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LUBRICATING OIL COMPOSITION

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This invention relates to a lubricating composition and more particularly to a light colored mineral lubricating oil composition having excellent thermal stability and rust-inhibiting characteristics.

Various lubricating compositions have heretofore been disclosed for lubricating internal combustion engines but the prior compositions have not been entirely satisfactory. Some of the prior compositions have exhibited good resistance to oxidation and sludge formation but they have not given prolonged protection against rusting of metal engine parts which are exposed to moisture. Other compositions have exhibited good rust inhibiting characteristics but they have failed to give adequate lubricating qualities in modern engines where the clearance between moving parts is extremely small.

The present invention is based upon a particularly effective lubricating composition having good resistance to oxidation and sludge formation combined with good lubricating characteristics, and anti-corrosion and rust-inhibiting properties.

The improved lubricating composition of this invention comprises a major proportion of a mineral lubricating oil and a minor proportion of each of (*a*) a metal salt of a thiophosphoric acid ester, (*b*) an oil-soluble alkaline earth metal sulfonate, and (*c*) an oil-soluble alkaline earth metal and sulfur containing, permanently thermoplastic, resinous condensation product of formaldehyde, a metal sulfide and an alkylated monohydric phenol. We have found that the constituents (*a*), (*b*) and (*c*) just mentioned can cooperate when admixed with a light colored highly refined paraffinic oil to give a light colored lubricating composition having excellent thermal stability at an elevated temperature combined with good corrosion and rust-inhibiting properties. The improved thermal stability and rust-inhibiting properties of the lubricating composition are unexpected in view of the performance of the individual additives and combinations of less than all of the additives when added to an oil.

The lubricating oil to which the other constituents are added is advantageously a highly refined paraffinic oil. By the term "highly refined paraffinic oil" we mean a pertoleum lubricating oil which has been refined by one of the more drastic refining methods known in the art, for example, by conventional aluminum chloride refining or by a solvent extraction adapted to remove all or substantially all of the unsaturated and aromatic constituents of the oil. Aluminum chloride refined and/or solvent extracted paraffinic base oil, such as a Pennsylanvia oil, provides an excellent base oil for the composition of the invention. However, drastically refined Mid-Continent and Gulf Coastal oil may also be used. Regardless of the type of oil employed, it is essential to use a light colored oil in order to obtain a final lubricating composition which has a light color.

The metal salts of the thiophosphoric acid esters which can be used in accordance with the invention are advantageously those whose metal component is a metal of Group II of Mendelyeevf's periodic arrangement of the

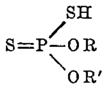
elements. Particularly desirable metals within this group are magnesium, calcium, zinc, strontium, cadmium and barium. In some instances other metals including aluminum and tin can also be employed. Of the Group II metals, we prefer zinc because the zinc salts when added to highly refined oils produce lubricating compositions having good antiwear and bearing corrosion inhibiting properties. Although the zinc salts of the thiophosphoric acid esters can impart these desirable properties to most oils, we have found that a relatively stable highly refined paraffinic lubricating oil containing a zinc salt of a thiophosphoric acid ester has a tendency to form sludge upon continued heating.

Also, such zinc salts do not confer antirust characteristics to the oil. In the past, anti-sludging properties have been obtained in lubricating compositions by utilizing a detergent and/or dispersant. Suitable dispersants have included various oil-soluble organic sulfonates including particularly the alkaline earth metal petroleum "mahogany" sulfonates. While these sulfonates have been found to confer sludge inhibiting properties to some oils when combined with some thiophosphates such as the alkaline earth metal thiophosphates and mixed metal salts of zinc and an alkaline earth metal thiophosphate, we have found that the sludging tendency of a highly refined paraffinic lubricating oil containing only a zinc thiophosphate is adversely affected by an alkaline earth metal petroleum sulfonate. Other stabilizers and detergents which have been used as sludge dispersants including various alkaline earth metal salts of certain sulfur-containing alkyl phenol-formaldehyde resins have also been found to adversely affect the sluding tendency of a highly refined paraffinic oil which contains the zinc salt of a thiophosphoric acid ester. It is surprising therefore that the addition of an oil-soluble alkaline earth metal petroleum sulfonate and an oil-soluble alkaline earth metal and sulfur containing, permanently thermoplastic, resinous condensation product of formaldehyde, a metal sulfide and an alkylated monohydric phenol to a highly refined paraffinic lubricating oil composition containing a zinc salt of a thiophosphoric acid ester will produce a composition having improved resistance to sludge formation. It is further surprising that an oil containing a combination of a metal salt of a thiophosphoric acid ester, an oil-soluble alkaline earth metal sulfonate, and an oil-soluble alkaline earth metal and sulfur containing, permanently thermoplastic, resinous condensation product of formaldehyde, a metal sulfide and an alkylated monohydric phenol will protect a ferrous metal surface against rusting for a period of time greater than the sum of the periods obtained with the same base oil containing each of the individual additives in proportions identical to those utilized in the combination.

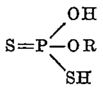
The metal salts of the thiophosphoric acid esters can be prepared by reacting a basic divalent metal compound with acidic thiophosphoric esters that are prepared in turn by reacting a monohydric alcohol with phosphorus pentasulfide. The monohydric alcohol can be either an open chain or cyclic aliphatic alcohol. Excellent additives for the purpose of our invention can be obtained with the alcohols containing an average of 6 to 8 carbon atoms. However, we can also use the aliphatic monohydric alcohols containing 6 to 14 carbon atoms on the average. Cyclohexanol and the Oxo octyl alcohols are exemplary of the alcohols which have given excellent additives for the purpose of our invention. The Oxo octyl alcohols, as is known, comprise mixed isomeric branched chain octyl alcohols, principally dimethyl hexanols, prepared by subjecting mixed isomeric heptenes to the well-known Oxo synthesis process. Examples of other alcohols which can be used are hexanol, heptanol, 2-ethylhexyl alcohol, lauryl alcohol, methyl cyclopentanol, cycloheptanol, methyl cyclohexanol and propyl cyclohexanol. Unsaturated, or olefinic, alcohols including octenol and dodecenol are also contemplated. It is not essential that the alcohol component consist entirely of alcohols containing 6 or more carbon atoms, and mixed alcohols, for example, mixtures of say 80–90 percent octyl alcohol and 20–10 percent propyl alcohol can be used in preparing compositions useful in our invention. The alcohols need not be pure as mixtures of two or more can be used.

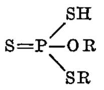
The acidic thiophosphoric esters are prepared with relative ease at moderately elevated temperatures and most conveniently at atmospheric pressure. Suitable temperatures for this reaction are generally between about 130° and about 350° F. In the early stages of the reaction, temperatures in the lower part of the range are suitable, but when the reaction nears completion as evidenced by a reduced rate of evolution of hydrogen sulfide, the temperature is preferably raised to at least about 200° F., preferably about 300° F., in order to insure essentially complete reaction of the phosphorus pentasulfide. The reaction of alcohol with phosphorus pentasulfide may be carried out in a solvent which does not interfere with the reaction, such as a mineral lubricating oil, naphtha or benzene, if desired. The reaction will normally be complete within 6 hours, the usual time being about 30 minutes to two hours.

