United States Patent Office 3,103,492 Patented Sept. 10, 1963

3,103,492

LUBRICATING COMPOSITION

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No Drawing. Original application July 30, 1958, Ser. No. 751,902. Divided and this application Aug. 12, 1960, Ser. No. 49,162

20 Claims. (Cl. 252—32.7)

This invention relates to certain new S-amine O,O-dialiphatic phosphorothioates and to improved lubricating compositions containing the same. A particular aspect of this invention relates to the improvement of the lubricating properties of hydrocarbon lubricating oils by the addition thereto of certain S-amine O,O-dialiphatic phosphorothioates.

The phosphorothioates contemplated by this invention generally improve the antiwear and extreme-pressure lubricating characteristics of the base oil. In addition, these phosphorothioates can be combined with certain other addition agents which together cooperate with each other and the base oil to provide lubricating compositions having performance levels more than adequate to meet the extreme requirements of vehicle differentials having both hypoid-type gears and limited-slip mechanisms.

Due to design, a conventional differential will always drive the wheel which offers the least resistance to turning. As a result, a vehicle equipped with a conventional differential, under adverse conditions, loses traction driving force as evidenced by wheel spinning when the traction wheels bounce over rough roads or non-uniform traction surface conditions such as ice and snow spots, wet and dry pavements, sand and gravel.

There has recently been commercialized for use with passenger cars, station wagons, light trucks, and the like, a mechanism known as a locking differential or limited-slip differential, which mechanism permits an automotive axle to transmit the major driving force to the wheel, with the better traction thus minimizing the disadvantages of driving, under adverse conditions, a vehicle equipped with a conventional differential.

With the commercial advent of limited-slip differentials, the use of known hydrocarbon lubricating oils and hydrocarbon lubricating oil compositions containing additives therein has not proved adequate to meet the lubrication requirements of both the hypoid gears and the limited-slip differential mechanism. The non-effectiveness of said known oils and compositions is apparent in the case of a limited-slip differential, for example, from the stick-slip action (resulting in an objectionable "chatter" which may reach the proportion of "thumping") resulting when a vehicle provided with such a device makes a turn, thus instigating action in the limited-slip mechanism.

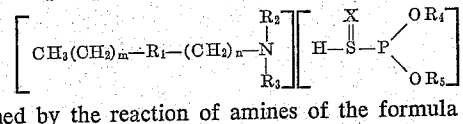
Various known lubricity agents have been added to gear lubricants in attempts to alleviate the stick-slip problem. In general, while these lubricity agents, such as methyl oleate, glycerol mono-oleate, desulfurized degras and sulfurized sperm oil, help to alleviate the stick-slip problem it was found that other properties which were "built" into the gear lubricants to meet the requirements of the hypoid gearing were deleteriously affected. Thus, for example, a hydrocarbon oil lubricant containing various multi-purpose additives, which lubricant would meet the

specifications of MIL-L-2105A, would not meet those specifications after the addition of one of these known lubricity agents in an amount sufficient to eliminate the stick-slip problem.

It is an object of this invention to provide a class of new compounds which, when combined with a hydrocarbon oil such as a mineral oil fraction of appropriate lubricating viscosity, are effective to improve the antiwear and extreme-pressure lubricating characteristics of such oils. A further object is to provide improved lubricating compositions which alleviate the stick-slip problem associated wtih limited-slip differentials and also eliminate the undesirable disturbance in automatic transmissions known as "squawk" which occurs when the "bands" of such a transmission are engaged. It is also an object of this invention to provide a class of compounds which, when combined with certain other classes of oil addition agents, cooperate with each other and the base oil to provide hydrocarbon oil compositions which pass the MIL-L-2105A specification and, in addition, satisfactorily alleviate the stick-slip problem of limited-slip differential mechanisms. It is also an object of this invention to provide a class of compounds which provide a significant improvement in the antiwear properties of a hydrocarbon oil or hydrocarbon oil containing various additives when added thereto in relatively small amounts.

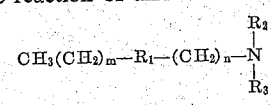
In its broadest aspect, the lubricating compositions of our invention comprise a major amount of a hydrocarbon oil, such as a mineral oil fraction of suitable lubricating viscosity, and a minor amount of certain S-amine O,O-dialiphatic phosphorothioates of the formula

(I)



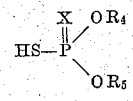
formed by the reaction of amines of the formula

(II)



with dialiphatic phosphorothioates of the formula

(III)



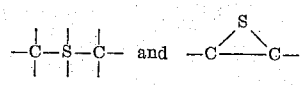
In each of the Formulae I, II and III above, m is an integer from 0 to 17, n is an integer from 0 to 17, the sum of m and n being from 9 to 17, R_1 is selected from

$$-CH_2-CH_2-$$

—CH=CH— and sulfurized —CH=CH—; R_2 and R_3 are selected from hydrogen and aliphatic radicals containing from 1 to 4 carbon atoms; X is selected from oxygen and sulfur, but preferably sulfur; and R_4 and R_5 are each aliphatic radicals containing from 1 to 12 carbon atoms, the sum of the carbon atoms of R_4 and R_5 being at least 3, but when the sum of m and n is 9, R_4 and R_5 each contain not more than 9 carbon atoms.

The aliphatic radicals from which R_2 and R_3 can be selected are preferably alkyl radicals containing from 1 to 4 carbon atoms, but can be other aliphatic radicals, such as hydroxypropyl, hydroxyethyl, beta-chloroethyl, etc. The aliphatic radicals from which R_4 and R_5 can

be selected are preferably alkyl radicals, such as methyl, ethyl, propyl (n- and iso-), butyl (n-, sec.-, iso- and tert.-), amyl (n-, sec.-, iso- and tert.-); hexyl radicals, such as n- and sec.-2,2-dimethyl-3-butyl, 2,2-dimethyl-4-butyl, 2,3-dimethyl-2-butyl, 2-methyl-1-pentyl, 2-methyl-2-pentyl, 3-methyl-1-pentyl, 3-methyl-2-pentyl; heptyl radicals, such as n- and sec.-2,3-dimethyl-pentyl, 2,4-dimethyl-2-pentyl, 2,4-dimethyl - 3 - pentyl, 2,2,3-trimethyl-3-butyl, 3-ethyl-2-pentyl, 2-methyl-2-hexyl; octyl radicals, such as n-2-ethylhexyl, diisobutyl, capryl; nonyl radicals, such as n-diisobutyl carbinyl; decyl radicals, such as n- and iso-decyl; undecyl radicals and dodecyl radicals; and especially those alkyl radicals derivable from the oxo process; halogen-containing alkyl radicals such as alkenyl radicals, such as vinyl; propenyl radicals, such as allyl and iso-propenyl; butenyl radicals, such as n-butenyl-1, n-butenyl-2, n-butenyl-3, iso-butenyl; pentenyl radicals, such as n-pentenyl-1, n-pentenyl-2, n-pentenyl-3; hexenyl radicals, such as n-hexenyl-1, n-hexenyl-2, n-hexenyl-3, 4,4-dimethylbutenyl-2, 3,4 - dimethylbutenyl - 1; heptenyl radicals, such as n-heptenyl; octenyl radicals, such as n-octenyl, diisobutenyl; nonenyl radicals, such as n-nonenyl; decenyl radicals, such as n-decenyl, iso-decenyl, undecenyl; dodecenyl radicals, such as n-dodecenyl and triisobutenyl; cycloalkyl radicals, such as cyclopentyl, alkylated cyclopentyl; cyclohexyl and alkylated cyclohexyl radicals, such as mono- and polymethyl cyclopentyl, mono- and polymethyl cyclohexyl, mono- and polyethyl cyclohexyl, mono- and polyisopropyl cyclohexyl, and mono-tert.-amyl cyclohexyl; cycloalkenyl radicals, such as cyclopentenyl, alkylated cyclopentenyl, cyclohexenyl, alkylated cyclohexenyl; cycloalkyl-substituted alkyl radicals, such as cyclopentylethyl, cyclohexylethyl, methylcyclohexylethyl; alkoxy-substituted alkyl radicals; cycloalkoxy-substituted alkyl radicals; alkenoxy-substituted alkyl radicals; alkoxy radicals;



