1966).

b. Cyclododecene-1,2-diol-O,O'-di-isobutyl dithiophosphate.

The product of (a) (54g, 0.275m) and toluene (200g) were placed in a 500ml flask fitted with a stirrer, condenser, N_2 cover, thermometer and dropping funnel containing 72.7g (0.275m) O,O'-di-isobutyl dithiophosphoric acid (product of part (a) of Example 6). The contents of the flask were heated on an oil bath to achieve a reasonably fluid mixture and the dithiophosporic acid run in quite quickly without any noticeable reaction. The reaction mixture was refluxed for 4 hours at a bath temperature of 105°–120°C and stood for 2 days. The acidity of the mixture was 16.2mg. KOH/g and refluxing was recommenced for a further 4 hours at a bath temperature of 120°C (some hydrogen sulphide evolved) followed by a further 2 hours at a bath temperature of 100°C.

The crude product (acidity 12.7mg. KOH/g) was placed in a separating funnel and washed with two 150ml portions of aqueous 2N Na_2CO_3, some CO_2 being evolved on the first washing. The aqueous layer, which was deep green in colour, was separated and the organic layer washed with 100ml water to give some solid, light brown precipitate. After some difficulty in separating the latter the liquid was dried over anhydrous magnesium sulphate and then stripped under high vacuum (0.1mm Hg) to a bath temperature of 140°C giving no distillate. The final product (yield 60g) was a medium brown semi-solid which was neutral to lacmoid and contained 8.4%P and 13.6%S (theory 7.08%P and 14.6%S).

EXAMPLE 8

Sulphurised cyclododeca-1,5,9-triene-di-isobutyl dithiophosporic acid reaction product

a. Sulphurised cyclododecatri-1,5,9-ene.

Cyclododeca-1,5,9-triene (162g, 1.0m) and triethylamine (2ml) were placed in a 500ml flask fitted with stirrer, condenser, thermometer, N_2 cover and side-arm addition assembly containing sulphur. The flask contents were heated to 150°C and sulphur added from the side-arm assembly over a period of 2½ hours while maintaining the temperature in the range 140°–150°C. A total of 32g (1.0m) sulphur was added giving no exotherm but giving an almost black liquid. The reaction mixture was stirred at 142°C for 50 minutes and then allowed to cool to room temperature under nitrogen. The crude product was stripped under high vacuum, giving only one discernible fraction. The final product (yield 82.5g) was a black viscous liquid containing 26.6% sulphur.

b. Sulphurised cyclododeca-1,5,9-triene-di-isobutyl dithiophosphoric acid reaction product.

The product of (a) (29.5g, 0.15m) and toluene (55g) were stirred at 40°C in a 250ml flask for 10 minutes to provide a fairly low viscosity solution. O,O'-di-isobutyl dithiophosphoric acid (35.4g, 0.15m of product of part (a) of Example 6) was added at 30°C over a period of 10 minutes, giving no obvious sign of reaction. The reaction mixture was stirred with heating on an oil bath at 110°C for 6 hours followed by a total of a further 15 hours at 100°C.

The crude product was placed in a separating funnel with an equal volume of petroleum ether (Boiling Point range 62°–68°C), washed with 100ml aqueous 2N Na_2. CO_3 (negligible CO_2 evolution), washed with two 100ml portions of water and finally dried over anhydrous magnesium sulphate to yield, after removal of the

solvent, 42g of a clear dark red liquid containing 6.2%P and 24.8%S (theory 6.74%P and 26.5%S).

EXAMPLE 9

S-(Acetoxycyclododecenyl)-O,O'-di-isobutyl dithiophosphate

a. 1-Acetoxy cyclododecadiene.

Cyclododeca-1,5,9-triene (162g, 1.0m), acetic acid (120g, 2.0m) and diethyl etherate of boron trifluoride (5ml) were placed in a 500ml flask fitted with thermometer, stirrer, condenser and N_2 bubbler. The reaction mixture was stirred for a total of 14 hours at 100°C followed by a total of a further 15 hours at 105°C. An equal volume of petroleum ether (Boiling Point range 62°–68°C) was added to the crude product and the resulting solution was washed with 500ml aqueous 2N Na_2CO_3 (with very considerable CO_2 evolution). The product was then quickly washed with a little water (50ml), dried over anhydrous magnesium sulphate and stripped to finally yield a middle fraction of B. Pt. 82°–92°C/0.1m Hg whose I.R. spectrum was consistent with it being the mono acetoxy derivative.

b. S(Acetoxycyclododecenyl)-O,O'-di-isobutyl dithiophosphate.