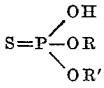
The principal product of the reaction of alcohol with phosphorus pentasulfide in a mol ratio of 4:1, respectively, is ordinarily considered to be a diester of dithiophosphoric acid having the formula:

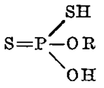


where R and R′ are like or unlike ester-forming radicals derived from alcohols of the kind disclosed above. The phosphorus:sulfur mol ratio of such a product is obviously about 1:2. Also possible, but in lesser amounts, are other thiophosphoric acid esters such as those having the following formulae:









where R and R′ are as indicated above.

The metal salts of the thiophosphoric acid esters can be prepared by reacting the thiophosphoric acid ester with an excess of the corresponding metal or a basic metal compound. This reaction can be conducted at a temperature between room temperature, i.e., 60° to 70° F., and 300° F., the reaction generally requiring about 1 to 8 hours or more to effect substantial completion thereof. The exact amount of time required for this reaction to take place will vary principally according to the reaction temperature, lower temperatures generally requiring a longer time. The time is also somewhat dependent upon the quantity of reactants employed and the effectiveness of the contacting means.

The metal salts of the thiophosphoric acid esters suitable for the purpose of our invention can comprise either a single metal salt obtained as described above or mixed metal salts of zinc and an alkaline earth metal as defined in application Serial No. 618,459 to Charles B. Welsh, filed October 26, 1956. According to the designated application to Charles B. Welsh, a crude thiophosphoric acid ester obtained as described above is reacted with zinc, or a basic zinc compound, preferably the latter, in a mol ratio of about 0.5 to about one mol of the zinc or basic zinc compound for each 2 mols of the crude thiophosphoric acid ester product. This corresponds to a ratio of about 0.5 to one mol of zinc or zinc compound per mol of phosphorus pentasulfide employed in the initial reaction. It is ordinarily desirable to carry out this reaction in the presence of an excess of the zinc or zinc compound.

The salt forming reaction begins to take place spontaneously with evolution of heat with gradual addition of zinc or the zinc compound, at atmospheric pressure, and at a temperature of 60° F., or above. In order to minimize side reactions, it is important to maintain the salt-forming reaction at a temperature not greater than 180° F. until the reaction is substantially complete. In this particular preparation, appreciable departure from the temperatures indicated will have a material effect on the ultimate composition. The reaction is further completed by raising the temperature to about 180° to about 280° F., preferably about 250° F., for at least 30 minutes, preferably about 2 hours. The product is then cooled, preferably to room temperature and filtered to remove unreacted zinc or zinc compound. The zinc thiophosphoric acid ester thus obtained is then reacted at a temperature of about 60° to about 300° F., preferably about 225° to about 275° F., with sufficient alkaline earth metal base to raise the pH of the reaction mixture to at least about 6 and preferably to about 7 and with about 0.5 to about 2 percent by weight of the mixture of benzoyl peroxide. The reaction is usually complete in about 15 minutes to about 2 hours. The product is filtered to remove undesired solids. Examples of the preferred basic alkaline earth metal compounds are calcium hydroxide and calcium oxide. Other basic alkaline earth metal compounds which can be used include barium hydroxide, barium oxide, strontium hydroxide and the like. The final product comprises principally mixed zinc-alkaline earth metal salts of thiophosphoric acid esters wherein the phosphorus:sulfur mol ratio is substantially more than 1:2, normally about 2:3.

The following Example I is illustrative of the preparation of mixed zinc and calcium salts of Oxo octyl esters of thiophosphoric acids which can be used in the compositions of our invention:

EXAMPLE I

A charge stock consisting of about 70 percent by weight of Oxo octyl alcohols (520 pounds) and 30 percent by weight of phosphorus pentasulfide (222 pounds) is charged to a stainless steel reaction vessel equipped with an agitator and means for heating and cooling. The mixture thus formed is reacted while maintaining the temperature of the reaction mixture between 130° and 200° F., until the rate of reaction has diminished substantially as evidenced by substantial disappearance of solid phosphorus pentasulfide. The foregoing reactant proportions correspond to a mol ratio of about 4 mols of alcohol per mol of phosphorus pentasulfide. The Oxo octyl alcohols referred to in this example have the following typical characteristics:

Gravity, ° API	38.5
Viscosity kinematic, 20° C., cs.	12.43
Flash, OC, ° F.	175
Distillation:	
Over point, ° C.	184
End point, ° C.	188
50% point, ° C.	186.4

The temperature of the foregoing mixture is then raised to 300° F. for an hour to insure completion of the reaction. The reaction product, consisting chiefly of the di Oxo octyl acid esters of dithiophosphoric acid, together with miscellaneous side reaction products, is then cooled to about 100° F., and zinc oxide (81 pounds) is gradually and slowly added in a ratio of one mol per mol of phosphorus pentasulfide, or in other words until the make-up of the overall reaction mass corresponds to 89.7 percent by weight of the crude di Oxo octyl acid ester of dithiophosphoric acid calculated as such and 10.3 percent by weight of zinc oxide. The temperature of the salt-forming reaction is kept just at or below about 180° F. during addition of most of the zinc oxide. The temperature of the reaction mixture is then raised to about 250° F., and maintained there for about 2 hours to complete the reaction, after which the mixture is cooled to room temperature.

An amount of hydrated lime (about 31 pounds), sufficient to raise the pH of the mixture from about 2 to about 7, and a small amount of benzoyl peroxide (about 8 pounds) are now added to the foregoing reaction product and thoroughly mixed. The make-up of this reaction mixture corresponds approximately to 94.0 weight percent of the zinc Oxo octyl thiophosphate ester reaction product, 5 weight percent lime and one percent by weight of benzoyl peroxide. After adding the lime and benzol peroxide and mixing the reactants, the reaction mixture is then heated to a temperature of about 250° F. for one hour to insure completion of the reaction. The product is then filtered.

A product prepared essentially according to the foregoing procedure consists essentially of highly stable, light colored, mixed zinc and calcium salts of Oxo octyl esters of thiophosphoric acids and has the following typical characteristics:

Specific gravity, 60°/60° F.		1.123
Viscosity, SUS:		
At 100° F.		1595
At 210° F.		130.0
Flash, OC, ° F.		380
Fire, OC, ° F.		395
Pour point, ° F.		—25
Color, ASTM Union		<1
Odor		Faint alcohol
Sulfur	percent	13.45
Phosphorus	do	8.86
Zinc	do	8.50
Calcium	do	1.13
pH value		7.0
Sulfated residue, ASTM D874	percent	27.7
Water by distillation	do	Trace
Mol ratio, phosphorus: sulfur		2:3

The metal salts of the thiophosphoric acid esters can be employed per se or they can be added to the lubricating oil in the form of a mineral oil concentrate. Formation of the thiophosphate is frequently facilitated by employing a solvent such as a light mineral oil, naphtha or benzene. When such a mineral oil solvent is used, the thiophosphate is readily recovered in the form of a mineral oil concentrate. This concentrate can then be added directly to the oil to be improved or it can be admixed with one or more of the other additive constituents. Regardless of whether the thiophosphate is employed per se or in the form of an oil concentrate, an amount is used sufficient to incorporate about 0.5 to about 5.0 percent by weight of the thiophosphate in the final lubricating composition. Thus, a concentrate containing 50 percent of the thiophosphate and 50 percent of light mineral oil can be employed in amounts of about 1.0 to about 10.0 percent by weight. The amount of thiophosphate is preferably not more than one half the amount of sulfonate employed. The thiophosphate and the alkaline earth metal and sulfur containing, permanently thermoplastic, resinous condensation products are preferably employed in about equal amounts.