and cycloalkyl radicals containing sulfur. Preferably, R_4 and R_5 are selected from normal and branched chain alkyl radicals containing 3 to 6 carbon atoms.

Examples of amines which can be used in our invention are dodecylamine, dodecenylamine, sulfurized dodecenylamine, tridecylamine, tridecenylamine, sulfurized tridecenylamine, tetradecylamine, N,N-2-hydroxypropyl octadecenylamine, N,N,N - di - 2 - hydroxypropyl octadecenylamine, N,N-hydroxyethyl octadecenylamine, N,N - hydroxybutyl octadecenylamine, tetradecenylamine, sulfurized tetradecyenylamine, pentadecylamine, pentadecenylamine, sulfurized pentadecyenylamine, hexadecylamine, hexadecenylamine, sulfurized hexadecyenylamine, heptadecylamine, heptadecenylamine, sulfurized heptadecyenylamine, octadecylamine, octadecenylamine, sulfurized octadecyenylamine, nondecylamine, nondecenylamine, sulfurized nondecyenylamine, eicosylamine, eicosylnylamine, sulfurized eicosyenylamine, methyldodecylamine, dimethyldodecylamine, diisopropyl pentadecylene amine, diethyl octadecenylamine, methylethyl octadecylamine, methylbutyl sulfurized octadecyenylamine and dimethyl eicosylamine. By "sulfurized," as used herein (for example, sulfurized dodecenylamine), we mean that sulfur has been introduced into an olefinic bond, although the precise chemical structure of the resulting product is uncertain. The sulfurization of the compounds disclosed herein can be accomplished by methods known to the art.

The compounds of Formula I can be prepared by methods known to the art. As non-limiting examples of the preparation of such compounds, the following are illustrative. Parts are parts by weight unless otherwise stated.

EXAMPLE 1

Into a clean, dry, suitable reaction vessel, having means for agitating, cooling and heating the contents thereof, there were charged 287 parts of oleylamine. While agitating and cooling, 318 parts of di(1,3-dimethylbutyl) phosphorodithioic acid were slowly added to the amine in the reactor. Reaction between the amine and the acid was almost instantaneous and was accompanied by the evolution of heat. The temperature of the vessel contents was maintained at 45° C. throughout the reaction period. After all of the acid had been added, agitation was continued for about 30 minutes, after which time a small additional portion of acid was added in order to obtain an essentially neutral mass. The resultant product, S-oleylamine O,O-di(1,3-dimethylbutyl) phosphorodithioate, was a dark amber liquid having a viscosity of about 314.69 centistokes at 100° C. and 24.96 centistokes at 210° C., and a specific gravity at 60°/60° of 0.0934.

EXAMPLE 2

Utilizing the equipment of Example 1, there were charged 280 parts of a technical grade stearylamine containing essentially 93% saturated C_{18}, 1% unsaturated C_{18}, and 6% saturated C_{16} primary amines. Three hundred parts of di(1,3-dimethylbutyl) phosphorodithioic acid were slowly added to the amines without cooling. After addition of the reactants was employed, the mixture was heated to about 60° C. to effect final solution of the materials in the vessel. Thereafter a small amount of acid was added in order to provide a neutral material. The resultant product, essentially S-stearylamine O,O-di-(1,3-dimethylbutyl) phosphorodithioate, was a fluid, viscous mass.

EXAMPLE 3

Utilizing the equipment of Example 1, 244 parts of isopropyl alcohol were added to the reaction vessel, to which were then slowly added 222 parts of P_2S_5 while maintaining the temperature of the reactants at about 60–70° C. After completing the P_2S_5 addition, the reaction product, diisopropyl phosphorodithioic acid, was filtered and then held under vacuum for about two hours to remove residual H_2S.

Thereafter 78 parts of the above prepared acid and 100 parts of oleylamine were reacted at about 60–70° C. An additional small quantity of said acid was added to adjust the pH to about 6.5–7.0 and the desired product, S-octadecenylamine O,O-diisopropyl phosphorodithioate, was recovered.

As hereinbefore stated, the amine portion of the additives of our invention can be saturated, unsaturated or sulfurized. Saturated amines are available commercially, but can also be prepared by hydrogenation of unsaturated amines by methods known to the art, as, for example, by hydrogenation using a nickel catalyst. Sulfurized amines can be prepared from unsaturated amines by known methods, such as, for example, by the slow addition of sulfur to unsaturated amines at a temperature of about 125° C.

The additives of the present invention can be employed in any hydrocarbon oil or hydrocarbon oil composition. Thus, for example, our additives can be employed in ordinary oil-base lubricants, as well as the so-called "heavy-duty" types of lubricants containing various functional additives. Suitable base stocks include, for example, mineral oils and synthetic oils. An example of a mineral oil is a petroleum fraction of lubricating viscosity. Examples of synthetic oils are those obtained by the polymerization of olefins, cracking coal tar fractions, animal, vegetable or fish oils or their hydrogenated products, and mixtures thereof with mineral oils. The viscosity of the oil may vary, depending upon the intended application of the finished lubricant, from about 1 to about 10,000 centistokes at 100° F. Particularly pre-

ferred for use in this invention, i.e., in the hypoid gears of automotive vehicles, are hydrocarbon oils having viscosities from about 10 to about 1500 centistokes at 100° F. The oil should, of course, also be selected on the basis of suitable pour point and viscosity index characteristics for the specific purpose intended, it being understood that the desired characteristics of the finished lubricant may be obtained by the addition of lubricating oil additives to provide the desired properties in the oil.

In addition to the foregoing, we contemplate using the additive of our invention in combination with certain preferred types of additives in hydrocarbon oils to provide a lubricating composition which will provide a level of performance hereinafter described. These preferred types of additives, which are referred to as types A, B and C, are as follows:

Type A.—A chlorinated aliphatic material or a chlorinated aliphatic material in which part of the chlorine has been replaced with a thiocarbonate group. Suitable aliphatic materials in either case are those containing from 5 to about 24 carbon atoms.