The product of (a) (28g) and O,O'-di-isobutyl dithiophosphoric acid (34.8g of product of part (a) of Example 6) were heated together at 100°–120°C for a total of 10 hours, followed by a further 6 hours at 100°C. The crude product was taken up in petroleum ether (Boiling Point range 62°–68°C), washed with aqueous 2N Na_2CO_3 and then water, dried over anhydrous magnesium sulphate and finally stripped to yield a light yellow oil containing 6.4%P and 13.1%S (theory 6.84%P and 14.1%S).

EXAMPLE 10

Phenol/cyclododeca-1,5,9-triene/di-isobutyl dithiophosphoric acid reaction product

a. Phenol/cyclododeca-1,5,9-triene reaction product.

Phenol (94g, 1.0m) and toluene (150ml) were placed in a 500ml flask fitted with thermocouple, dropping funnel, stirrer, condenser and N_2 cover. The diethyl etherate of boron trifluoride (5ml) was carefully added to the reaction mixture, giving no sign of reaction. A cold water bath was then placed around the flask. With an internal temperature for the reaction mixture at 12°C, cyclododeca-1,5,9-triene was run into the flask. A total of 162g (1.0m) of the cyclododeca-1,5,9-triene was added, with vigorous stirring, over a period of ¾ hour giving an exotherm which was easily controlled to maintain the reaction temperature in the range 12°–23°C and during which the reaction mixture became progressively deeper red in colour. The reaction mixture was then stirred at 23°C for a further 3 hours.

The crude product was placed in a separating funnel, 300ml petroleum ether (Boiling Point range 62°–68°C) added and the mixture washed with three 100ml portions of 10% aqueous NaOH solution, during which time the aqueous layer became progressively lighter purple in colour and the organic layer changed from deep red to yellow/orange. The organic layer was dried over anhydrous magnesium sulphate and the petroleum ether stripped off to yield a light orange liquid. The latter was stripped to 150° C under high vacuum to yield 78.6g of a clear, medium brown liquid whose I.R. spectrum was consistent with the product being an adduct of phenol and CDT.

b. Phenol/cyclododeca-1,5,9-triene/di-isobutyl dithiophosphoric acid reaction product.

The product of (a) (64g, 0.25 mole) and O,O'-di-isobutyl dithiophosphoric acid (66g, 0.25 mole) were heated together for 7 hours at 100°C, followed by 7 hours at 115°C and finally a total of a further 21 hours at 120°C. The crude product so produced was taken up in petroleum ether (Boiling Point range 62°–68°C), washed with aqueous 2N Na_2CO_3 and water, dried over anhydrous magnesium sulphate and finally stripped to yield a viscous red oil which was neutral and contained 5.04%P and 11.4%S (theory 6.2%P and 12.8%S for a 1:1:1 reaction product).

EXAMPLE 11

Phosphosulphurised S-tetrahydrocyclododecatrienyl bis (O,O'-di-isobutyl dithiophosphate)

a. S-tretrahydrocyclododecatrienyl bis (O,O'-di-isobutyl dithiophosphate).

A further sample of the product of Example 2 was prepared by adding cyclododeca-1,5,9-triene (486g, 3.0m) to O,O'-di-isobutyl dithiophosphoric acid (1572g, 6.0m) and heating the mixture at 120°C for 21 hours, whereafter the acidity of the reaction mixture had fallen to 16.5mg KOH/g. The crude product was taken up in petroleum ether, washed with sodium carbonate solution and water, dried over anhydrous magnesium sulphate and the petroleum ether stripped off to yield a clear, yellow, viscous liquid.

b. Phosphosulphurised S-tetrahydrocyclododecatrienyl bis (O,O'-di-isobutyl dithiophosphate).

The product of (a) (129g, 0.2m) and P_2S_5 (11.1g, 0.5m) were placed in a 250ml flask fitted with stirrer, thermometer, condenser and N_2 cover. The reaction mixture was then stirred with heating on an oil bath to 120°C for 2 hours, whereafter the reaction temperature was raised to 170°C for a further 6 hours (momentarily to an internal temperature of 182°C and a bath temperature of 194°C).