The alkaline earth metal sulfonate which we employ can be prepared from sulfonic acids such as sulfonates obtained in the sulfonation of mineral oils or alkyl aryl compounds, such as didodecyl benzene, as well as sulfonates obtained in the sulfonation of organic acids including the naphthenic and fatty acids occurring in animal and vegetable oil. In some instances it may be desirable to employ a mixture of sulfonates such as a mixture of a petroleum sulfonate with one or more of the other named sulfonates. It is essential, of course, that the alkaline earth metal sulfonate or mixture of sulfonates be soluble in a mineral oil. In general, we prefer to employ the sulfonic acids derived from the sulfuric acid treatment of petroleum fractions. Of these, the sulfonic acids having an average molecular weight of about 400 to about 450 are particularly advantageous. The sulfonates can be prepared by saponification of the corresponding acids with the metal oxide or hydroxide or an alkaline salt of a metal. In some instances we may start with an alkali metal sulfonate such as the sodium salt of the oil-soluble petroleum sulfonic acids. When such an alkali metal sulfonate is utilized as the starting material, a double decomposition procedure is employed to obtain the desired oil-soluble alkaline earth metal sulfonate such as calcium or barium sulfonate. The sulfonation reaction is conventional and needs no elaboration here.

The sulfonate can be employed, per se, or it can be added to the lubricating oil in the form of a mineral oil concentrate. We prefer to employ the sulfonate in the form of a mineral oil concentrate because homogeneous mixtures are more readily obtained when the sulfonate is added in this form.

The following Example II is illustrative of the preparation by double decomposition of a suitable mineral oil concentrate of calcium petroleum sulfonate which can be used in the compositions of our invention:

EXAMPLE II

Into a stainless steel reaction vessel equipped with an agitator and means for cooling are charged 1424 pounds of an oil-soluble sodium petroleum sulfonate having an average molecular weight of about 445. The sodium petroleum sulfonate is then heated to about 140° F., and thoroughly admixed with 219 pounds of calcium chloride dihydrate dissolved in an equal amount of water. The reaction mass is then heated to 270° F. and held at that temperature for about 30 minutes to complete the reaction. The reaction mass is then dried at a temperature not exceeding 300° F. The dried product is then admixed with about 3 pounds of hydrated lime to raise the pH of the sulfonate and to prevent gelling of the finished product. The resulting dried product is then diluted with about 1200 pounds of a dilution mineral oil having a viscosity of about 58 SUS at 100° F., and 34.5 SUS at 210° F. The diluted product is then filtered to remove any undesired solids. The filtered product comprises a mineral oil concentrate containing 33 percent by weight active ingredient, i.e., calcium petroleum sulfonate. The concentrate thus obtained has the following typical properties:

Gravity, ° API		20.4
Viscosity, SUS, 210° F.		2353
Average molecular weight, ASTM D 1216		884
Flash, OC, ° F.		365
Fire, OC, ° F.		390
Pour, ° F.		+20
Color, ASTM Union		<4.5
Sulfur, B	percent	2.1
Calcium	do	1.57
Sodium	do	0.04
Water by distillation	do	0.2
Sulfated residue, ASTM D 874	do	6.9

The amount of the sulfonate which we employ is between about 0.5 and about 5.0 percent by weight based on the weight of the total composition. While we can use more than about 5.0 percent of the sulfonate, we prefer to use the least amount required to give good detergent properties for obvious economic reasons. An amount less than about 0.5 percent is generally undesirable because the detergent properties given to the oil with such a small amount of sulfonate is generally insufficient for modern engines. Higher concentrations are frequently required in heavy duty engines. Preferred compositions comprise about 1.5 to about 3.0 percent by weight of sulfonate, the ratio of sulfonate to thiophosphate being about 2 to 1. When the sulfonate is employed in the form of a mineral oil concentrate, the concentrate is employed in an amount sufficient to incorporate between about 0.5 and about 5.0 percent by weight of sulfonate in the final composition. Thus, a concentrate containing 33 percent of sulfonate in a light mineral oil diluent can be employed in amounts between about 1.5 and about 15 percent by weight.

The alkaline earth metal and sulfur containing, permanently thermoplastic, resinous condensation product of formaldehyde, metal sulfide and alkylated monohydric phenol which we employ can be prepared directly or by metathesis according to the processes defined, respectively, in U.S. Patent Nos. 2,736,702 and 2,736,703, which issued February 28, 1956, to H. G. Smith, T. L. Cantrell and J. G. Peters. As disclosed in the respective patents, the condensation can be carried out in the presence of an alkali metal hydroxide or alkaline earth metal hydroxide in place of some of the alkali metal sulfide or alkaline earth metal sulfide in which case sufficient of the sulfide is employed in relation to the hydroxide to yield not less than about 0.5 percent by weight of sulfur in the final resinous product. The total amount of metal compound employed, that is, the amount of metal sulfide plus metal hydroxide is in the proportion of at least one equivalent of total metal compound for every two mols of the phenol. It will be understood, of course, that if an alkali metal is employed the salt so obtained is converted to an alkaline earth metal compound by metathesis with a water soluble salt of an alkaline earth metal.

In preparing the condensation product it is necessary not to permit substantial reaction between the phenol and formaldehyde in the absence of the alkali metal sulfide or alkaline earth metal sulfide and the alkali metal hydroxide or alkaline earth metal hydroxide, if the hydroxide is employed. Accordingly, it is preferred to mix all of the ingredients and react them simultaneously. However, the alkali metal sulfide or alkaline earth metal sulfide and formaldehyde, with or without the hydroxide, can first be mixed and partially reacted followed by addition of the phenol to the reaction mass and further reaction; or the alkali metal sulfide or alkaline earth metal sulfide and phenol, with or without the hydroxide, can first be reacted followed by reaction with the formaldehyde.

The condensation reaction takes place spontaneously at room temperature, but it is preferred to employ moderately elevated temperatures in order to obtain reasonably rapid reaction rates. When the reaction sequence of first reacting the phenol and alkali metal sulfide or alkaline earth metal sulfide and then reacting the formaldehyde is followed, the phenol and alkali metal sulfide or alkaline earth metal sulfide, with or without the hydroxide, can be reacted first at temperatures as high as 400° F. Thereafter, for the subsequent reaction with formaldehyde, the reaction mass is cooled to about 120° to about 180° F. to avoid excessive volatilization of formaldehyde. In any instance where formaldehyde is present in the reacting mass, whether initially or otherwise, it is desirable not to exceed a reaction temperature of about 200° to about 210° F. in order to avoid loss of formaldehyde, although this loss can be reduced to some extent when employing temperatures higher than about 210° F. by the use of closed reaction vessels.

Since the formaldehyde is most conveniently used in the form of commercial aqueous formalin, containing 37 percent by weight of formaldehyde, sufficient water for the reaction is generally contained in the formalin solution. However, the alkali metal or alkaline earth metal sulfides, and the alkali metal or alkaline earth metal hydroxides may be conveniently dispersed and/or dissolved in water to form an aqueous slurry or solution even when formalin is used.