When a chlorinated aliphatic material is to be used, the higher carbon content materials are preferred, especially petroleum wax or similar material, and chlorination is carried to the level where the average amount of chlorine substituted is about 30% to 70% of the theoretical maximum, and preferably to about 40% to 50% of the theoretical maximum in order to obtain maximum benefit of such an additive without a serious decrease in solubility, which normally occurs when a highly chlorinated material is used.

When a chlorinated aliphatic material-thiocarbonate reaction product is used, it is usually preferable to use aliphatic materials having from about 5 to about 15 carbon atoms, since the extremely short-chain and extremely long-chain materials are more difficult to react and are less efficient in their effect upon the final formulation. Preferably, a kerosene containing about an average of 10 carbon atoms and having a boiling range of from about 150° C. to about 275° C. is used.

The thiocarbonate group which is used to replace a part of the chlorine is derived from an alkali (Na, K, Li) or alkaline earth (Ca, Sr, Ba) metal salt of a thiocarbonic acid, preferably an alkyl thiocarbonic acid. The thiocarbonate radical may be a mono-, di- or trithiocarbonate, but, in general, preference is given to the dithiocarbonate (xanthate) compounds, characterized by the divalent group (OCS_2). The trithiocarbonate type of compounds, characterized by the divalent group (CS_3), have also been prepared and have been found to form effective extreme-pressure agents in combination with the chlorinated aliphatic material, but from the standpoint of odor and cost, we prefer products in which the thiocarbonate constituent is a xanthate group.

A procedure which may be followed in synthesizing this material involves substantial chlorination of an aliphatic compound or a predominantly aliphatic material, such as a petroleum naphtha, followed by reaction of the chlorinated material with an alkali or alkaline earth metal salt of an alkyl thiocarbonic acid in such proportions and under such conditions that only part of the chlorine is replaced by the alkyl thiocarbonate.

As to the substituents in the thiocarbonate or xanthate groups which are substituted in the chlorinated aliphatic material, it is preferable that such substituents be derived from aliphatic compounds of relatively low molecular weight, e.g., methyl, ethyl, propyl and butyl. There is no particular advantage to be gained by having a long-chain alkyl group in the xanthate or thiocarbonate substituent from the standpoint of solubility, etc., and the lower molecular weight alkyl groups give a finished product in which the content of the chlorine and characterizing divalent thiocarbonate groups (O_2CS, OCS_2 or CS_3) is somewhat more highly concentrated.

Examples of the thiocarbonate or xanthate materials which may be reacted with chlorinated aliphatic materials to provide extreme-pressure agents of the type discussed are sodium or potassium methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, octyl, decyl or dodecyl xanthates or the corresponding mono- or trithiocarbonates.

It is desired that the proportions of reactants used and the conditions of reaction be controlled so that the final product contains both chlorine and thiocarbonate characterizing groups in chemical combination with the aliphatic hydrocarbon material. The relative amounts of chlorine and sulfur, or, more specifically, of chlorine and thiocarbonate characterizing groups, in the finished product may be varied over a relatively wide range, but, in general, it may be said that the finished product should preferably be one which contains from about 25% to 40% of chlorine and from about 7% to 15% of sulfur. Expressing the sulfur content as the equivalent amount of characterizing thiocarbonate groups present in the product, such preferred products are more accurately identified as containing from about 10% to about 22% characterizing dithiocarbonate or xanthate (divalent OCS_2) groups or from about 7% to about 17% characterizing trithiocarbonate (divalent CS_3) groups. For general purposes, it may be said that the characterizing thiocarbonate group content is preferably from about 7% to about 22%.

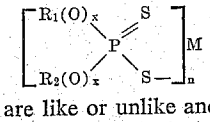
A specific non-limiting example of the preparation of a chlorinated aliphatic-thiocarbonate reaction product is given below. Parts are in parts by weight.

EXAMPLE A

A chlorinated naphtha is first prepared by chlorinating petroleum naphtha (Stoddard solvent) until it contains about 54% by weight of chlorine. Two hundred parts of the chlornaphtha are then dissolved in about 500 parts of acetone and placed in a reaction vessel heated by a water jacket and equipped with stirrer and reflux condenser. To this solution, 120 parts of potassium isopropyl xanthate are added and the mixture held at its boiling temperature with stirring under reflux for about 2 hours. The resulting mixture is cooled to room temperature, filtered, and the filtrate subjected to distillation to remove the acetone. After removal of the acetone, the product is washed to remove potassium salts and is dried and filtered. The finished reaction product obtained by the foregoing procedure is a dark brown liquid containing about 11% sulfur, or, more specifically, about 16% of the characterizing xanthate (divalent OCS_2) group, and 34% chlorine.

Variation in xanthate and chlorine content of the reaction product can be obtained by varying the degree of chlorination of the naphtha, by varying the amount of alkali xanthate used, and by varying the hydrocarbon substituent in the alkali xanthate. Thus, products of widely varying chlorine and xanthate content are readily possible.

Type B.—A metal salt of a dithio acid of phosphorous represented by the structure,



where R_1 and R_2 are like or unlike and are selected from acyclic, alicyclic, aromatic and substituted aromatic radicals, M is a metal selected from Zn, Ba, Mg and Ca, but preferably Zn, n is the valence of M, and x is 1 (phosphoric acids) or 0 (phosphinic acids).

Examples of acyclic radicals are propyl, butyl, isobutyl, sec.-butyl, amyl, isoamyl, hexyl, isohexyl, 2-ethylamyl, octyl, iso-octyl, 2-ethylhexyl, decyl, dodecyl, tetradecyl and hexadecyl; of alicyclic radicals are cyclopentyl, cyclohexyl, methylcyclohexyl, ethylcyclohexyl, amylcyclohexyl; of aromatic radicals and substituted aromatic radicals are those radicals having six or more carbon atoms, such as phenyl, methylphenyl, ethylphenyl, dimethylphenyl, propylphenyl, butylphenyl, chlorophenyl and cyclohexylphenyl.

A non-limiting example of the preparation of a metal salt of a dithio acid of phosphorus is the following:

EXAMPLE B

To a suitable reaction vessel are added and intimately mixed approximately 4 molecular proportions of methyl isobutyl carbinol and approximately one molecular proportion of phosphorus pentasulfide. The mixture is heated at 90–100° C. for about three hours employing a pressure slightly below atmospheric. Thereafter the reaction product (a dithiophosphoric acid) is decanted from the unreacted phosphorus pentasulfide and admixed with a small amount of water and zinc oxide in excess of that theoretically required. The mixture is heated at about 60° C. for about three hours, cooled and filtered. The dark oily zinc salt of di(1,3-dimethylbutyl) dithiophosphoric acid so obtained analyzes approximately, in weight ratio, one part of phosphorus and approximately 2.2 parts of sulfur per one part of zinc.

Type C.—A phosphorized-sulfurized dicyclic terpene obtained by reacting a dicyclic terpene, such as carene, pinene, camphene, fenchene and similar terpenes containing one double bond in the molecule and comprising two-ring systems, with a phosphorus sulfide at a temperature of about 100–160° C. While any phosphorus sulfide, such as P_2S_5, P_3S_6, P_4S_6, P_4S_3, P_4S_7, etc., can be employed in the preparation of said reaction products, the preferred reaction products are those obtained employing phosphorus pentasulfide (P_2S_5). While the proportions of these reactants will vary depending upon the oil-solubility and oil-improvement properties desired, the preferred product is that obtained by the reaction of about one mol of a phosphorus sulfide with about four mols of a dicyclic terpene at a reaction temperature in the range of about 100–160° C.