The crude product was allowed to cool under nitrogen and then petroleum ether (Boiling Point range 62°–68°C) added thereto. The resulting mixture was filtered, using a filter aid, and stripped to 25mm Hg and 100°C to yield a cloudy yellow liquid which was very faintly acidic to lacmoid indicator and contained 10.8%P and 26.2%S (theory 11%P and 22%S).

EXAMPLE 12

S-dihydrocyclododecatrienyl-O,O'-di-tridecyl dithiophosphate

O,O'-di-tridecyl dithiophosphoric acid (240g, 0.46 mole) and cyclododeca-1,5,9-triene (74.5g, 0.46 mole) were heated together for 6 hours at 120°C. The crude product was taken up in petroleum ether (Boiling Point range 62°–68°C), washed with aqueous 2N Na_2CO_3 (a little CO_2 evolved) and water, dried over anhydrous magnesium sulphate and finally stripped to yield 199.6g of a yellow liquid containing 5.1%P and 10.05%S (theory 4.72%P and 9.75%S) and which was neutral to lacmoid indicator.

EXAMPLE 13

S-dihydrocyclooctadienyl-O,O'-di-(p-nonylphenyl-/isobutyl) dithiophosphate

a. O,O'-di-(p-nonylphenyl/isobutyl) dithiophosphoric acid.

A sample of O,O'-di-(p-nonyphenyl/isobutyl) dithiophosphoric acid was prepared by reacting equimolar proportions of isobutanol and p-nonylphenol with P_2S_5 in a manner similar to that described for O,O'-di-isobutyl dithiophosphoric acid in Example 6, but at a temperature of 90°–110°C.

b. S-dihydrocyclooctadienyl-O,O'-di-(p-nonylphenyl/isobutyl) dithiophosphate.

O,O'-di-(p-nonylphenyl/isobutyl) dithiophosphoric acid (205g, 0.5 mole) and cycloocta-1,5-diene(54g 0.5m) were heated together for 7 hours at 120°C. The resulting crude product was worked up in the same manner as in Example 12 to yield 162g of a slightly cloudy, yellow liquid which was neutral to lacmoid indicator and contained 6.1%P and 13.7%S (theory 6.25%P and 12.9%S).

EXAMPLE 14

S-Tetrahydrocyclododecatrienyl bis (O,O'-di-capryl dithiophosphate)

Cyclododeca-1,5,9-triene (40.5g, 0.25 mole) and O,O'-di-capryl dithiophosporic acid (181g, 0.5 mole) were heated together at 100°C for a total of 27 hours. The crude product so obtained was worked up in similar manner to Example 12 to yield 143.4g of a clear, yellow liquid which was neutral to lacmoid indicator and contained 6.3%P and 14.2%S (theory 7.14%P and 14.7%S)

EXAMPLE 15

S-dihydrocyclooctadienyl-O,O'-di-isodecyl dithiophosphate

Cycloocta-1,5-diene (23.6g, 0.218 mole) and O,O'-di-isodecyl dithiophosphoric acid (100g, 0.218 mole) were heated together for 6 hours at 100°–120°C followed by a total of a further 21 hours at 120°C. The crude product so obtained was worked up in the same manner as in Example 12 to yield 65.4g of a clear, colourless liquid which was neutral to lacmoid indicator and which contained 6.2%P and 9.8%S (theory 5.94%P and 12.2%S).

EXAMPLE 16

S-tetrahydrocyclododecatrienyl bis O,O'-di-capryl-O,O'-di-p-nonylphenyl/isobutyl) dithiophosphate

Cyclododeca-1,5,9-triene (40.5g, 0.25 mole) and O,O'-di-capryl dithiophosphoric acid (90.5g, 0.25 mole) were heated together at 120°C for a total of 13 hours (acidity of reaction mixture 13.1mg KOH/g), whereafter O,O'-di-(isobutyl/p-nonylphenyl) dithiophosphoric acid (102.2g, 0.25 mole) was added to the reaction mixture and reaction continued for a further 7 hours at 120°C. The crude product so obtained was taken up with petroleum ether (Boiling Point range 62°–68°C) and washed with aqueous 2N Na_2CO_3. During this washing a green liquid was continually precipitated and this was removed and a little toluene added, whereafter no further precipitate was formed. The product was then washed with water, dried over anhydrous magnesium sulphate and stripped to yield 153.1g of a yellow liquid which was neutral to lacmoid indicator and which contained 6.4%P and 12.9%S (theory 6.87%P and 14.2%S).