In order to obtain the oil-soluble metal and sulfur-containing resins at least one mol of formaldehyde is used for every two mols of the phenol. Amounts of formaldehyde less than this tend to yield oil-insoluble resins. Amounts of formaldehyde in excess of the amounts stated can be employed since any formaldehyde in excess of the amount reacted is either volatilized off in the reaction or in the subsequent dehydration of the resin.

When an alkali metal hydroxide or alkaline earth metal hydroxide is employed in place of some of the alkali metal sulfide or alkaline earth metal sulfide, it is necessary to use such an amount of hydroxide that the sulfur content of the resulting resin, which is derived from the alkali metal sulfide or alkaline earth metal sulfide, does not fall below about 0.5 percent by weight. In general, it is preferred that the relative molar proportions of alkali metal sulfide or alkaline earth metal sulfide to alkali metal hydroxide or alkaline earth metal hydroxide, respectively, should be about 1:1. The use of an alkali metal monosulfide or alkaline earth metal monosulfide is preferred.

After the condensation reaction is completed, the product is subjected to dehydration as by distillation to distill off the water. Dehydration is completed as rapidly as possible to avoid darkening the product. If an alkali metal product is prepared first, then conversion to the alkaline earth metal product by double decomposition is advantageously carried out prior to dehydration of the alkali metal product. Although the condensation reaction can be carried out solely in an aqueous medium, it is advantageous to use additionally a light naphtha solvent or a mineral lubricating oil of the same general type as the oil to which the resin is to be added. There is then obtained, after dehydration, a concentrate of the alkaline earth metal resin in solution in the naphtha or mineral lubricating oil as the case may be. These concentrates are convenient for incorporating the additive into the lubricating composition.

The phenolic compounds employed in preparing the condensation product are alkylated monohydric phenols having at least one alkyl group of at least four carbon atoms. As will be understood by those skilled in the art, such phenols must have at least one reactive position in the nucleus which is free of substituents. The presence of at least one alkyl group of at least four carbon atoms in the phenol insures oil solubility of the resinous condensation products prepared therefrom. Phenols not containing such groups tend to yield products which are insoluble in mineral lubricating oils.

The alkylated phenols can readily be prepared by alkylating phenol or the simple monohydric homologues thereof, such as the naphthols, cresols, and ethyl and propyl phenols, with an alkyl halide or an alkanol in the presence of a Friedel-Crafts catalyst. Alternatively, alkylation can be performed with an olefin in the presence of concentrated sulfuric acid as a catalyst. The alkyl halides, alkanols and olefins employed in these alkylation reactions contain at least four carbon atoms and are selected to yield such alkyl radicals as butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, stearyl and cetyl. The long chain groups derived from paraffin wax are also suitable; these yield the so-called "wax" phenols. Alkyl substituents containing from four to twelve carbon atoms form a preferred class. The alkylation reactions described are conventional and need not be further elaborated here.

Representative alkyl phenols of the class described include n-butylphenol; sec-butylphenol; tert-butylphenol; 2-tert-butyl-4-methylphenol; 2,4-di-tert-butylphenol; 2,6-di-tert-butylphenol; 2-tert-butyl-4-ethylphenol; n-amylphenol; di-tert-amylphenol; hexyl phenols; heptyl phenols; n-octylphenol; iso-octyl phenol (alpha, alpha, gamma, gamma tetramethylbutyl phenol); nonyl phenol; decyl phenol; tri-isobutyl phenol; "wax" phenols; and the like.

The alkali metal sulfides which can be used include the mono- and poly-sulfides of sodium, potassium, lithium, rubidium and caesium. When an alkali metal resin is prepared it is converted to the corresponding alkaline earth product by metathesis. The metathesis can be carried out by employing an alkaline earth metal nitrate, sulfate, chloride or alcoholate salt which is water soluble. The alkaline earth metal sulfides which can be used include the mono- and poly-sulfides of calcium, barium, strontium and magnesium.

The following Examples III and IV are illustrative of the preparation of alkaline earth metal and sulfur containing, permanently thermoplastic, resinous products which can be used in the compositions of our invention. Example III illustrates the preparation of a calcium-sulfur containing resin directly, whereas Example IV illustrates the preparation of a barium-sulfur containing resin by double decomposition of the corresponding sodium resin.

EXAMPLE III

Into a stainless steel reaction vessel equipped with an agitator and means for heating and cooling are charged 412 pounds (2 mols) of tetramethylbutyl phenol and 494 pounds of a dilution mineral oil having a viscosity of about 58 SUS at 100° F., and 34.5 SUS at 210° F. The mixture thus formed is agitated and heated to a temperature of about 160° F. While maintaining this temperature, 85 pounds (1 mol) of 85 percent calcium sulfide are slowly admixed with the tetramethylbutyl phenol and dilution oil. Thirty-six pounds (2 mols) of water are then added and the mixture is heated to 185° F. for about one hour. The iron content of the water should preferably not exceed two parts per million parts of water. The mixture is then cooled to 160° F. One hundred sixty-two pounds (2 mols) of 37 percent formaldehyde are introduced below the surface of the reaction mass at a rate which will maintain the reaction temperature between about 160° and about 175° F. without the aid of external cooling. The iron content of the formaldehyde solution should preferably not exceed 150 parts per million. After the formaldehyde has been added, the reaction mass is heated at a temperature of 175° to 185° F. for two hours to complete the reaction. The reaction mass is then dried at a temperature not exceeding 300° F. as rapidly as possible in order to obtain a light colored product. The preferred method of drying this material utilizes a stainless steel flash evaporator. The dried product is then further diluted with 494 pounds of the dilution oil to obtain a concentrate containing 33 percent by weight active ingredient. The diluted product is filtered to remove any undesired solids. The concentrate thus obtained has the following typical properties:

Gravity, ° API		21.7
Viscosity, SUS:		
100° F.		548
210° F.		62.1
Flash, OC, ° F.		340
Fire, OC, ° F.		355
Pour: ° F.		0
Color, ASTM Union		2.75
Sulfur, B	percent	0.46
Calcium	do	1.8
Water by distillation	do	0.1
Sulfated residue ASTM D 874	do	6.3

EXAMPLE IV

Into a stainless steel reaction vessel equipped with an agitator and means for heating and cooling are charged 752 pounds of tetramethylbutyl phenol and 943 pounds of a dilution mineral oil having a viscosity of about 58 SUS at 100° F., and 34.5 SUS at 210° F. The mixture thus formed is agitated and heated to a temperature of about 160° F. While maintaining this temperature, 208 pounds of sodium sulfide in an aqueous solution (297 pounds of water) are slowly admixed with the tetramethylbutyl phenol and dilution oil. The iron content of the water should preferably not exceed two parts per million. The mixture is then heated to about 350° F. and further diluted with 943 pounds of the dilution oil. The diluted product is then cooled to about 160° F. Three hundred and three pounds of formaldehyde (37 percent) are then introduced below the surface of the reaction mass at a rate which will maintain the reaction temperature between about 160° and about 180° F. The iron content of the formaldehyde solution should preferably not exceed 150 parts per million. After the formaldehyde has been added, the reaction mass is heated at a temperature of about 180° F. for two hours to complete the reaction. Double decomposition is then accomplished by adding 403 pounds of barium chloride in an aqueous solution (297 pounds of water). The mixture is agitated and heated to 300° F. to dry the product. Fast drying is preferred in order to avoid an undesired color change. Flash evaporation in a stainless steel flash evaporator is preferred. The dried product is then filtered to remove any undesired solids. The dried product comprises a mineral oil concentrate containing 33 percent by weight active ingredient. The concentrate has the following typical properties:

Gravity: ° API		13.5
Viscosity, SUS, 210° F.		102.5
Flash, OC, ° F.		340
Fire, OC, ° F.		355
Pour, ° F.		0
Color, ASTM Union		3.25
Sulfur, B	percent	1.04
Barium	do	6.5
Water by distillation	do	0.1
Sulfated residue, ASTM D 874	do	11.3

The alkaline earth metal and sulfur containing, permanently thermoplastic, resinous condensation products diluted with a mineral lubricating oil obtained as described above can be added to the lubricating oil of our invention either per se or they can be further diluted with additional mineral oil if desired. While the condensation products can be prepared in the absence of dilution oil, their preparation is facilitated by the presence of oil. The condensation product is employed in the lubricating composition in amounts of about 0.5 to about 5.0 percent by weight based on the weight of the final lubricating composition. Thus, a concentrate containing 33 percent of active ingredient in a light mineral oil diluent can be employed in amounts of about 1.5 to about 15.0 percent by weight. The condensation product and the thiophosphate are preferably employed in about equal amounts, the sum of the respective amounts being about equal to the amount of the sulfonate. Thus, a preferred ratio of condensation product:thiophosphate:sulfonate is 1:1:2.

The lubricating oil compositions of this invention can contain other additive agents, if desired, to improve other specific properties without deleteriously affecting the beneficial properties of the compositions. For example, pour point depressors, viscosity and viscosity index improvers, dyes, and the like can be used. Also, if desired, the oil can contain a foam inhibitor such as organi-silicon oxide condensation products, organo-silicol condensation products, and the like.

The individual constituents employed in the composition of this invention may be added to the lubricating oil base in any order or simultaneously, either per se, or in the form of a mineral oil concentrate.

We have found that it is particularly advantageous to form a concentrate of the metal salts of the thiophosphoric acid esters and the metal sulfide phenol-formaldehyde condensation product. We have found, for example, that the addition of the thiophosphate to the metal sulfide phenol-formaldehyde condensation product prevents undesirable darkening of the condensation product during storage prior to its addition to the oil. This is extremely important in producing a light colored lubricating composition. While the sulfonate can be added to the lubricating composition either prior or subsequent to the addition of a concentrate of the thiophosphate and metal sulfide phenol-formaldehyde condensation product, the sulfonate is compatible with the thiophosphate and condensation product thus permitting the preparation of a concentrate of all three constituents. The preparation of such a three component concentrate greatly facilitates the compounding and blending procedure. In the preparation of such concentrates, it is desirable, of course, to employ a light naphtha solvent or, preferably, a mineral lubricating oil of the same general type as the oil to which the concentrate is to be added. In preparing concentrates, the weight ratio of sulfonate to thiophosphate is advantageously maintained between about 1:10 and 10:1; the weight ratio of sulfonate to alkaline earth-su'fur-containing phenol, formaldehyde resin is maintained between about 1:10 and 10:1; and the weight ratio of thiophosphate to alkaline earth-sulfur-containing phenol-formaldehyde resin is maintained between about 1:10 and 10:1. An example of a preferred concentrate within these weight ratios is one which contains about 2 parts of sulfonate, 1 part thiophosphate and 1 part alkaline earth-sulfur-containing phenol-formaldehyde resin.

The advantages of the improved lubricating composition of the invention as compared with similar compositions containing the individual components are illustrated hereinafter with reference to several of the preferred embodiments of our invention but it is to be understood that they are given by way of illustration and not in limitation thereof. The base oil used in preparing the various compositions, unless otherwise indicated, was a highly refined, aluminum chloride treated, paraffinic oil stock having an API gravity of about 29.3° and a viscosity of about 340 SUS at 100° F. The mixed zinc and calcium salts of Oxo octyl thiophosphate were prepared according to the procedure illustrated in Example I. The calcium and barium petroleum sulfonates were prepared by double decomposition from the corresponding sodium salts of the oil-soluble petroleum sulfonic acids having an average molecular weight of about 420. Example II is illustrative of the procedure employed. The calcium and barium sulfur containing phenol-formaldehyde resins were prepared according to the procedures illustrated in Examples III and IV, respectively.

The thermal stability of the lubricating composition of our invention has been demonstrated by subjecting the respective compositions to the Sligh oxidation test. In brief, the Sligh oxidation test comprises placing a ten gram sample of the oil to be tested in a Sligh oxidation flask. The air atmosphere over the oil is changed to oxygen by purging with oxygen delivered at a rate of about 5 liters per minute for a period of 30 seconds. The flask is then quickly stoppered with a ground glass stopper to which is attached a convection plug to confine

the atmosphere of oxygen over the oil. The flask is then placed in an oil bath held at 392° F.±1° F., the flask being immersed to a depth such that the surface of the oil of the oil bath is about one inch above the body of the flask. The flask remains in the oil bath for 2½ hours. The flask is then removed and cooled to room temperature. The contents of the flask are then removed with the aid of dilution naphtha and filtered through a Gooch crucible. The precipitate or sludge which remains in the crucible after being dried in a desiccator and drying oven at about 220° F. is weighed to the nearest milligram. The weight of sludge thus obtained constitutes the Sligh oxidation number. Thus, a Sligh oxidation number of 1 indicates a relatively thermally stable composition as compared with a composition having a much higher Sligh oxidation number. The make-up of the compositions and the results of the Sligh oxidation tests are shown in Table 1.

In laboratory work, amounts are usually designated in terms of weight percent while in commercial operations where liquid concentrates are frequently employed, amounts are advantageously given as volume percents. Since the specific gravities of the materials used in the preparation of the various compositions reported hereinafter are approximately 0.9 to 1.0 the figures will not be substantially different whether reported as weight percent or volume percent. While the make-up of the compositions reported in the subsequent tables are given as volume percents, these percents can be readily converted to weight percents by reference to the following specific gravities for the materials used.

Base oil:	Specific gravity, 60°/60° F.
28.5° API	0.8844
29.3° API	0.8800
30.6° API	0.8729
Barium-sulfur-containing product of Example IV (33% active ingredient)	0.9759
Calcium-sulfur-containing product of Example III (33% active ingredient)	0.9236
Barium petroleum sulfonate (33% active ingredient)	0.9593
Calcium petroleum sulfonate product of Example II (33% active ingredient)	0.9315
Zinc di-cyclohexyl dithiophosphate	1.110
Mixed zinc-calcium Oxo octyl thiophosphate product of Example I	1.123
Acrylate resin	0.8927

Table 1

Composition, percent by volume	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
Base Oil—29.3° API	100	99.5	97	97	93.2	93.2	99	99	89.2	88.7	88.7	89.2	96	96	92.2	92.2	90.2
Barium-sulfur-containing product of Example IV (33% active ingredient)	------	------	3	------	------	------	------	------	------	------	3	------	------	------	------	------	------
Calcium-sulfur-containing product of Example III (33% active ingredient)	------	------	------	3	------	------	------	------	3	3	------	3	3	3	------	------	3
Barium petroleum sulfonate (33% active ingredient)	------	------	------	------	6.8	------	------	------	------	------	6.8	------	------	------	------	6.8	------
Calcium petroleum sulfonate product of Example II (33% active ingredient)	------	------	------	------	------	6.8	------	------	6.8	6.8	------	6.8	------	------	6.8	------	6.8
Zinc di-cyclohexyl dithiophosphate	------	------	------	------	------	------	1	------	1	------	------	------	1	------	1	1	------
Mixed Zinc-calcium Oxo octyl thiophosphate product of Example I	------	------	------	------	------	------	------	1	------	1	1	1	------	1	------	------	------
Viscosity index improver (acrylate resin)	------	0.5	------	------	------	------	------	------	------	0.5	0.5	------	------	------	------	------	------
Inspection: Sligh Oxidation No., mg. of sludge	1	1	1	1	1	1	42	47	1	1	1	1	63	68	108	67	1