As a non-limiting example of the preparation of an oil-soluble sulfurized- and phosphorized-dicyclic terpene, the following is illustrative. Parts are parts by weight.

EXAMPLE C

A mixture of 245 parts of pinene (substantially 1.8 mol) and 220.5 parts of mineral oil (SAE–10) grade motor oil) is charged into a suitable reaction vessel and is heated to 110–115° C. While stirring, 100 parts of phosphorus pentasulfide (substantially 0.45 mol) are added slowly while maintaining the temperature at 110–120° C. The temperature of the mixture is then increased to about 150° C. and stirred at that temperature for one hour. After partial cooling of the reaction mixture, there is added a small amount of clay and the mixture filtered. The filtered product is a clear red viscous oil having a specific gravity of 1.02 at 15.6/15.6° C., a Saybolt viscosity of 145 at 210° F., analyzing about 4.7% phosphorus and about 13% sulfur and containing 43% by weight mineral oil.

Due to the sludge-forming characteristics of the phosphorized-sulfurized dicyclic terpene while in storage, it may be desirable to incorporate in the composition of this invention a small amount (e.g., 2% to 10% by weight based on the weight of the phosphorized-sulfurized dicyclic terpene) of an oil-soluble alkali metal or alkaline earth metal hydrocarbon sulfonate such as sodium, barium or calcium wax-alkylated benzene sulfonates or petroleum sulfonates.

In general, in the preferred lubricating compositions of this invention, the weight ratio of the zinc dihydrocarbon dithiophosphate to the phosphorized- and sulfurized-dicyclic terpene will be approximately 1 to 9 parts of the former to 1 part of the latter, and the weight ratio of the chlorinated aliphatic material to the zinc dihydrocarbon dithiophosphate is approximately 0.5 to 3 parts of the former to 1 part of the latter, and the total weight percent based on the mineral oil base is in the range of about 4% to 20%. Optimum results, however, are obtained when the weight ratio of the zinc dihydrocarbon dithiophosphate to the phosphorized-sulfurized dicyclic terpene is about 4 to 6.5 parts of the former to 1 part of the latter and wherein the weight ratio of the chlorinated aliphatic material, in which part of the chlorine has been replaced with a thiocarbonate group, to the zinc dihydrocarbon dithiophosphate is approximately 1 to 1.5 parts of the former to 1 part of the latter. Generally, we employ the aforedescribed three components so that their total weight is in the range of about 8% to 15% by weight based on the hydrocarbon oil.

In order to demonstrate the effectiveness of the compounds described above in fulfilling the objects hereinbefore stated, the following tests were utilized:

Shell Four-Ball Test

To demonstrate the increase in antiwear and extreme-pressure lubrication properties of a hydrocarbon oil by the addition of a small amount of the additives of our invention to such an oil, a Shell Four-Ball machine containing EP grade steel balls was employed using a 50 kg. load for 15 minutes at 1800 r.p.m. and 250° F. The following results were observed. In all cases, 1% by weight of additive was used in a solvent refined Mid-Continent SAE 90 oil, herein referred to as the "SAE 90 Base."

Composition	Seizure	Scar width, mm.
SAE 90 Base	Yes	[1] 2.3
SAE 90 Base plus S-octadecenylamine O,O-diethyl phosphorodithioate.	No	0.50
SAE 90 Base plus S-octadecenylamine O,O-diisopropylphosphorodithioate.	No	0.375
SAE 90 Base plus S-octadecenylamine O,O-di(1,3-dimethylbutyl) phosphorodithioate.	No	0.27
SAE 90 Base plus S-octadecenylamine O,O-dioctyl phosphorodithioate.	No	0.375
SAE 90 Base plus S-octadecenyl O,O-didodecyl phosphorodithioate.	No	0.375
SAE 90 Base plus S-dodecylamine O,O-di(1,3-dimethylbutyl) phosphorodithioate.	No	0.425
SAE 90 Base plus S-dodecylamine O,O-dioctyl phosphorodithioate.	No	0.575
SAE 90 Base plus S-dodecylamine O,O-didecyl phosphorodithioate (some insolubility).	Yes	0.675
SAE 90 Base plus S-dodecyl O,O-didodecyl phosphorodithioate (some insolubility).	Yes	0.675

[1] After 8 min.

From these results, it is seen that compounds within the range of limits described for the addition agents of our invention impart a marked improvement in antiwear and extreme-pressure lubrication properties to a hydrocarbon oil, and that compounds outside the range of limits described for the additives of our invention do not possess the ability to impart these improved lubricant properties.

High-Speed Axle Test

This test is a research technique for determining load-carrying and extreme-pressure lubrication characteristics of universal gear lubricants in axles under conditions of high speed and shock loading. All tests were performed according to the procedure established by the Coordinating Research Committee (CRC) and given the designation L–42458. This test differs from CRC test L–19–645 in that the peak torques are approximately two to three times those obtained in the L–19 procedure. Results of the L–42 test are stated as "pass" or "fail," a pass being equivalent to the performance which is obtained with CRC Reference Gear Oil (R60)–110–57.

High-Torque Axle Test

This test is a research technique for determining load-carrying, antiwear and extreme-pressure lubrication properties of universal gear lubricants in axles under conditions of high speed low-torque and low-speed high-torque using a single gear set. All tests were performed according to the procedure established by the CRC and given the designation L–37–956, usually known as L–37. This test differs from CRC L–20–545 in that there is high speed

running on the gears prior to the high torque run and a 30% increase in load during the high torque portion of the test. Thus, the L–37 test is more severe than the L–20. In the L–37 test, results are normally stated as pass, borderline (BL) and fail.

Limited-Slip Test

This is a test devised to enable evaluation of the effectiveness of various additives in hydrocarbon oils in alleviating the stick-slip problem. The test is as follows: The apparatus to be used is assembled as required for a high speed and shock-loading test (CRC designation L–42). In our tests we used a Spicer Model 44–1 rear axle equipped with gears having a 47:12 ratio (as required for the L–42 test), which had incorporated therein a limited-slip or locking differential device manufactured by the Dana Corporation. The clutch plates in the differential (which are part of the slip-limiting mechanism) are arranged for the milder setting (i.e., two splined plates between two tonged plates, giving three friction surfaces). The field current on the right dynamometer (i.e. the dynamometer occupying the position of the right rear wheel if the test equipment were a vehicle) is adjusted to give a 65-pound load at 100 r.p.m., and the field current on the left dynamometer is adjusted to give a 15-pound load at 100 r.p.m. The carburetor idle screw is adjusted to give a 30-wheel r.p.m. at no load (i.e., no differentialing). After completing the above, maximum axle dif ferentialing is obtained, using second gear of a four-speed transmission, by accelerating to 100-wheel r.p.m. using a 10-inch manifold vacuum. Differentialing and noises due to the action of the clutches are observed. The above cycle is repeated once using a 10-inch manifold vacuum and twice using a 5-inch manifold vacuum. The complete evaluation of the additive undergoing test is accomplished using the following dynamometer load combinations:

Rating	Right	Left	Rating	Right	Left
1	65	15	1	15	65
2	165	15	2	15	165
3	265	15	3	15	265
4	365	15	4	15	365

The test composition is given a two-number rating, which rating is dependent upon the load conditions at which the first reproducible noise is observed. Thus, if under "right turn" conditions a reproducible noise (as a grind or chatter) occurred at 265–15, and under "left turn" conditions, at 15–165, the additive would be rated 3–2. If no noise is observed under any of the test conditions, an additive would be rated 5–5. The temperature of the hydrocarbon oil composition within the axle is maintained between 150° C. and 200° C. As a precautionary measure, a break-in and warm-up period for each composition is provided by running at speeds not greater than 100-wheel r.p.m., under conditions resulting in differentiating, first in one direction and then in the other. For a more stringent test, the clutch plates are arranged to provide five friction surfaces (i.e., by alternating the splined and tongued plates). In expressing the results, the average of a rating is usually expressed. Thus, a 5–3 rating (or a 4–4 rating) would be expressed as a 4 rating. The significance of the ratings is as follows:

5—Pass ——— No chatter under any of the test conditions.
4—Pass ——— Some chatter under severe test conditions.
3—Borderline — Chatter under severe test conditions.
2 or 1—Fail —— Chatter under mild test conditions.

The results observed in the latter three tests are tabulated below. The percent additive is percent by weight based on the weight of the hydrocarbon oil.

Spl. No.	Test composition	Weight percent of additive	Limited-slip test		L–42	L–37
			Three friction surfaces	Five friction surfaces		
1	Gear Oil "A"		2	1	Pass	Pass.
2	"A" plus S-octadecenylamine O,O-diethyl phosphorodithioate.	0.25	5			
		0.35	5	4½	Pass	
3	"A" plus S-octadecenylamine O,O-di-2-chloroethyl phosphorodithioate.	0.5	5	5		
4	"A" plus S-octadecenylamine O,O-diisopropyl phosphorodithioate.	0.25	4	3		
		0.35	5	5	Pass	Pass.
5	"A" plus S-octadecenylamine O,O-di-*n*-propyl phosphorodithioate.	0.35		4		
6	"A" plus S-octadecenylamine O,O-di-sec.-butyl phosphorodithioate.	0.35		4		
7	"A" plus S-octadecenylamine O,O-di-isobutyl phosphorodithioate.	0.35		4		
8	"A" plus S-octadecenylamine O,O-di-sec.-amyl phosphorodithioate.	0.25		5		
9	"A" plus S-octadecenylamine O,O-di-1,3-dimethylbutyl phosphorodithioate.	0.15	4		Pass	Pass.
		0.25	5	4		
		0.35	5	5		
		0.50		5		
10	"A" plus S-octadecenyl 9,10-episulfide amine O,O-di-1,3-dimethylbutyl phosphorodithioate.	0.35		4½		
11	"A" plus S-octadecenylamine O,O-didodecyl phosphorodithioate.	0.35		4		BL. Pass.
12	"A" plus S-dimethylstearylamine O,O-di-1,3-dimethylbutyl phosphorodithioate.	0.25		4		
		0.35		5		
13	"A" plus S-stearylamine O,O-diisopropyl phosphorodithioate.	0.50	5			
		0.70	5			
14	"A" plus S-stearylamine O,O-di-1,3-dimethylbutyl phosphorodithioate.	0.35		5		
15	"A" plus S-Armeen HT [1] O,O-di-1,3-dimethylbutyl phosphorodithioate.	0.35		5	Pass	
16	"A" plus S-dodecylamine O,O-didodecyl phosphorodithioate.	0.35		4		
17	"A" plus S-dodecylamine O,O-di-1,3-dimethylbutyl phosphorodithioate.	0.25		5		
		0.35		5		
18	"A" plus S-(N,N-2-hydroxypropyl octadecenyl) amine O,O-di-1,3-dimethylbutyl phosphorodithioate.	0.25		4		
		0.35		5		
19	Gear Oil "B" plus S-octadecenylamine O,O-di-1,3-dimethylbutyl phosphorodithioate.	0.75		5		
20	Gear Oil "C" plus S-octadecenylamine O,O-di-1,3-dimethylbutyl phosphorodithioate.	1.0		5		

[1] Armeen HT, a product of Armour and Company, contains, by weight, 25% saturated C_{16}, 70% saturated C_{18}, and 5% unsaturated C_{18} primary amines.

The following table presents the results observed from using S-amine O,O-dialiphatic phosphorothioates not within the aforedescribed class of suitable compounds:

Spl. No.	Test composition	Weight percent of additive	Limited-slip test: Three friction surfaces	Limited-slip test: Five friction surfaces	L–42	L–37
21	"A" plus S-octadecenylamine O,O-dimethyl phosphorodithioate.	0.125	2	----------	Fail	BL.
		0.50	5	----------	do	Pass.
22	"A" plus S-octylamine O,O-di-1,3-dimethylbutyl phosphorodithioate.	0.35	----------	3	----------	
23	"A" plus S-isoamylaniline O,O-di-1,3-dimethylbutyl phosphorodithioate.	0.35	----------	2	----------	
24	"A" plus S-diethylamine O,O-oleyl, t-butyl phosphorodithioate.	0.35	----------	2	----------	
25	"A" plus S-methylamine O,O-dioleyl phosphorodithioate.	0.25	----------	2	----------	
26	"A" plus S-Primene JMT [1] O,O-diisopropyl phosphorodithioate.	0.35	2	----------	----------	
		0.50	2	----------	----------	

[1] Primene JMT, a product of Rohm and Haas, is a mixture of C_{18}–C_{24} highly branched primary amines.

The amount of the new additives of our invention used with a hydrocarbon oil or hydrocarbon oil composition can vary over a range dependent to some extent upon the particular application in which said oil is to be used. Generally, not over about 10% by weight is sufficient. When these additives are used in combination with additives in a hydrocarbon oil designed to give performance sufficient to pass the L–19, L–20, L–37 and L–42 tests, the amount which is used will generally be from about 0.1% to about 1.5% by weight, based upon the amount of said oil, although we prefer to use from about 0.25% to about 1% by weight, based upon the oil content.

As is seen from the above results, the base composition (Gear Oil "A") used would pass the L–42 and L–37 tests, but would not pass the LSD test (sample 1). Gear Oils "A," "B" and "C" contained the aforedescribed preferred additives in quantities falling within the specified ranges for such additives and, more particularly, had the following composition:

GEAR OIL "A"

Ingredient:	Percent by weight of composition
Solvent-refined Mid Continent SAE 90 oil	90.1
Reaction product of Example A	4.3
Reaction product of Example B	4.3
Reaction product of Example C	1.3
Total	100.0

GEAR OIL "B"

Ingredient:	Percent by weight of composition
Solvent-refined Mid-Continent SAE 90 oil	85.8
Reaction product of Example A	6.2
Reaction product of Example B	6.2
Reaction product of Example C	1.8
Total	100.0

GEAR OIL "C"

Ingredient:	Percent by weight of composition
Solvent-refined Mid-Continent SAE 90 oil	86.0
Reaction product of Example A	6.1
Reaction product of Example B	6.1
Reaction product of Example C	1.8
Total	100.0

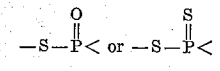
The additives used to make the base oil composition can be varied within the prescribed limits for those additives while maintaining performance levels adequate to pass the L–37 and L–42 tests. However, for purposes of showing the performance results of the additives of our invention, the base oil composition was not varied.