EXAMPLE 17

S-dihydrocyclododecatrienyl-O,O'-di-p-nonylphenyl dithiophosphate

Cyclododeca-1,5,9-triene (40.5g, 0.25 mole) and O,O'-di-p-nonylphenyl dithiophosphoric acid (140.8g, 0.25 mole) were heated together for 5 hours at 120°C. The crude product was then worked up in the same manner as Example 12 to yield 128g of a viscous, red-brown liquid which was neutral to lacmoid indicator and contained 4.4%P and 9.0%S (theory 4.46%P and 9.2%S).

EXAMPLE 18

S-tetrahydrocyclooctadienyl bis (O,O'-di-2-ethylhexyl-O,O'-di-p-nonylphenyl) dithiophosphate

Cycloocta-1,5-diene (21.6g, 0.2 mole) and O,O'-di-2-ethylhexyl dithiophosphoric acid (82.0g, 0.2 mole) were heated together for 6 hours at 120°C. To the resulting product (acidity 3.1mg KOH/g) was added O,O'-di-p-nonyphenyl dithiophosphoric acid (112.6g, 0.2 mole) and the resulting mixture was heated at 120°C for a further 7 hours. Thereafter, the resulting crude product was worked up in the same manner as Example 12 to yield 171.3g of a clear brown liquid which was neutral to lacmoid indicator and contained 6.4%P and 12.7%S (theory 6.23%P and 12.8%S).

EXAMPLE 19

S-dihydrocyclododecatrienyl-O,O'-di-(tridecyl/p-cresyl dithiophosphate

a. O,O'-di-(tridecyl/p-cresyl) dithiophosphoric acid.

A sample of O,O'-di-(tridecyl/p-cresyl dithiophosphoric acid was prepared by reacting equimolar proportions of tridecanol and p-cresol with P_2S_5 in a manner similar to that described for O,O'-di-isobutyl dithiophosphoric acid in Example 6, but at a temperature of 90°–110°C.

b. S-dihydrocyclododecatrienyl-O,O'-di-(tridecyl/p-cresyl) dithiophosphate.

Cyclododeca-1,5,9-triene (81g, 0.5 mole) and O,O'-di-(tridecyl/p-cresyl) dithiophosphoric acid (210.5g, 0.5 mole) were heated together for 5 hours at 100°C. The resulting crude product was worked up in the same manner as in Example 12 to yield 182g of a clear, yellow liquid which was neutral to lacmoid indicator and contained 5.58%P and 11.4%S (theory 5.5%P and 11.3%S).

EXAMPLE 20

1,2-Dithiocyanocyclooctane-O,O'-di-tridecyl dithiophosphate

a. 1,2-Dithiocyanocyclooct-5-ene.

1,2-Dithiocyanocyclooct-5-ene was prepared from 1,5-cyclo-octadiene using the method given in U.S. Pat. No. 3,308,150 to yield 41.5g of an orange oil that slowly crystallised and contained 27.2%S and 12.37%N (theory) 28.6%S and 12.5%N).

b. 1,2-Dithiocyanocyclooctane-O,O'-di-tridecyl dithiophosphate.

The product of (a) (41.5g, 0.185m) was mixed with O,O'-di-tridecyl dithiophosphoric acid (95.4g, 0.185 m) and heated to 100°C for 6 hours. The crude product was then worked up in the same manner as Example 12 to yield 79.3g of a neutral, red oil containing 14.6%S, 2.4%N and 4.9%P (theory 17.4%S, 3.8%N and 4.2%P).

EXAMPLE 21

S-hexahydrocyclododecatrienyl tris(O,O'-di-isobutyl dithiophosphate)

Cyclododeca-1,5,9-triene (54g, 0.33m) was added to O,O'-di-isobutyl dithiophosphoric acid (268g, 1.0m) and the mixture heated to 120°C for 13 hours, at which time the acidity of the reaction mixture had fallen to 36mg. KOH/g. The crude product was worked up in the same manner as Example 12 to yield 236.3g of a slightly cloudy viscous liquid containing 10.5%P and 23.0%S (theory 10.5%P and 21.6%S).