It will be noted from the data in Table 1 that the base oil (Composition A) is substantially thermally stable as evidenced by the Sligh oxidation number of 1. It will be still further noted that the thermal stability of the base oil was not adversely affected by the addition of (1) the viscosity index improver (acrylate resin), Composition B, (2) the barium-sulfur-containing product of Example IV, Composition C, (3) the calcium-sulfur-containing product of Example III, Composition D, (4) barium petroleum sulfonate, Composition E, or (5) calcium petroleum sulfonate, Composition F, as further evidenced by Sligh oxidation numbers of 1 for each of the respective compositions. However, when either zinc di-cyclohexyl dithiophosphate or the mixed zinc-calcium Oxo octyl thiophosphate product of Example I was added to the base oil, the resulting composition was less stable as evidenced by the Sligh oxidation numbers of 42 and 47 for Compositions G and H, respectively. It will be noted that when the calcium-sulfur-containing product of Example III is added to a composition containing either the zinc di-cyclohexyl dithiophosphate or the mixed zinc-calcium Oxo octyl thiophosphate product of Example I, the resulting compositions are even less stable than Compositions G and H as evidenced by the Sligh oxidation numbers of 63 and 68 for Compositions M and N, respectively.

The sulfonates, like the calcium-sulfur-containing product of Example III, have the same detrimental effect on the composition containing the zinc di-cyclohexyl dithiophosphate as evidenced by Compositions O and P where the Sligh oxidation numbers were increased from 42 to 108 and 67, respectively, by the addition of calcium sulfonate and barium sulfonate, respectively. The detrimental effect of the calcium-sulfur-containing product of Example III and the calcium and barium sulfonates is indeed surprising in view of the fact that these materials by themselves or combined (Composition Q) do not exhibit such tendencies in the absence of the zinc thiophosphate compound. It is still further surprising (see Compositions I, J, K and L) that compositions containing the zinc thiophosphate compound in combination with the calcium or barium sulfonate and the calcium- or barium- sulfur-containing alkyl phenol-formaldehyde resins exhibit a thermal stability equal to that of the base oil. While the calcium and barium sulfonates have detrimental effects on the thiophosphate compound having only zinc as its metal component (Compositions O and P), these sulfonates do not have the same effect on compositions wherein the thiophosphate contains both zinc and an alkaline earth metal. For example, when barium petroleum sulfonate and calcium petroleum sulfonate in amounts of 6.8 percent by volume are separately added to Composition H containing the mixed zinc-calcium Oxo octyl thiophosphate product of Example I having a Sligh oxidation number of 47, the resulting compositions have Sligh oxidation numbers of 19 and 3, respectively.

The lubricating composition of this invention not only has excellent thermal stability but also has excellent rust-inhibiting characteristics. The rust-inhibiting characteristics, like the thermal stability, are unexpected in the light of the performance of the individual additives.

The effectiveness of the rust-inhibiting properties has been demonstrated by subjecting the lubricating compositions to the procedure of ASTM Test D665–54, Procedure B., and also to the Humidity Cabinet Corrosion Test according to the Army-Navy Standard Specification No. JAN–H–792. In brief, Procedure B of ASTM D665–54 involves placing a 300 milliliter sample of the oil in a 400 milliliter beaker which is, in turn, immersed in a constant temperature bath maintained at a temperature of 140° F. The beaker is fitted with a cover provided with openings for a stainless steel, motor-driven stirrer and for insertion of a standard steel test bar having a diameter of 0.5 inch and a length of approximately 5.5 inches which has been carefully cleaned and polished according to a prescribed procedure just prior to the test. The stirrer is started and when the oil sample in the beaker reaches a temperature of 140° F., the test bar is lowered through the proper opening and is suspended from the beaker cover. After 30 minutes, 50 milliliters of the oil are removed and replaced with 30 milliliters of synthetic sea water. Stirring is then continued for 24 hours with the temperature maintained at 140° F. At the end of this period the steel bar is removed and examined for rust spots.

In the Army-Navy Humidity Cabinet Test JAN–H–792, steel panels coated with the comparative lubricating compositions are placed in a closed cabinet which is maintained at a temperature of 120° F., and a humidity of 100 percent. The 100 percent humidity is achieved by heating water in the bottom of the cabinet and simultaneously bubbling air through the water. The steel panels slowly revolve around the inner periphery of the cabinet. The steel panels are examined daily for evidence of rust. The results of the tests according to ASTM D665–54 and JAN–H–792 are shown in Table 2.

Table 2

Composition, percent by volume	A	B	C	D	E	F	G	H	I	J	K
Base Oil—29.3° API	100.0	99.5	97.0	97.0	93.2	93.2	99.0	99.0	89.2	88.7	88.7
Barium-sulfur-containing product of Example IV (33% active ingredient)	--------	--------	3.0	--------	--------	--------	--------	--------	--------	3.0	--------
Calcium-sulfur-containing product of Example III (33% active ingredient)	--------	--------	--------	3.0	--------	--------	--------	--------	3.0	--------	3.0
Barium petroleum sulfonate (33% active ingredient)	--------	--------	--------	--------	6.8	--------	--------	--------	--------	6.8	--------
Calcium petroleum sulfonate product of Example II (33% active ingredient)	--------	--------	--------	--------	--------	6.8	--------	--------	6.8	--------	6.8
Zinc di-cyclohexyl dithiophosphate	--------	--------	--------	--------	--------	--------	1.0	--------	1.0	--------	--------
Mixed Zinc-calcium Oxo octyl thiophosphate product of Example I	--------	--------	--------	--------	--------	--------	--------	1.0	--------	1.0	1.0
Viscosity index improver (acrylate resin)	--------	0.5	--------	--------	--------	--------	--------	--------	--------	0.5	0.5
Inspection:											
Rust Preventive Tests—											
ASTM D665-54, Procedure B. Rusting after 24 hrs	severe	severe	light	moderate	none	none	severe	severe	none	none	none
JAN-H-792, Days to failure	<1	<1	<1	<1	17	21	<1	<1	39	48	45

As can be noted from the data in Table 2, compositions of the invention, Compositions I, J and K, containing all three of the respective additives, are strikingly superior to compositions containing only one of the additives. It is indeed surprising to note that the number of days of metal protection obtained by the compositions of the invention are greater than the sum of the number of days of protection obtained by the individual additives. It will be noted, for example, that the base oil, Composition A, the base oil in combination with the viscosity index improver (acrylate resin), Composition B, the base oil in combination with the barium-sulfur-containing product of Example IV, Composition C, the base oil in combination with the calcium-sulfur-containing product of Example III, Composition D, the base oil in combination with the zinc di-cyclohexyl dithiophosphate, Composition G, and the base oil in combination with the mixed zinc-calcium Oxo octyl thiophosphate product of Example I, Composition H, each gave less than one day of protection according to the JAN–H–792 test. While the base oil in combination with the barium and calcium petroleum sulfonates, Compositions E and F, respectively, did not fail to give protection until 17 and 21 days, respectively, Compositions I, J and K did not fail to give protection until 39, 48 and 45 days, respectively. Thus, it is evident that the days of protection obtained by a combination of the additives are greater than the sum of the days of protection obtained by the additives individually.