In addition to the aforedescribed, the additives of our invention are suitable for use in hydrocarbon oils of lubricating viscosity which, although not "built" to a level which will give a performance capable of passing the L–37 and L–42 tests, can be used for applications where only a performance level as defined by the L–19–645 and L–20–545 tests is needed. Examples of such compositions are those containing about 2% to about 15% by weight of those preferred additives designated as type A and about 1% to about 5% by weight of those preferred additives designated as type B. Such compositions can also contain a small amount of an oil-soluble alkali metal or alkaline earth metal hydrocarbon sulfonate as previously described. More particular examples of such compositons which also contain an additive of our invention are as follows. Percentages are by weight, based upon the hydrocarbon oil content.

(D) SAE 90 oil plus—
- 7.5% chlorinated wax (about 40% chlorination)
- 2.5% zinc dialkyl dithiophosphate
- .35% S-octadecenylamine O,O-di-1,3-dimethylbutyl phosphorodithioate

(E) SAE 90 oil plus—
- 5.0% reaction product of chlorinated kerosene (containing about 10 carbon atoms) and sodium ethyl xanthate
- 4.2% zinc dihexyl dithiophosphate
- .35% S-octadecenylamine O,O-di-1,3-dimethylbutyl phosphorodithioate

As stated above, the portion of the molecule of the additives of our invention, which is derived from dialiphatic phosphorothioates of Formula III, above, may be



with a preference for the latter. This preference is due to the fact that the presence of the oxygen markedly decreases the solubility of the additives. It should be noted that in either case the



linkage is necessary, as we have found that if there is an



linkage, in addition to the decreased solubility due to the presence of the oxygen, the extreme-pressure properties of a hydrocarbon oil containing additives with such a linkage is significantly lower than a hydrocarbon oil containing additives with a



linkage.

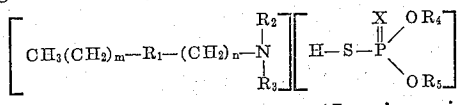
Since the aliphatic radicals of the phosphorothioate portion of the molecule of the compounds of our invention (i.e., R_4 and R_5) can be the same or different, it is intended to include the isomeric mixtures of diesters and mixed esters which are obtained in some cases by the

methods used to prepare such compounds. Thus, for example, to prepare an aliphatic phosphorothioate in which the aliphatic groups are ethyl and butyl, P_2S_5 can be reacted with a mixture of ethyl and butyl alcohols to yield a mixture of diethyl, dibutyl and ethyl, butyl phosphorothioates. We contemplate using such a mixture without separation of the isomers or using any of the specific isomers or combination of insomers.

This application is a division of copending application Serial Number 751,902, filed July 30, 1958 (now Patent Number 3,002,014).

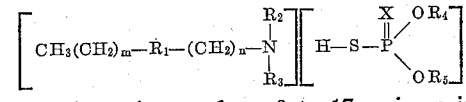
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and, in an amount sufficient to improve the antiwear and extreme pressure properties of said oil but not over about 10% by weight, an S-amine O,O-dialiphatic phosporothioate having the structure,



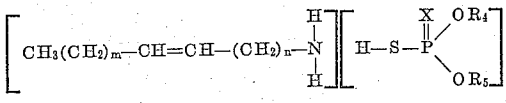
wherein m is an integer from 0 to 17, n is an integer from 0 to 17, the sum of m and n is from 9 to 17; R_1 is selected from the group consisting of —CH_2—CH_2—, sulfurized —CH=CH— and —CH=CH—; R_2 and R_3 are selected from the group consisting of hydrogen and aliphatic radicals containing from 1 to 4 carbon atoms; X is selected from the group consisting of oxygen and sulfur, and R_4 and R_5 are aliphatic radicals containing from 1 to 12 carbon atoms, the sum of the carbon atoms of R_4 and R_5 being at least 3, but when the sum of m and n is 9, R_4 and R_5 each contain not more than 9 carbon atoms.

2. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and, in an amount sufficient to improve the antiwear and extreme pressure properties of said oil but not over about 10% by weight, an S-amine O,O-dialiphatic phosphorothioate having the structure,



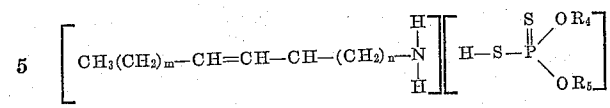
wherein m is an integer from 0 to 17, n is an integer from 0 to 17, the sum of m and n is from 9 to 17; R_1 is selected from the group consisting of —CH_2—CH_2—, sulfurized —CH=CH— and —CH=CH—; R_2 and R_3 are selected from the group consisting of hydrogen and aliphatic radicals containing from 1 to 4 carbon atoms; X is selected from the group consisting of oxygen and sulfur; and R_4 and R_5 are aliphatic radicals each containing from 3 to 6 carbon atoms.

3. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and, in an amount sufficient to improve the antiwear and extreme pressure properties of said oil but not over about 10% by weight, an S-octadecenylamine O,O-dialiphatic phosphorothioate having the structure,



wherein m is 7, n is 8, X is selected from the group consisting of oxygen and sulfur, and R_4 and R_5 are aliphatic radicals containing from 1 to 12 carbon atoms and the sum of the carbon atoms of R_4 and R_5 is at least 3.

4. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and, in an amount sufficient to improve the antiwear and extreme pressure properties of said oil but not over about 10% by weight, an S-octadecenylamine, O,O-dialiphatic phosphorodithioate having the structure,

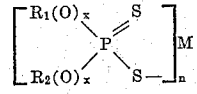


wherein m is 7, n is 8, and R_4 and R_5 are alkyl radicals each containing from 3 to 6 carbon atoms.

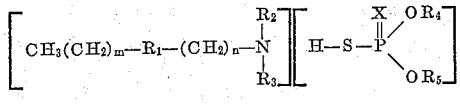
5. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and, in an amount sufficient to improve the antiwear and extreme pressure properties of said oil but not over about 10% by weight, an S-octadecenylamine O,O-diisopropyl phosphorodithioate.

6. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and, in an amount sufficient to improve the antiwear and extreme pressure properties of said oil but not over about 10% by weight, an S-octadecenylamine O,O-di-1,3-dimethylbutyl phosphorodithioate.

7. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and, based on said oil, about 2% to about 15% by weight of a chlorinated aliphatic material having from 5 to about 24 carbon atoms selected from the group consisting of chlorinated aliphatic hydrocarbons wherein the amount of chlorine is from about 30% to about 70% of the theoretical and the product obtained by chemically substituting a part only of the chlorine in a chorinated aliphatic hydrocarbon with an alkyl thiocarbonate group, about 1% to about 5% by weight of a metal salt of a dithio acid of phosphorous of the structure,



where R_1 and R_2 are selected from the group consisting of acyclic, alicyclic, and aromatic hydrocarbon radicals, M is a metal selected from the group consisting of Zn, Ba, Mg and Ca, n is the valence of M, and x is an integer from 0 to 1, and about 0.1% to about 1% by weight of an S-amine O,O-dialiphatic phosphorothioate of the structure



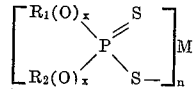
wherein m is an integer from 0 to 17, n is an integer from 0 to 17, the sum of m and n being from 9 to 17; R_1 is selected from the group consisting of

—CH_2—CH_2—

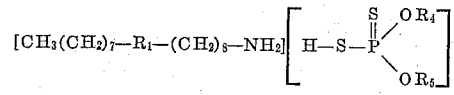
sulfurized —CH=CH— and —CH=CH—; R_2 and R_3 are selected from the group consisting of hydrogen and aliphatic radicals containing from 1 to 4 carbon atoms; X is selected from the group consisting of oxygen and sulfur; and R_4 and R_5 are each aliphatic radicals containing from 1 to 12 carbon atoms, the sum of the carbon atoms of R_4 and R_5 being at least 3, but when the sum of m and n is 9, R_4 and R_5 each contain not more than 9 carbon atoms.

8. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and, based on said oil, about 2% to about 15% by weight of a chlorinated aliphatic material having from 5 to about 24 carbon atoms selected from the group consisting of chlorinated aliphatic hydrocarbons wherein the amount of chlorine is from about 30% to about 70% of the theoretical and the product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon with an alkyl thiocarbonate group, about 1% to about

5% by weight of a metal salt of a dithio acid of phosphorous of the structure,



where R_1 and R_2 are selected from the group consisting of acyclic, alicyclic, and aromatic hydrocarbon radicals, M is a metal selected from the group consisting of Zn, Ba, Mg and Ca, n is the valence of M, and x is an integer from 0 to 1, and about 0.1% to about 1% by weight of an S-amine O,O-dialiphatic phosphorothioate of the structure,

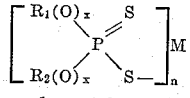


where R_1 is selected from the group consisting of —CH_2—CH_2—, sulfurized —CH=CH— and

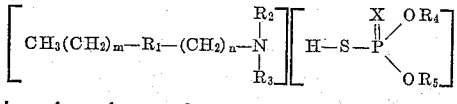
—CH=CH—,

and R_4 and R_5 are each aliphatic radicals containing from 3 to 6 carbon atoms.

9. A lubricating composition comprising a major proportion of a hydrocarbon oil and (*a*) a chlorinated aliphatic material having from 5 to about 24 carbon atoms selected from the group consisting of chlorinated aliphatic hydrocarbons wherein the amount of chlorine is from about 30% to about 70% of the theoretical and the product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon with an alkyl thiocarbonate group, (*b*) a metal salt of a thio acid of phosphorus represented by the structure,

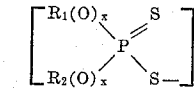


where R_1 and R_2 are selected from the group consisting of acyclic, alicyclic, and aromatic hydrocarbon radicals, M is a metal selected from the group consisting of Zn, Ba, Mg and Ca, n is the valence of M, and x is an integer from 0 to 1 (*c*) a phosphorized-sulfurized dicyclic terpene, the weight ratio of (*a*) to (*b*) being from about 1 to 1.5:1, the weight ratio of (*b*) to (*c*) being from about 4 to 6.5:1, the total weight percent of (*a*), (*b*) and (*c*), based on said oil, being about 4% to 15%, and (*d*) about 0.1% to about 1% by weight, based on said oil, of an S-amine O,O-dialiphatic phosphorothioate of the structure,

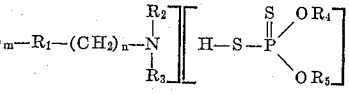


wherein m is an integer from 0 to 17, n is an integer from 0 to 17, the sum of m and n being from 9 to 17; R_1 is selected from the group consisting of —CH_2—CH_2—, sulfurized —CH=CH— and —CH=CH—; R_2 and R_3 are selected from the group consisting of hydrogen and aliphatic radicals containing from 1 to 4 carbon atoms; X is selected from the group consisting of oxygen and sulfur; and R_4 and R_5 are each aliphatic radicals containing from 1 to 12 carbon atoms, the sum of the carbon atoms of R_4 and R_5 being at least 3, but when the sum of m and n is 9, R_4 and R_5 each contain not more than 9 carbon atoms.

10. A lubricating composition comprising a major proportion of a hydrocarbon oil and (*a*) a chlorinated aliphatic material having from 5 to about 24 carbon atoms selected from the group consisting of chlorinated aliphatic hydrocarbons wherein the amount of chlorine is from about 30% to about 70% of the theoretical and the product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon with an alkyl thiocarbonate group, (*b*) a metal salt of a thio acid of phosphorus represented by the structure,

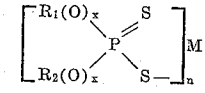


where R_1 and R_2 are selected from the group consisting of acyclic, alicyclic, and aromatic hydrocarbon radicals, M is a metal selected from the group consisting of Zn, Ba, Mg and Ca, n is the valence of M, and x is an integer from 0 to 1, (*c*) a phosphorized-sulfurized dicyclic terpene, the weight ratio of (*a*) to (*b*) being from about 1 to 1.5:1, the weight ratio of (*b*) to (*c*) being from about 4 to 6.5:1, the total weight percent of (*a*), (*b*) and (*c*), based on said oil, being about 4% to 15%, and (*d*) about 0.1% to about 1% by weight, based on said oil, of an S-amine O,O-dialiphatic phosphorothioate of the structure

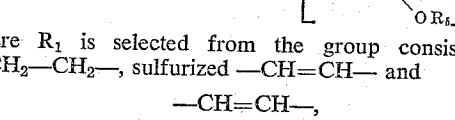


where m is an integer from 0 to 17, n is an integer from 0 to 17, the sum of m and n being from 9 to 17; R_1 is selected from the group consisting of —CH_2—CH_2—, sulfurized —CH=CH— and —CH=CH—; R_2 and R_3 are selected from the group consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms; and R_4 and R_5 are each aliphatic radicals containing from 1 to 12 carbon atoms, the sum of the carbon atoms of R_4 and R_5 being at least 3, but when the sum of m and n is 9, R_4 and R_5 each contain not more than 9 carbon atoms.

11. A lubricating composition comprising a major proportion of a hydrocarbon oil and (*a*) a chlorinated aliphatic material having from 5 to about 24 carbon atoms selected from the group consisting of chlorinated aliphatic hydrocarbons wherein the amount of chlorine is from about 30% to about 70% of the theoretical and the product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon with an alkyl thiocarbonate group, (*b*) a metal salt of a thio acid of phosphorus represented by the structure,



where R_1 and R_2 are selected from the group consisting of acyclic, alicyclic, and aromatic hydrocarbon radicals, M is a metal selected from the group consisting of Zn, Ba, Mg and Ca, n is the valence of M, and x is an integer from 0 to 1, (*c*) a phosphorized-sulfurized dicyclic terpene, the weight ratio of (*a*) to (*b*) being from about 1 to 1.5:1, the weight ratio of (*b*) to (*c*) being from about 4 to 6.5:1, the total weight percent of (*a*), (*b*) and (*c*), based on said oil, being about 4% to 15%, and (*d*) about 0.1% to about 1% by weight, based on said oil, of an S-amine O,O-dialiphatic phosphorothioate of the structure,

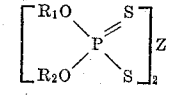


where R_1 is selected from the group consisting of —CH_2—CH_2—, sulfurized —CH=CH— and

—CH=CH—,

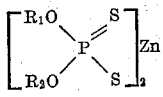
and R_4 and R_5 are each aliphatic radicals containing from 3 to 6 carbon atoms.

12. The lubricating composition of claim 10 wherein (*b*) is a zinc salt of a dithio acid of phosphorous represented by the structure,

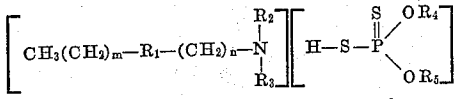


wherein R_1 and R_2 are selected from the group consisting of acyclic, alicyclic, and aromatic hydrocarbon radicals.

13. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and (*a*) the product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon having from 5 to 15 carbon atoms with an alkyl thiocarbonate group, (*b*) a zinc salt of a dithio acid of phosphorus represented by the structure,

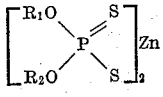


wherein R_1 and R_2 are selected from the group consisting of acyclic, alicyclic, and aromatic hydrocarbon radicals, (*c*) a phosphorized-sulfurized dicyclic terpene obtained by reacting said terpene with a phosphorus sulfide at 100–160° C., the weight ratio of (*b*) to (*c*) being from about 4 to 6.5:1, the weight ratio of (*a*) to (*b*) being from about 1 to 1.5:1, the total weight percent of (*a*), (*b*) and (*c*), based on said oil, being about 8% to 15%, and (*d*) about 0.1% to 1% by weight, based on said oil, of an S-amine O,O-dialiphatic phosphorothioate of the structure,

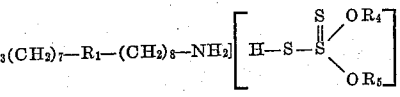


where *m* is an integer from 0 to 17, *n* is an integer from 0 to 17, the sum of *m* and *n* being from 9 to 17; R_1 is selected from the group consisting of $—CH_2—CH_2—$, sulfurized —CH=CH— and —CH=CH—; R_2 and R_3 are selected from the group consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms; and R_4 and R_5 are each aliphatic radicals containing from 1 to 12 carbon atoms, the sum of the carbon atoms of R_4 and R_5 being at least 3, but when the sum of *m* and *n* is 9, R_4 and R_5 each contain not more than 9 carbon atoms.

14. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and (*a*) the product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon having from 5 to 15 carbon atoms with an alkyl thiocarbonate group, (*b*) a zinc salt of a dithio acid of phosphorus represented by the structure,



wherein R_1 and R_2 are selected from the group consisting of acyclic alicyclic, and aromatic hydrocarbon radicals, (*c*) a phosphorized-sulfurized dicyclic terpene obtained by reacting said terpene with a phosphorus sulfide at 100–160° C., the weight ratio of (*b*) to (*c*) being from about 4 to 6.5:1, the weight ratio of (*a*) to (*b*) being from about 1 to 1.5:1, the total weight percent of (*a*), (*b*) and (*c*), based on said oil, being about 8% to 15%, and (*d*) about 0.1% to 1% by weight, based on said oil, of an S-amine O,O-dialiphatic phosphorothioate of the structure,

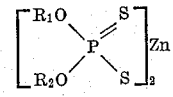


where R_1 is selected from the group consisting of $—CH_2—CH_2—$, sulfurized —CH=CH— and

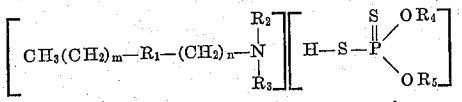
—CH=CH—

and R_4 and R_5 are each aliphatic radicals containing from 3 to 6 carbon atoms.

15. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and (*a*) a chlorinated petroleum naphtha-alkyl xanthate group reaction product wherein said product contains about 25% to about 40% by weight chlorine, (*b*) a zinc salt of a dithio acid of phosphorus represented by the structure,



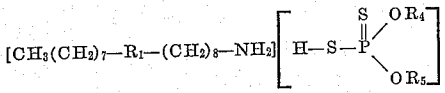
wherein R_1 and R_2 are alkyl radicals, (*c*) a phosphorized-sulfurized dicyclic pinene obtained by reacting said pinene with a phosphorus sulfide at 100–160° C., the weight ratio of (*b*) to (*c*) being from about 4 to 6.5:1, the weight ratio of (*a*) to (*b*) being from about 1 to 1.5:1, the total weight percent of (*a*), (*b*) and (*c*), based on said oil, being about 8% to 15%, and (*d*) about 0.1% to 1% by weight, based on said oil, of an S-amine O,O-dialiphatic phosphorothioate of the structure,



where *m* is an integer from 0 to 17, *n* is an integer from 0 to 17, the sum of *m* and *n* being from 9 to 17; R_1 is selected from the group consisting of $—CH_2—CH_2—$, sulfurized —CH=CH— and —CH=CH—; R_2 and R_3 are selected from the group consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms; and R_4 and R_5 are each aliphatic radicals containing from 1 to 12 carbon atoms, the sum of the carbon atoms of R_4 and R_5 being at least 3, but when the sum of *m* and *n* is 9, R_4 and R_5 each contain not more than 9 carbon atoms.

16. A lubricating composition of claim 15 wherein the alkyl xanthate group is an isopropyl xanthate, and the alkyl radicals of the zinc dialkyl dithiophosphoric acid are hexyl radicals.

17. A lubricating composition of claim 16 wherein the S-amine O,O-dialiphatic phosphorothioate is a compound of the structure,

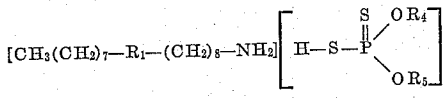


where R_1 is selected from the group consisting of $—CH_2—CH_2—$, sulfurized —CH=CH— and

—CH=CH—

and R_4 and R_5 are each aliphatic radicals containing from 1 to 12 carbon atoms, the sum of the carbon atoms of R_4 and R_5 being at least 3.

18. A lubricating composition of claim 16 wherein the S-amine O,O-dialiphatic phosphorothioate is a compound of the structure,



where R_1 is selected from the group consisting of $—CH_2—CH_2—$, sulfurized —CH=CH— and

—CH=CH—

and R_4 and R_5 are each aliphatic radicals containing from 3 to 6 carbon atoms.

19. A lubricating composition of claim 16 wherein the S-amine O,O-dialiphatic phosphorothioate is S-octadecenylamine O,O-diisopropyl phosphorodithioate.

20. A lubricating composition of claim 16 wherein the S-amine O,O-dialiphatic phosphorothioate is S-octadecenylamine O,O-di-1,3-dimethylbutyl phosphorodithioate.

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