EXAMPLE 22

S-tetrahydrocyclododecatrienyl bis (O,O'-di-isobutyl-O,O'-di-isopropyl) dithiophosphate

O,O'-di-isopropyl dithiophosphoric acid (244g 1.0m) was added to cyclododeca-1,5,9-triene and heated for 12 hours at 100°–120°C, at which time the acidity of the reaction mixture had fallen to 8.6mg KOH/g. To the reaction mixture was added O,O'-di-isobutyl dithiophosphoric acid (259g, 1.0m) and the mixture then heated to 120°C for 11 hours, at which time the acidity of the resulting crude product was 13.1mg. KOH/g. The crude product was worked up in the same manner as in Example 12 to yield 543g of a cloudy liquid containing 9.8%P and 20.5%S (theory 10.0%P and 20.7%S).

EXAMPLE 23

S-tetrahydrocyclododecatrienyl bis (O,O'-di-isopropyl dithiophosphate

O,O'-di-isopropyl dithiophosphoric acid (732g, 3.0m) was added to cyclododeca-1,5,9-triene (243g, 1.5m) and the mixture heated at 100°–110°C for 53 hours. The resulting crude product was worked up in the same manner as Example 12 to yield a final product containing 9.4%P and 22.1%S (theory 12.3%P and 23.4%S).

EXAMPLE 24

S-tetrahydrocyclododecatrienyl bis (O,O'-di-allyl-O,O'-di-2-ethylhexyl) dithiophosphate

Cyclododeca-1,5,9-triene (64.8g, 0.4m) and O,O'-di-allyl dithiophosphoric acid (101-6g, 0.4m) were heated together for 3 hours at 90°C. O,O'-di-2-ethyl-hexyl dithiophosphoric acid (164g, 0.4m) was then added and heating continued for a further 5 hours at 90°C. The crude product was worked up in the same manner as in Example 12, during which a small amount of polymeric material formed in the reaction was removed, to yield 200g of a final product containing 8.1%P and 16.7%S (theory 8.55%P and 17.6%S).

To demonstrate the suitability of the compounds of the present invention for use in lubricating oils, mineral oil blends containing the compounds were tested by standard methods and compared with blends containing olefin/dithiophosphoric acid reaction products not in accordance with the invention. The following Examples 25 to 30 describe the preparation of said reaction products not in accordance with the invention.

EXAMPLE 25

1:1 Reaction Product of O,O'-di-isobutyl dithiophosphoric acid and Dicyclopentadiene

The same apparatus was used as in Example 1. The dithiophosphoric acid (0.3 mole) was placed in the flask and a solution of 2g concentrated H_2SO_4 in 3g of water added thereto. Dicyclopentadiene (0.3 mole) was added dropwise over a period of 15 minutes, an exotherm of 42°C being noticed. The reaction mixture was stirred for 10 minutes and then heated to 60°C on a water bath, whereafter it was maintained at that temperature, with stirring for 5 hours.

The crude reaction product was poured into 150ml water and a yellowish oil extracted with 400ml petroleum ether (Boiling Point 62°–68°C). The extract was washed with 200ml 2N Na_2CO_3 solution, then washed with two 200ml portions of water, dried over $MgSO_4$ and stripped to yield 102g (90.9%) of a cloudy yellow liquid.

Analysis: Calculated: 8.3%P; 17.1%S. Found: 8.1%P; 17.6%S.

EXAMPLE 26

1:1 Reaction Product of O,O'-di-isobutyl dithiophosphoric acid and Cycloocta-1,3-diene

The same apparatus was used as in Example 1. The olefin (0.5 mole) was placed in the flask and the dithiophosphoric acid (0.5 mole) added thereto. The reaction mixture was then heated on a water bath (temp. 100°C) for a total of 23 hours. A determination of acidity indicated that the reaction was proceeding very slowly and therefore 2ml of boron trifluoride diethyl etherate was added and heating continued for a further 21 hours. The crude reaction product was worked up in a similar manner to Example 3 to yield 140.2g (80.1%) of a clear golden liquid.

Analysis: Calculated: 8.86%P; 18.3%S. Found: 9.7%P; 18.8%S.

EXAMPLE 27

S-dihydrocycloheptatriethyl-O,O'-di-isobutyl dithiophosphate

Cycloheptatriene (92g, 1.0m) and O,O'-di-isobutyl dithiophosphoric acid (264g, 1.0m) were heated together for 5 hours at 115°C. The crude product was worked up in the same manner as in Example 12 to yield 285.2g of a final product containing 10.5%P and 21.1%S (theory 9.4%P and 19.2%S).

EXAMPLE 28

S-tetrahydrocycloheptatrienyl bis O,O'-di-isobutyl dithiophosphate)

Cycloheptatriene (46g, 0.5m) and O,O'-di-isobutyl dithiophosphoric acid (264g, 1.0m) were heated together for 14 hours at 120°C. The crude product was worked up in the same manner as in Example 12 to yield 276g. of a final product containing 10.6%P and 23.0%S (theory 10.8%P and 22.2%S).

EXAMPLE 29

S-dihydrocyclododecenyl-O,O'-di-isobutyl dithiophosphate

Cyclododecene (166g, 1.0m) and O,O'-di-isobutyl dithiophosphoric acid (264g, 0.1m) were heated together for 27 hours at 120°C. The crude product was worked up in the same manner as in Example 12 to yield 380g of a final product containing 7.6%P and 15.4%S (theory 7.6%P and 15.7%S).

EXAMPLE 30

2:1 Reaction Product of O,O'-di-isobutyl dithiophosphoric acid and Cycloocta-1,3-diene

An attempt was made to prepare this reaction product in the same way as Example 26, except in that 1.0 mole of the dithiophosphoric acid was used and that heating was continued for a total of 84 hours, 2ml and 3ml of the boron trifluoride etherate being added after 23 hours and 56 hours respectively. After this period a determination of acidity indicated that the reaction had not gone further than a 1:1 reaction, i.e. the product was the same as Example 26. The crude reaction product was worked up in the same way as in Example 26.

Analysis: Calculated (for a 2:1 product): 10.5%P; 21.6%S. Found: 9.6%P; 22.1%S.

The infra-red spectra of the products of all of Examples 1 to 29 were consistent with the expected products having been obtained, but in the case of Example 30 the infra-red spectrum was more consistent with a 1:1 reaction product having been obtained.

Mineral oil blends containing additives in accordance with the present invention and the products of Examples 25 to 30 were evaluated by Rotary Bomb Tests, Petter W1 Engine Tests and Hot Oil Oxidation Tests. The Rotary Bomb Test was carried out in the manner described in the left-hand column of page 220 of the article entitled, "Evaluation of Antioxidants for Automotive Lubricants Using the Rotary Bomb" in the Journal of the Institute of Petroleum, Vol. 55, No. 544, July 1969, pages 219 to 226. The tests were carried out at 150°C, with water present as described in the aforementioned article. The blends tested consisted of 2.0% by weight of the antioxidant being tested dissolved in 98% by weight of a 500 Solvent Neutral mineral oil.

The Petter W1 Engine Tests were carried out for 36 hours, using a Petter W1 laboratory engine built and run according to the standard IP 176/69 procedure, except in that a sample of the oil was not taken after 16 hours.

The blends tested in this were fully formulated blends prepared by modifying a blend formulated to comply with the U.S. Military Specification MIL-L-46152. The blend complying with this specification consisted of a mineral oil base stock containing an additive package, the latter consisting of a detergent/dispersant/inhibitor system containing a zinc dialkyl dithiophosphate antioxidant. The blends tested in the Petter W1 engine were identical with the blend complying with MIL-L-46152, except in that the zinc dialkyl dithiophosphate was omitted and replaced by the antioxidant being tested, the latter being used in an amount such as to provide a phosphorus concentration in the test blend of 0.9%.

In the Hot Oil Oxidation Test 30ml samples of test blends and 0.7ml of iron naphthenate containing 2.3% iron were placed in 10 × 1 inch test tubes, heated to 150°C and dry air blown therethrough at a rate of 10 liters/hour while maintaining the temperature at 150°C. The test was of 56 hours duration and the total acid number (TAN) and viscosity (at 100°F) of the blends after the tests were determined. The test blends consisted of the additive blended into a 150 solvent neutral base oil to give a constant level of 0.072% phosphorus.

The results of the Rotary Bomb Tests, Petter W1 Engine Tests and Hot Oil Oxidation Tests are set out in the following Table. From the results set out in the Table it will be noted that compounds in accordance with the present invention exhibit antioxidant properties and furthermore inhibit excessive bearing weight losses. For example the current Ministry of Defence Specification DEF-2101-D requires that bearing weight loss under the test conditions used should not exceed 25mg. Compounds in accordance with the present invention satisfied this requirement; whereas corresponding derivatives of a diene having a carbon atom content in the range 8 to 12 but being bicyclic (Example 25), a monocyclic diene having a carbon atom content in the range 8 to 12 but being conjugated (Example 26), a monocyclic triene not having a carbon atom content in the range 8 to 12 (Examples 27 and 28) and a monocyclic olefin having a carbon atom content in the range 8 to 12 but being a mono-olefin (Example 29) all failed to satisfy this important requirement.

TABLE

Test Additive Product of Example:	TEST RESULTS Rotary Bomb Test Time to Induction Break (minutes)**	36 hr. Petter W1 Engine Tests Bearing Weight Loss (mg)	56hr. Hot Oil Oxidation Tests TAN ϕ (mg KOH/g)	Viscosity+ (cSt at 100°F)
1	104*	6	10.2	131.5
2	104*	14	10.9	112.7
3	357*	—	11.1	135.0
4	965 (355)*	14	10.6	128.0
5	259*	—	—	—
6	92	19	—	—
7	496 (200)*	—	—	—
8	—	—	—	—
9	160	—	—	—
10	115	—	9.79	115.4
11	68*	—	—	—
12	132	—	11.3	116.7
13	82	—	—	—
14	98	—	—	—
15	44	—	—	—
16	89	—	8.72	86.82
17	30	32 ≠		
18	175	—	9.68	103.4

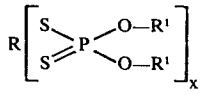
TABLE-continued

Test Additive Product of Example:	TEST RESULTS Rotary Bomb Test Time to Induction Break (minutes)**	36 hr. Petter W1 Engine Tests Bearing Weight Loss (mg)	56hr. Hot Oil Oxidation Tests TAN ϕ (mg KOH/g)	Viscosity+ (cSt at 100°F)
19	140	—	—	—
20	243 (82)*	—	—	—
21	375*	14	10.9	112.6
22	300*	—	—	—
23	325*	10	8.75	88.2
24	179*	15	—	—
25	57	146	—	—
26	250*	33	—	—
27	80*	35	—	—
28	130*	43	—	—
29	80	1278	—	—
30	—	13	—	—

* (time to 25 p.s.i. pressure loss)
** Base oil 35 minutes.
ϕ Base oil 14.0mg KOH/g.
+ Base oil 570.5cSt.
≠ Bearings were in excellent condition, the high weight loss being attributable to mechanical scoring.

We claim:

1. A lubricating composition comprising a major amount by weight based on the total weight of the composition, of a lubricating oil and a minor amount, conferring antioxidant or anti-wear properties, by weight of an oil-soluble, ashless additive compound having the formula:



wherein:

i. R is selected from the group consisting of (a) a residue of a monocyclic, non-conjugated olefin containing from 8 to 12 carbon atoms and at least two ethylenically unsaturated double bonds in the ring and (b) the residue of the product formed by reacting at least one, but not all, of the ethylenically unsaturated double bonds in said monocyclic, non-conjugated olefin with a compound selected from the group consisting of sulphur, phosphorus pentasulphide, a mercaptan, phenol, thiopenol, and thiocyanate anion;

ii. each R^1 is the same or different and is phenyl, alkyl-substituted phenyl group containing from 7 to 18 carbon atoms and an alkyl group containing from 3 to 10 carbon atoms; and

iii. x is an integer selected from the group consisting of 1, 2, and 3.

2. A lubricating composition according to claim **1** wherein R is the residue of a monocyclic, non-conjugated olefin containing 8 to 12 carbon atoms and at least two ethylenically unsaturated double bonds in the ring, the ring bearing at least one substituent selected from the group consisting of alkyl groups, alkoxy groups and hydroxy groups.

3. A lubricating composition according to claim **1** wherein R^1 is a phenyl or alkyl-substituted phenyl group containing from 7 to 18 carbon atoms.

4. A lubricating composition according to claim **1** wherein R^1 is an alkyl group containing from 3 to 10 carbon atoms.

5. A lubricating composition according to claim **1** wherein:

R is selected from the group consisting of the residue of a monocyclic, non-conjugated olefin containing from 8 to 12 carbon atoms and at least two ethylenically unsaturated double bonds in the ring.

6. A lubricating composition according to claim **5** wherein R is the residue of a monocyclic, non-conjugated olefin containing 8 to 12 carbon atoms and at least two ethylenically unsaturated double bonds in the ring, the ring bearing at least one substituent selected from the group consisting of alkyl groups and alkoxy groups.

7. A lubricating composition according to claim **5** wherein R^1 is a phenyl or alkyl-substituted phenyl group containing from 7 to 18 carbon atoms.

8. A lubricating composition according to claim **5** wherein R^1 is an alkyl group containing from 3 to 10 carbon atoms.

9. A lubricating composition according to claim **1** wherein:

i. R is the residue of an olefin selected from the group consisting of cyclododeca-1,5,9-triene, cyclooctа-1,5-diene, benzylthiocyclododecadiene, cis-5-trans-9-cyclododecadiene-trans-1,2-diol, sulphurised cyclododecatri-1,5,9-ene, 1-acetoxy cyclododecadiene, phenol/cyclododeca-1,5,9-triene reaction product, phosphosulphurised cyclododeca-1,5,9-triene and 1,2-dithiocyanocyclooct-5-ene;

ii. each R^1 is the same or different and is selected from the group consisting of isobutyl, tridecyl, p-nonylphenyl, capryl, isodecyl, 2-ethylhexyl, p-cresyl, isopropyl and allyl groups; and

iii. x is an integer selected from the group consisting of 1, 2 and 3.

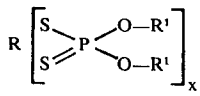
10. A lubricating composition according to claim **1** comprising the additive in an amount of from 0.1 to 10% by weight based on the total weight of the composition.

11. A lubricating composition according to claim **1** comprising the additive in an amount of from 0.25 to 5% by weight, based on the total weight of the composition.

12. A lubricating composition according to claim **1** comprising at least one conventional lubricant additive selected from the group consisting of ancillary antioxidants and antiwear additives, corrosion inhibitors, dis-

persants, detergents, thickeners, pour-point depressants and viscosity index improvers.

13. An additive concentrate comprising a concentrated solution of a major amount, conferring antioxidant or antiwear properties, by weight of an oil soluble, ashless additive compound having the formula:



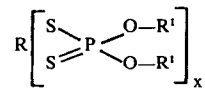
wherein:

i. R is selected from the group consisting of (a) the residue of a monocyclic, non-conjugated olefin containing from 8 to 12 carbon atoms and at least two ethylenically unsaturated double bonds in the ring and (b) the residue of the product formed by reacting at least one, but not all, of the ethylenically unsaturated double bonds in said monocyclic, non-conjugated olefin with a compound selected from the group consisting of sulphur, phosphorus pentasulphide, a mercaptan, phenol, thiopenol, and thiocyanate anion;

ii. each R^1 is the same or different and is phenyl, alkyl-substituted phenyl group containing from 7 to 18 carbon atoms and an alkyl group containing from 3 to 10 carbon atoms; and

iii. *x* is an integer selected from the group consisting of 1, 2 and 3 and a minor amount of mineral oil.

14. An additive package comprising a concentrated solution in mineral oil of a major amount, conferring antioxidant or anti-wear properties, by weight of an oil-soluble, ashless additive compound having the formula:



wherein:

i. R is selected from the group consisting of (a) a residue of a monocyclic, non-conjugated olefin containing from 8 to 12 carbon atoms and at least two ethylenically unsaturated double bonds in the ring and (b) the residue of the product formed by reacting at least one, but not all, of the ethylenically unsaturated double bonds in said monocyclic, non-conjugated olefin with a compound selected from the group consisting of sulphur, phosphorus pentasulphide, a mercaptan, phenol, thiophenol and thiocyanate anion.

ii. each R^1 is the same or different and is phenyl, alkyl-substituted phenyl group containing from 7 to 18 carbon atoms and an alkyl group containing from 3 to 10 carbon atoms; and

III. *x* is an integer selected from the group consisting of 1, 2 and 3 with at least one conventional additive.

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