The data in Tables 1 and 2 show that the cooperative effect can be obtained with the calcium as well as with the barium salts regardless of whether the metal thiophosphate is a single metal salt of a thiophosphoric acid ester such as zinc di-cyclohexyl dithiophosphate or a mixed metal salt such as the mixed zinc and calcium Oxo octyl thiophosphate.

Other compositions within the scope of the invention wherein thermal stability combined with good antiwear, antioxidant, antirust and bearing corrosion inhibiting properties can be obtained are illustrated in Table 3.

Table 4

Composition, percent by volume	Z	Z_1
Base Oil—30.6° API	89.2	89.2
Barium-sulfur-containing product of Example IV (33% active ingredient)	3.0	------
Calcium-sulfur-containing product of Example III (33% active ingredient)	------	3.0
Barium petroleum sulfonate (33% active ingredient)	6.8	------
Calcium petroleum sulfonate product of Example II (33% active ingredient)	------	6.8
Mixed Zinc-calcium Oxo octyl thiophosphate product of Example I	1.0	1.0
Inspection:		
Gravity, ° API	28.8	29.3
Viscosity, SUS—		
at 100° F	231	231
at 210° F	49.9	49.4
Viscosity Index	114	109
Flash, OC, ° F	440	435
Fire, OC, ° F	500	475
Pour Point, ° F	−30	−20
Color, ASTM Union	2−	2½−
Sulfur, B, percent	0.36	0.39
Phosphorus, percent, ASTM D1091-54T	0.08	0.11
Carbon Residue, Conradson, percent	1.22	1.01
Copper Strip Test, 212° F., 3 hrs	0	0
Neutralization Value, ASTM D974-54T, Total Acid No	0.71	2.00
Ash as Oxide, percent	1.04	0.65
Ash as Sulfate, percent	1.22	0.80
Metals—		
Barium, percent	0.48	Nil
Calcium, percent	0.02	0.18
Zinc, percent	0.10	0.11

Table 3

Composition, percent by volume	R	S	T	U	V	W	X	Y
Base Oil:								
30.6° API—181 SUS @ 100° F	88.7	88.5	------	86.3	------	------	------	------
29.3° API—340 SUS @ 100° F	------	------	------	------	96.5	95.0	65.0	75.0
28.5° API—517 SUS @ 100° F	------	------	88.5	------	------	------	------	------
Barium-sulfur-containing product of Example IV (33% active ingredient)	3.0	------	------	3.0	1.5	1.5	------	------
Calcium-sulfur-containing product of Example III (33% active ingredient)	------	3.0	3.0	------	------	------	15.0	7.5
Barium petroleum sulfonate (33% active ingredient)	6.8	7.5	7.5	9.0	1.5	------	------	------
Calcium petroleum sulfonate product of Example II (33% active ingredient)	------	------	------	------	------	3.0	15.0	15.0
Zinc di-cyclohexyl dithiophosphate	------	------	------	------	0.5	------	------	------
Mixed Zinc-calcium Oxo Octyl thiophosphate product of Example I	1.0	1.0	1.0	1.0	------	0.5	5.0	2.5
Viscosity index improver (acrylate resin)	0.5	------	------	0.7	------	------	------	------

It will be noted that Compositions S, T and W as illustrated in Table 3 contain a mixture of calcium and barium salts in combination with the mixed zinc and calcium Oxo octyl thiophosphate product of Example I. These compositions, like those wherein the salts are not mixed, are substantially thermally stable compositions as evidenced by the fact that they have Sligh oxidation numbers of 1.

As noted hereinabove, the composition of this invention can contain other additive agents to improve other specific properties of the composition. It will be further understood that other oxidation inhibitors including 2,4,6-tri-tert-butylphenol and 2,6-di-tert-butyl-4-methylphenol can be used in combination with the thiophosphoric acid ester, the sulfonate and permanently thermoplastic, resinous condensation product disclosed herein. The amounts of the various additives will vary depending upon the particular base oil employed and the severity of the conditions to which the lubricating composition is subjected. In any event, the respective additives are employed in amounts sufficient to confer their desired effect on the resulting composition.

Typical make-up and inspection properties of light lubricating oils within the scope of the invention containing the calcium and barium salts are shown in Table 4. Each of these compositions also contained 0.5 percent of an acrylate resin as a viscosity index improver, 0.00075 percent of a green dye and 0.0006 to 0.0009 percent of Dow-Corning silicone Fluid 200, as a foam inhibitor. The acrylate resin used in these compositions and the others reported hereinabove is known as Acryloid 618, which can be purchased from Rohm & Haas Co., Philadelphia, Pennsylvania. The acrylate resin is a viscous liquid at room temperature having a specific gravity of 0.8927 at 60°/60° F., a furol viscosity of 395 seconds at 210° F., a flash point (P-M) of 250° F., a fire point (OC) of 375° F., a pour point of +20° F., an ASTM Union color of 1.25, a neutralization number (ASTM D974) of 0.13 and only a trace of water. Dow-Corning silicone Fluid 200 can be purchased from Dow-Corning Corporation, Midland, Michigan. This antifoam agent is a liquid polymer of a dialkyl silicone. Typical properties of this antifoam agent are: specific gravity at 60°/60° F., 0.9779; viscosity at 100° F., 3696 SUS; viscosity at 210° F., 1532 SUS; flash point (OC), 650° F.; and a pour point, below —50° F.

While the invention has been described above with reference to certain specific embodiments thereof by way of illustration, it is to be understood that the invention is not limited to such embodiments except as hereinafter defined in the appended claims.

We claim:

1. A lubricating composition having improved resistance to sludge formation upon continued heating and

rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 0.5 to about 5.0 percent by weight of a zinc salt of a thiophosphoric acid ester obtained by reacting phosphorus pentasulfide with a monohydric alcohol containing 6 to 14 carbon atoms on the average in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to about 1 mol of said member per mol of phosphorus pentasulfide at a temperature of about 60° to 300° F.; about 0.5 to about 5.0 percent by weight of an oil-soluble alkaline earth metal sulfonate; and about 0.5 to about 5.0 percent by weight of an oil-soluble alkaline earth metal and sulfur containing, permanently thermoplastic, resinous condensation product obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, a sulfide selected from the group consisting of an alkali metal sulfide and an alkaline earth metal sulfide, and an alkylated monohydric phenol having at least one free reactive position in the nucleus and at least one alkyl group containing from 4 to 12 carbon atoms, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of alkaline earth metal sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of said sulfide, said resinous condensation product when obtained when employing said alkali metal sulfide being subjected to metathesis with a water soluble salt of an alkaline earth metal.

2. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 0.5 to about 5.0 percent by weight of a mixed metal salt of a thiophosphoric acid ester, wherein the mixed metal is zinc and an alkaline earth and the mixed metal salt is obtained by reacting phosphorus pentasulfide and an aliphatic monohydric alcohol containing 6 to 14 carbon atoms per molecule on the average in a mol ratio, respectively, of about 1:4, said reaction being effected at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic alkaline earth compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 0.5 to about 5.0 percent by weight of an oil-soluble alkaline earth metal sulfonate; and about 0.5 to about 5.0 percent by weight of an oil-soluble alkaline earth metal and sulfur containing permanently thermoplastic, resinous condensation product obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, a sulfide selected from the group consisting of an alkali metal sulfide and an alkaline earth metal sulfide, and an alkylated monohydric phenol having at least one free reactive position in the nucleus and at least one alkyl group containing from 4 to 12 carbon atoms, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of alkaline earth metal sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of said sulfide, said resinous condensation product when obtained when employing said alkali metal sulfide being subjected to metathesis with a water soluble salt of an alkaline earth metal.

3. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 0.5 to about 5.0 percent by weight of zinc dicyclohexyl dithiophosphate; about 0.5 to about 5.0 percent by weight of an oil-soluble calcium sulfonate; and about 0.5 to 5.0 percent by weight of the calcium and sulfur containing condensation product obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, calcium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of calcium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the calcium sulfide.

4. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 0.5 to about 5.0 percent by weight of a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 0.5 to about 5.0 percent by weight of an oil-soluble calcium sulfonate; and about 0.5 to about 5.0 percent by weight of the calcium and sulfur containing condensation product obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, calcium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of calcium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the calcium sulfide.

5. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 0.5 to about 5.0 percent by weight of a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 0.5 to about 5.0 percent by weight of an oil-soluble calcium sulfonate; and about 0.5 to about 5.0 percent by weight of the calcium and sulfur containing condensation product obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, calcium sulfide and tetramethyl-

butyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of calcium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the calcium sulfide, wherein the weight ratio of said thiophosphate to said sulfonate to said calcium and sulfur containing condensation product is about 1:2:1.

6. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 0.5 to about 5.0 percent by weight of a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 0.5 to about 5.0 percent by weight of an oil-soluble calcium sulfonate; and about 0.5 to about 5.0 percent by weight of the calcium and sulfur containing product obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, sodium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of sodium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the sodium sulfide, the condensation product thus obtained being subjected to metathesis with calcium chloride.

7. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 0.5 to about 5.0 percent by weight of a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 0.5 to about 5.0 percent by weight of an oil-soluble calcium sulfonate; and about 0.5 to about 5.0 percent by weight of the calcium and sulfur containing product obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, sodium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of sodium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the sodium sulfide, the condensation product thus obtained being subjected to metathesis with calcium chloride, wherein the weight ratio of said thiophosphate to said sulfonate to said barium and sulfur containing metathesis product is about 1:2:1.

8. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 1 percent by weight of a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 7 percent by weight of a solution consisting of about 33 percent calcium petroleum sulfonate in a light mineral oil; and about 3 percent by weight of a solution consisting of about 33 percent calcium and sulfur containing condensation product in a light mineral oil, said condensation product being obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, calcium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of calcium sulfide being employed for every two mols of the phenol, the condensaiton being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the calcium sulfide.

9. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 1 percent by weight of a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 7 percent by weight of a solution consisting of about 33 percent barium petroleum sulfonate in a light mineral oil; and about 3 percent by weight of a solution consisting of about 33 percent barium and sulfur containing product in a light mineral oil, said product being obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, sodium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of sodium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the sodium sulfide, the condensation product thus obtained being subjected to metathesis with barium chloride.

10. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 1 percent by weight of

a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 7 percent by weight of a solution consisting of about 33 percent calcium petroleum sulfonate in a light mineral oil; about 3 percent by weight of a solution consisting of about 33 percent calcium and sulfur containing condensation product in a light mineral oil, said condensation product being obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, calcium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of calcium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the calcium sulfide; and at least one agent selected from the group consisting of a viscosity index improver, an antifoam agent and a dye.

11. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 1 percent by weight of a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 7 percent by weight of a solution consisting of about 33 percent calcium petroleum sulfonate in a light mineral oil; about 3 percent by weight of a solution consisting of about 33 percent calcium and sulfur containing condensation product in a light mineral oil, said condensation product being obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, calcium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of calcium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the calcium sulfide; and a viscosity index improving amount of an acrylate resin.

12. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 1 percent by weight of a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 2 percent by weight of calcium petroleum sulfonate in a light mineral oil solution; about 1 percent by weight of a calcium and sulfur containing condensation product in a light mineral oil solution, said condensation product being obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, calcium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of calcium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the calcium sulfide; and a small amount, sufficient to confer to the lubricating composition their respective characteristics, of each of a viscosity index improver; an antifoam agent; and an oil-soluble dye.

13. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 0.5 to about 5.0 percent by weight of a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 0.5 to about 5.0 percent by weight of an oil-soluble barium sulfonate; and about 0.5 to about 5.0 percent by weight of the barium and sulfur containing product obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, sodium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of sodium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the sodium sulfide, the condensation product thus obtained being subjected to metathesis with barium chloride.

14. A lubricating composition having improved resistance to sludge formation upon continued heating and rust inhibiting characteristics comprising a major proportion of a highly refined mineral lubricating oil and minor proportions consisting of about 0.5 to about 5.0 percent by weight of a mixed metal salt of zinc and calcium branched chain octyl thiophosphate obtained by reacting phosphorus pentasulfide and a mixture of branched-chain octyl alcohols in a mol ratio, respectively, of about 1:4 at a temperature of about 130° to 350° F., and reacting the resultant product with a member selected from the group consisting of zinc metal and a basic zinc compound in a mol ratio of about 0.5 to 1 mol of said member per mol of phosphorus pentasulfide at temperatures of about 60° to about 180° F., then reacting the resulting reaction product with sufficient basic calcium compound to raise the pH of the reaction mixture to at least about 6 and

about 0.5 to about 2 percent by weight of benzoyl peroxide, at a temperature of about 60° to about 300° F.; about 0.5 to about 5.0 percent by weight of an oil-soluble barium sulfonate; and about 0.5 to about 5.0 percent by weight of the barium and sulfur containing product obtained by condensing in an aqueous medium reactants consisting essentially of formaldehyde, sodium sulfide and tetramethylbutyl phenol, at least one mol of formaldehyde being employed for every two mols of the phenol, and at least one equivalent of sodium sulfide being employed for every two mols of the phenol, the condensation being conducted to avoid any substantial reaction between the phenol and formaldehyde in the absence of the sodium sulfide, the condensation product thus obtained being subjected to metathesis with barium chloride, wherein the weight ratio of said thiophosphate to said sulfonate to said barium and sulfur containing product is about 1:2:1.

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UNITED STATES PATENT OFFICE

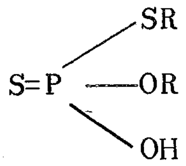
CERTIFICATION OF CORRECTION

Patent No. 2,966,460 December 27, 1960

Troy L. Cantrell et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 72, for "Mendelyeevf's" read -- Mendeleeff's --; column 2, line 32, for "sluding" read -- sludging --; column 3, lines 44 to 47, the right-hand portion of the formula should read as shown below instead of as in the patent:



column 10, line 58, for "organi" read -- organo --; column 18, line 8, for "0.5 to 5.0" read -- 0.5 to about 5.0 --.

Signed and sealed this 30th day of May 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents