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COMPLEX METAL SALTS OF PHOSPHORIC ACID ESTERS AND MINERAL OIL COMPOSITIONS CONTAINING THE SAME

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This application is a continuation-in-part of copending application Serial No. 246,501, filed September 13, 1951, now abandoned.

This invention relates to improved lubricating oil compositions, particularly mineral lubricating oils for use in internal combustion engines.

As is well known, mineral lubricating oils refined for use as lubricants have a tendency to oxidize in use in an engine with attendant formation of oxidized products which are acidic in character and which exert a strong corrosive action on the engine parts, such as the hard metal alloy bearings. The oxidation of the oil also produces carbonaceous sludge deposits in the engine, particularly around the pistons and oil rings causing them to stick, thus materially lowering the efficiency of the engine.

To counteract these conditions, there have been developed in the art chemical agents which, when added to a mineral lubricating oil designed for use in internal combustion engines, have the ability to inhibit or retard oxidation of the oil. These agents are designated as antioxidants. Other agents have been developed which have the ability to suspend the carbonaceous oxidation products formed in the oil, thereby keeping the engine parts clean and free from clogging and sticking effects normally encountered. These materials are known as detergents. The present invention is concerned with chemical additives which exhibit a two-fold ability, viz., (1) the ability to inhibit the formation of acidic, corrosive, oxidation products in the oil during use in an engine and (2) the ability to keep the engine parts clean and free from sticking. These additives are, therefore, antioxidants as well as detergents. This two-fold action of these materials is, of course, of great advantage from an economic standpoint since ordinarily separate additives are employed to impart each of these characteristics to an oil.

It is, therefore, the object of this invention to provide a mineral lubricating oil composition which is stabilized against the formation of corrosive bodies therein during use and which is also fortified as to its detergent ability. Other and further objects will appear from the following detailed description of the invention.

The additives contemplated herein may be designated broadly as complex metal salts of partial esters of phosphoric acid. Due to the complex nature of these compounds, no exact chemical formula can be ascribed to them at this time and they are, therefore, best described by the process of producing them.

Broadly, the complex salts of the present invention are prepared by the method which comprises the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of an organic hydroxy compound selected from the group consisting of a hydroxyaromatic compound that has an alkyl substituent having at least 8 carbon atoms in place of a nuclear hydrogen atom thereof and a primary, aliphatic alcohol having at least 8 carbon atoms per molecule, to form an acidic, partial ester of phosphoric acid, and (2) reacting

said acidic, partial ester of phosphoric acid with a metal salt reagent, the metal constituent of which is selected from the group consisting of zinc, cadmium, magnesium, cobalt, barium, calcium and strontium, in an amount sufficient to furnish at least about two equivalents of metal per equivalent of acid-hydrogen content in said acidic partial ester of phosphoric acid, and of which at least about one of said equivalents of metal is furnished by a metal carboxylate selected from the group consisting of metal acetates and metal caproates.

In the practice of the invention, the reaction of the partial ester of the phosphoric acid with the metal salt can be accomplished by reacting the ester first with about one equivalent of a metal salt reagent which may be a metal carboxylate or a salt other than a metal carboxylate, such as a metal hydroxide, metal carbonate or metal alcoholate, this reaction being followed by reaction with about one equivalent of a metal carboxylate, such as a metal formate, acetate or caproate, the metal constitutent of which is the same as that of the reagent utilized in the first reaction. However, more than one equivalent of the metal salt reagent can be utilized in the first step, amounts up to and including about two equivalents or more being entirely suitable. It will be understood, therefore, that the use of about one equivalent of the metal salt reagent in the first reaction and about one equivalent of metal carboxylate reagent in the second reaction represents about the least amounts of these reagents which can be successfully employed. Obviously, in instances where a metal carboxylate is used in the first reaction and more than one equivalent is employed the second reaction will not require an additional full equivalent of the reagent but only an amount thereof necessary to supply up to a minimum of two equivalents of metal. Thus, alternatively, the reaction of the partial ester with the metal salt reagent may be conducted in a single step by utilizing at least about two equivalents of metal carboxylate exclusively. Here again, this represents about the least amount which can be used. It can be said then that the upper limit with respect to the amounts of the several metal salt reagents which can be employed is not a critical factor but is governed largely by practical considerations. Thus, although the use of amounts considerably higher than those above indicated provides no particular advantage the employment of large excess amounts of the salts reagents tends to reduce the fluidity of the reaction mass which, in turn, may create handling and filtration difficulties.

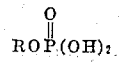
The complex metal salts herein contemplated have metal contents substantially greater than "normal" salts of the phosphoric acid partial esters. Generally, these complex salts contain at least about two equivalents of metal per equivalent of acid-hydrogen in the partial ester. We have found that these complex metal acetate salts when utilized in mineral lubricating oils provide outstanding detergent properties in the oil. They also generally improve the antioxidant properties of the oil.

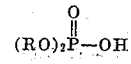
We are aware of the fact that the "normal" metal salts of the organo-substituted phosphoric acids have been disclosed heretofore as oil additives. Patents Nos. 2,228,658 and 2,228,659 to B. B. Farrington et al. and No. 2,228,671 to George L. Neeley, for example, describe normal metal salts of this type and oil compositions thereof. However, in so far as is known there has been no disclosure in the art of "complex" metal salts of the type herein contemplated, or that these "complex" metal salts possess markedly improved detergent powers in lubricating oils over the normal salts. Since the complex metal salts have not been known heretofore, they are believed to be new compositions of matter.

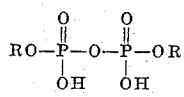
As aforesaid, due to the complex nature of the reactions involved in the formation of the complex metal

salts, their exact structure has not as yet been determined. However, in order that the nature of these products may be understood to the fullest possible extent, and without intending to limit the invention in any way, the following theoretical observations may be made.

When an alkylated hydroxyaromatic compound, such as an alkyl phenol reacts with phosphorus pentoxide in a 3:1 mol ratio, indications are that the product obtained consists essentially of a mixture of (1) monoalkaryl phosphoric acids, (2) di-alkaryl phosphoric acids and (3) pyrophosphoric acids. These products may be represented by the following formulae in which R represents the organic (alkaryl) substituent.

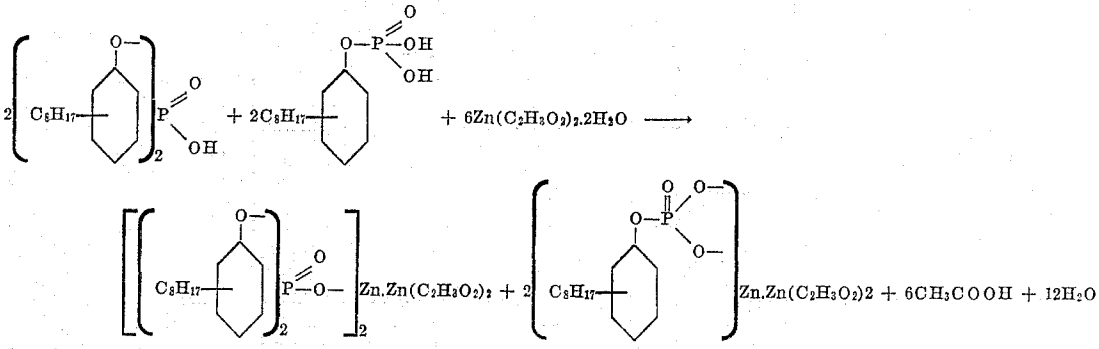
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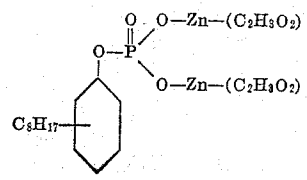
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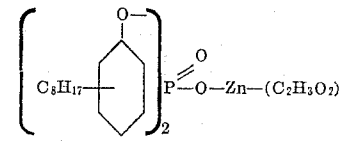
The relative proportions of these compounds present in the product would be expected to be governed to some extent by the proportions of hydroxyaromatic compound and phosphorus pentoxide used in the reaction. For example, when the mol ratio of the hydroxyaromatic compound to phosphorus pentoxide is 3:1, the major components of the reaction product are considered to be most probably the mono- and di-esters of phosphoric acid with minor amounts of pyrophosphoric acid.

We have found, for example, that when the octylphenol-phosphorus pentoxide product is reacted with an amount of zinc acetate at least twice that which would be equivalent to the acid-hydrogen of the said product, the resulting salt will contain at least about two, and as high as three, equivalents of zinc per equivalent of acidity in the octylphenol-phosphorus pentoxide product. Although, as stated previously, the structure of these complex metal salt products is not known, it is believed that the extra equivalents of zinc are incorporated into the molecule through a coordination or "complexing" of the zinc salt with the normal zinc salt of the phosphoric acid ester. Thus, the reaction of zinc acetate with octylphenol-phosphorus pentoxide (3:1) product in the proportion of about two equivalents of zinc acetate per acid-hydrogen equivalent of the octylphenol-phosphorus pentoxide product may be represented as follows:



Another possible structure for these products would be that corresponding to a mixed acetate-phosphate zinc salt. This product, when employing the octylphenol-phosphorus pentoxide (3:1) product, would be represented as follows:





However, indications are that the structure is of the complex type rather than the latter possibility. Thus, it is possible to prepare products containing more than two equivalents of zinc. Also, a normal zinc salt of the phosphoric acid ester, prepared with a basic salt reagent other than zinc acetate, such as zinc hydroxide, zinc carbonate, zinc alcoholate, etc., may be further reacted with zinc acetate to form products similar to those obtained by treatment of the ester with two equivalents of zinc acetate.

ALKYL HYDROXYAROMATIC COMPOUND

The preparation of the compounds of the invention involves, first, the alkylation of a hydroxyaromatic compound, such as phenol. Alkylation of the aryl hydroxide may be accomplished by methods known to the art, such as by a Friedel-Crafts synthesis using a halogenated hydrocarbon. The alkylation may also be effected by reaction of the aryl hydroxide with unsaturated hydrocarbons, or alcohols, in the presence of a suitable catalyst, such as H_2SO_4, $ZnCl_2$, BF_3, HF, etc.

Typical aryl hydroxides which may be used as the starting material for the alkylation reaction are: phenol, resorcinol, hydroquinone, catechol, cresol, xylenol, hydroxydiphenyl, benzyl - phenol, phenyl - ethyl - phenol, phenol resins, methyl-hydroxydiphenyl, guaiacol, alpha and beta naphthol, alpha and beta methyl naphthol, tolyl naphthol, xylyl naphthol, benzyl naphthol, anthranol, phenyl methyl naphthol, phenathrol, chlorphenol and the like. Preference in general is to the monohydroxy phenols otherwise unsubstituted, particular preference being given to phenol and alpha and beta naphthol.

The hydroxyaromatic compound may have one or several alkyl groups attached to the nucleus thereof. In any case, the alkyl portion of this compound should contain a total of at least eight carbon atoms. Thus, if the alkyl substituent contains less than eight carbon atoms, the aromatic nucleus should contain more than one such substituent to bring the carbon atom content of the side chains so attached to about eight in order to provide ultimate complex salts which are completely oil soluble. On the other hand, the hydrocarbon from which the alkyl group is derived may suitably contain up to 30 or even 40 carbon atoms. In fact a preferred source of the alkyl substituent is petroleum wax which contains hydrocarbon molecules having from about 20 to about 30 carbon atoms and an average of about 24 carbon atoms per molecule. Other suitable alkyl hydroxyaromatic compounds are, for example, octylphenol, diamylphenol, decylphenol, laurylphenol, tetradecylphenol, hexadecylphenol and octadecylphenol, octylphenol being particularly preferred.

Where a primary aliphatic alcohol is used for reaction with phosphorus pentoxide, rather than an alkaryl hydroxy compound, it should likewise contain at least about

8 carbon atoms and suitably as high as 20, or even 30, carbon atoms. Of the alcohols suitable for use in the invention there may be mentioned, as non-limiting examples, the following: octyl alcohol, nonyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl, octadecyl, carnaubyl, ceryl and melissyl alcohols. Unsaturated alcohols, such as oleyl alcohol, may also be used.

The various alkylphenols and aliphatic alcohols utilized in the invention, with the exception of the wax-alkylated phenols, are either available commercially or the methods for their preparation are within the skill of those versed in the art. The preparation of a wax-alkylated type of product, however, is illustrated by the following procedure.

WAX-PHENOL

A paraffin wax melting at approximately 120° F. and predominantly comprised of hydrocarbons, having at least 20 and an average of about 24 carbon atoms in their molecules, is melted and heated to about 200° F., after which chlorine is bubbled therethrough until the wax has absorbed about 14%, by weight, of chlorine. A sufficient quantity of this chlorinated wax to provide three atomic proportions of chlorine is then heated to a temperature varying from just above its melting point to not over 150° F. One mol of phenol (C_6H_5OH) is then mixed with the chlorowax. The mixture is then heated to about 150° F. and a quantity of anhydrous aluminum chloride, corresponding to about 3% of the weight of the chlorowax in the mixture, is slowly added with active stirring. The rate of addition of the aluminum chloride should be sufficiently slow to avoid violent foaming and during the addition the temperature should be held at about 150° F. After the aluminum chloride has been added, the temperature of the mixture may be increased slowly over a period of from 15 to 25 minutes to a temperature of about 250° F. and then should be more slowly increased to about 350° F. To control the evolution of HCl gas, the temperature of the mixture is preferably raised from 250° F. to 350° F. at a rate of approximately one degree per minute, the whole heating operation occupying approximately two hours from the time of adding the aluminum chloride. If the emission of HCl gas has not ceased when the final temperature is reached, the mixture may be held at 350° F. for a short time to allow completion of the reaction. However, to avoid possible cracking of the wax, the mixture should not be heated appreciably above 350° F., nor should it be held at that temperature for any extended length of time.

It is important that all unreacted, or non-alkylated phenol remaining in the reaction mixture, as well as aluminum chloride, be removed. This can be conveniently effected by washing the product several times with a mixture of water and an alcohol, such as butanol, preferably at elevated temperature, say 175° F. The product may then be treated with steam. This latter step will insure complete removal of the unreacted material and also dry the product.

It will be understood that a wax-substituted phenol prepared according to the above procedure in which a quantity of chlorowax containing three atomic proportions of chlorine and having a chlorine content of 14% is reacted with one mol of phenol is designated as "wax-phenol (3–14)." Similarly, "wax-phenol (3–10)" and "wax-phenol (1–10)" may also be prepared by the reaction of sufficient amounts of chlorinated wax, containing 10%, by weight, of chlorine, to provide three atomic proportions and one atomic proportion of chlorine per mol of phenol, respectively, in the reaction and are useful in the invention. In general, the amount of chlorowax, containing from about 10% to 18%, by weight, of chlorine, used in the reaction is sufficient to supply between one and four atomic proportions of chlorine per mol of phenol used.

PARTIAL ESTER OF PHOSPHORIC ACID

In preparing the alkaryl phosphoric acid ester, the alkyl hydroxyaromatic compound and the phosphorus pentoxide are heated together at a temperature of from about 50° C. to about 150° C. for a period of time to insure substantially complete reaction, usually from about 5 to 15 hours. An inert solvent, such as toluene, xylene or the like, may be used to facilitate the reaction. A mineral oil may also be conveniently used as the solvent, in which case the product is an oil concentrate which may be used directly in the preparation of the ultimate complex metal salt. In this way, the ultimate complex metal salt product is obtained in the form of an oil concentrate and may be conveniently utilized as such for addition to mineral lubricating oils. Where a solvent other than mineral oil is used, the reaction mixture is filtered and topped at elevated temperature and reduced pressure to remove the solvent.

The proportions of alkyl hydroxyaromatic compound and phosphorus pentoxide used in the reaction can be varied between from about one to about three mols of the alkyl hydroxyaromatic compound to one mol of phosphorus pentoxide, although our preferred products are obtained by the use of about three mols of the alkyl hydroxyaromatic compound (or alcohol) per mol of phosphorus pentoxide.

COMPLEX METAL SALT

As indicated previously, in preparing the "complex" metal salt of the phosphoric acid ester, a salt of the ester may first be prepared by reaction of the ester with a suitable metal salt, such as a hydroxide, carbonate, alcoholate, etc., and the desired complex salt then formed by further reaction of the ester salt with a metal carboxylate, preferably the acetate, of the same metal constituent as the metal salt reagent used in the formation of the ester salt. On the other hand, the desired complex salt may be prepared directly by reacting the ester with a sufficient amount of a metal acetate salt to provide more than the amount of metal which would be equivalent to the acid-hydrogen content of the phosphoric acid partial ester. This direct "one-step" procedure is generally preferred.

The reactions required to produce the complex salts by either the indirect method, i. e., by first forming the ester salt or by forming the complex metal salt with the metal acetate reactant directly, are within the skill of those familiar with the art, both reactions being accomplished at temperatures of from about 50° C. to about 200° C. and in a relatively short time, generally from about one-half hour to two hours. As already stated, the total amount of metal salt reactant used in forming the complex salt by the indirect method (i. e., through initial formation of the ester salt) and by the direct method, should be sufficient to provide an amount of metal which will completely replace the acid-hydrogen of the phosphoric acid ester and also supply the additional amount (at least equivalent to that required to form the ester salt) of metal necessary to form the complex metal salt product; the complex salts generally containing at least about two equivalents of metal for each equivalent of acid-hydrogen in the phosphoric acid ester. A suitable solvent medium, such as benzene, toluene, xylene and the like, or a mineral oil may be used as the solvent. In the latter case, an oil concentrate of the complex salt is obtained.

We have found that, in forming the zinc complexes, it is more convenient and economical to supply the zinc acetate to the reaction in the form of zinc oxide and glacial acetic acid.

The following specific examples and test results will serve to fully illustrate the nature and outstanding utility as oil additives of the complex salts herein contemplated.

Example 1

WAX-PHENOL (3–14)-P_2O_5 (3:1) PRODUCT

Reaction mixture:

Wax-phenol (3–14) (phenol content=approx. 11.9%)	grams	300
P_2O_5	do	18
Toluene	ml	300

Procedure.—The wax-phenol (3–14) and toluene were placed in a 2-liter, 4-necked, round-bottom flask containing a reflux condenser, thermometer and mechanically driven stirrer. After heating to 100° C., phosphorus pentoxide was gradually added to the mixture over a 4-hour period. Following this, the temperature of the mixture was held at 100° C. for a period of 8 hours to insure complete reaction. The product was then filtered through filtering clay and the filtrate was topped to 150° C. under diminished pressure to remove the toluene solvent. The residue, representing the finished product, contained 2.2% phosphorus and had a neutralization number of 48.

Example 2

NORMAL ZINC SALT OF WAX-PHENOL (3–14)-P_2O_5 (3:1) PRODUCT

Reaction mixture:

Wax-phenol (3–14)-P_2O_5 (3:1) product (Ex. 1)	grams	100
$Zn(C_2H_3O_2)_2.2H_2O$	do	9.5
Mineral oil (S. U. V. of 296 sec. at 100° F.; solvent-refined Penna. oil)	grams	300
Ethyl alcohol	ml	100

Procedure.—The wax phenol (3–14)-phosphorus pentoxide (3:1) product and the mineral oil were placed in a 2-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and a mechanically driven stirrer. The zinc acetate dihydrate was dissolved in the ethyl alcohol and the solution added to the other reactant at room temperature. The reaction mixture was heated, removing alcohol by distillation to 175° C., and held at that temperature for one hour. After cooling, the reaction product was dissolved in benzene and the solution filtered through a Buchner funnel packed with filtering clay. The zinc salt was recovered as the distillation residue by topping to 175° C. under diminished pressure. This material contained 0.78% zinc and 0.52% phosphorus.

Example 3

WAX-PHENOL (3–14)-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Wax-phenol (3–14)	1000
Mineral oil (S. U. V. of 296 sec. at 100° F.; solvent-refined Penna. oil)	2000
P_2O_5	60

Procedure.—The wax-phenol (3–14) and mineral oil were placed in a 5-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and were warmed with agitation to 100° C. The phosphorus pentoxide was added portionwise at 100° C. over 2½ hours, followed by a reaction period of 7½ hours at 100° C. The clear amber colored reaction product was filtered through filtering clay contained on a heated Buchner funnel. The product was found to have an N. N. (neutralization number) of 19.2 and a phosphorus content of 0.84%.

Example 4

COMPLEX ZINC ACETATE SALT OF WAX-PHENOL (3–14)-P_2O_5 (3:1) PRODUCT

Reaction mixture:

Wax-phenol (3–14)-P_2O_5 (3:1) product (Ex. 3)	grams	400
$Zn(C_2H_3O_2)_2.2H_2O$	do	30.6
Ethyl alcohol, Formula 30 [1]	ml	175

[1] A denatured alcohol containing 10 gals. pure methanol per 100 gals. 190° proof ethyl alcohol.

Procedure.—The wax-phenol (3–14)-phosphorus pentoxide (3:1) product was added to a 1-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer, and mechanically driven stirrer. The zinc acetate dihydrate was dissolved in formula 30 alcohol and the solution added to the reaction flask at 60° C. The reaction mixture was heated with agitation and a nitrogen flush to remove alcohol and aqueous acetic acid and then held at the attained temperature of 165° C. under diminished pressure for one hour. The reaction product was cooled to 90° C. and filtered through filtering clay on a heated Buchner funnel. The filtrate representing the finished product was a dark amber liquid containing 2.64% zinc and 0.75% phosphorus.

Example 5

OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Octylphenol	800
P_2O_5	180

Procedure.—The octylphenol was placed in a 2-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and was heated to 100° C. with agitation. The temperature was maintained at 100° C. ±5° during the portionwise addition of phosphorus pentoxide over a two-hour period and during the reaction period proper of eight hours duration. The clear light amber reaction product was filtered through filtering clay contained on a heated Buchner funnel. The product had an N. N. (neutralization number) of 210 and contained 7.99% phosphorus.

Example 6

NORMAL ZINC SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Octylphenol-P_2O_5 (3:1) product (Ex. 5)	400
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	800
$ZnCO_3$	94

Procedure.—The octylphenol-phosphorus pentoxide (3:1) product and the mineral oil were placed in a 3-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer. The zinc carbonate was added gradually over a 15-minute period and the mixture heated to and maintained at 100° C. for two hours. The reaction product was filtered through filtering clay contained on a heated Buchner funnel giving a product containing 3.90% zinc.

Example 7

COMPLEX ZINC ACETATE SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:

Octylphenol-P_2O_5 (3:1) product (Ex. 5)	grams	400
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	grams	800
$Zn(C_2H_3O_2)_2.2H_2O$	do	329
Ethyl alcohol, Formula 30	ml	1450

Procedure.—The octylphenol-phosphorus pentoxide (3:1) product and the mineral oil were placed in a 5-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and were heated with agitation to 70° C. The

$Zn(C_2H_3O_2)_2.2H_2O$

was dissolved in the formula 30 alcohol and the solution was added at 60° C. to the reaction flask. The mixture was then heated to 165° C. allowing alcohol and aqueous acetic acid to distill. After three hours at this temperature, the last two hours under diminished pressure, the reaction product was filtered through filtering clay contained on a heated Buchner funnel. The filtrate contained 8.35% zinc and 2.73% phosphorus.

Example 8

COMPLEX ZINC ACETATE SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Pounds
Octylphenol-P_2O_5 (3:1) product (Ex. 5)	13.0
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	13.0
Zinc oxide	3.98
Acetic acid (glacial)	6.17

Procedure.—The octylphenol-phosphorus pentoxide (3:1) product and mineral oil were mixed in a 5-gallon glass lined kettle equipped with a mechanical stirrer and heated to 146° F. Acetic acid was then added followed by zinc oxide. Upon heating to 238° F., at which point refluxing began, a nitrogen stream was introduced to facilitate distillation of acetic acid. The temperature was then raised to 330° F. and held there for two hours at atmosphere pressure and one-half hour under diminished pressure. After cooling to 190° F., the reaction product filtered through filtering clay contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 10.55% zinc and 3.38% phosphorus.

Example 9

NORMAL ZINC SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Octylphenol-P_2O_5 (3:1) product (similar to Example 5, but N. N.=212)	600
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	600
$ZnCO_3$	156

Procedure.—The octylphenol-phosphorus pentoxide (3:1) product and mineral oil were mixed in a 5-liter, 4-neck, round-bottom flask equipped with a condenser, thermometer, and a mechanically driven stirrer. Zinc carbonate was added at 650° C. and the mixture was heated to 100° C. with a nitrogen flush and held at 100° C. for two hours. The reaction mixture was pretreated with 5%, by weight, of filtering clay and then filtered through filtering clay contained on a heated Buchner funnel. The filtered product contained 5.55% zinc.

Example 10

COMPLEX ZINC ACETATE SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Normal zinc salt of octylphenol-P_2O_5 (3:1) product (Ex. 3)	150
ZnO (charge on basis of N. N. of octylphenol-P_2O_5 product used in Ex. 9)	13.6
Acetic acid (glacial)	20.2
H_2O	34.0

Procedure.—The normal zinc salt of octylphenol-phosphorus pentoxide (3:1) product was placed in a 500-ml., 4-neck, round-bottom flask equipped with a distillation assembly, a submerged gas inlet tube, a thermometer, and a mechanically driven stirrer, and was heated with agitation. When the temperature reached 70° C., aqueous zinc acetate, prepared by heating zinc oxide, acetic acid and water to 90° C., was added directly and the heating rate increased. Nitrogen was introduced at 125° C., aiding removal of acetic acid and water, and the reaction temperature of 165° C. was reached within 1¼ hours after the $Zn(C_2H_3O_2)_2$ (Aq.) addition. The reaction mixture was held as 165° C. under diminished pressure for an additional hour. The reaction product was pretreated at 100° C. with 4%, by weight, of filtering clay and then filtered through 1%, by weight, of the clay contained on a heated Buchner funnel. The filtrate representing the finished product contained 12.58% zinc and 3.46% phosphorus.

Example 11

COMPLEX ZINC ACETATE SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Normal zinc salt of octylphenol-P_2O_5 (3:1) product (Ex. 9)	150.0
ZnO (charge of Zn based on Zn content of Ex. 9)	10.4
Acetic acid (glacial)	14.4
H_2O	24.8

Procedure.—The normal zinc salt of octylphenol-phosphorus pentoxide (3:1) product was placed in a 500-ml., 4-neck, round-bottom flask, equipped with a distillation assembly, a submerged gas inlet tube, a thermometer and a mechanically driven stirrer and was heated with agitation. When the temperature reached 80° C., aqueous zinc acetate, prepared from zinc oxide, acetic acid and water heated to 90° C., was added directly and the heating rate increased. Aqueous acetic acid was recovered by distillation during attainment of the reaction temperature of 165° C. and this temperature was held, with a nitrogen flush, for ¾ hour, followed by like treatment under diminished pressure for ¼ hour.

The reaction product was treated at 100° C. with 4%, by weight, of filtering clay and then filtered through 1%, by weight, of the clay contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 11.27% zinc and 3.60% phosphorus.

Example 12

DI-SECONDARY AMYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Di-secondary amylphenol	1404
P_2O_5	285

Procedure.—The di-secondary amylphenol was placed in a 3-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and was heated to 100° C. The phosphorus pentoxide addition was made portionwise over a 3-hour period at 100° C. for eight hours. The clear amber reaction product was filtered through filtering clay contained on a heated Buchner funnel. The product contained 7.68% phosphorus and had an N. N. (potentiometric) of 165.

Example 13

NORMAL ZINC SALT OF DI-SECONDARY AMYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Di-secondary amylphenol-P_2O_5 (3:1) product (Ex. 12)	135
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	270
$ZnCO_3$ (100% excess)	50.2

Procedure.—The di-secondary amylphenol-phosphorus pentoxide (3:1) product and the mineral oil were placed in a 1-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer, and mechanically driven stirrer and the $Zn(CO)_3$ was added at room temperature. The reaction mixture was heated with agitation and nitrogen flush to 165° C. and held at 165° C. under diminished pressure for 2¼ hours. The reaction mixture was cooled to 90° C., dissolved in benzene and the solution was filtered through filtering clay on a Buchner funnel. The filtrate was topped under diminished pressure and the product residue contained 3.4% of zinc and 2.49% phosphorus.

Example 14

NORMAL ZINC SALT OF DI-SECONDARY AMYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:

Di-secondary amylphenol-P_2O_5 (3:1) product (Ex. 12)	grams	400
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	grams	800
$Zn(C_2H_3O_2)_2.2H_2O$	do	132
Ethyl alcohol, Formula 30	ml	1200

Procedure.—The di-secondary amylphenol-phosphorus pentaoxide (3:1) product and the mineral oil were placed in a 5-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and the zinc acetate di-hydrate in alcohol solution was added thereto. The reaction mixture was heated with agitation to 165° C. with recovery of alcohol-aqueous acetic acid condensate and then reacted at 165° C. for 1¼ hours under diminished pressure. The reaction mixture was cooled and filtered through filtering clay contained on a heated Buchner funnel. The filtrate, a dark amber colored oil, contained 3.38% zinc and 2.48% phosphorus.

Example 15

COMPLEX ZINC ACETATE SALT OF DI-SECONDARY AMYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:

Di-secondary amylphenol-P_2O_5 (3:1) product (Ex. 12)	grams	400
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	grams	800
$Zn(C_2H_3O_2)_2.2H_2O$	do	264
Ethyl alcohol, Formula 30	ml	2500

Procedure.—The di-secondary amylphenol-phosphorus pentoxide (3:1) product and the mineral oil were placed in a 5-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and the solution of $Zn(C_2H_3O_2)_2.2H_2O$ in alcohol was added thereto. The reaction mixture was heated with agitation and nitrogen flush to 165° C., recovering a mixture of alcohol and aqueous acetic acid. After heating at 165° C. for three hours under diminished pressure, the reaction product was cooled, filtering clay added, and then filtered through filtering clay contained on a heated Buchner funnel. The product contained 6.44% zinc and 2.45% phosphorus.

Example 16

NONYL ALCOHOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:

	Grams
Nonyl alcohol (3,5,5-trimethylhexanol)	400
P_2O_5	128

Procedure.—The nonyl alcohol was placed in a 1-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer, and mechanically driven stirrer and was heated with agitation to 100° C. and then the phosphorus pentoxide was added portionwise, keeping the temperature constant, over a two-hour period. The reaction mixture was maintained at 100° C. for four hours and then filtered through filtering clay contained on a heated Buchner funnel. The product contained 10.5% phosphorus and had an N. N. of 305.

Example 17

NORMAL ZINC SALT OF NONYL ALCOHOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:

	Grams
Nonyl alcohol-P_2O_5 (3:1) product (Ex. 16)	450
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	450
$ZnCO_3$	170

Procedure.—The nonyl alcohol-phosphorus pentoxide (3:1) product and the mineral oil were placed in a 3-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and the zinc carbonate was added thereto at room temperature. The reaction mixture was heated to 175° C. with recovery of water of reaction and maintained at 175° C. ± 50° C. for two hours. The reaction mixture was filtered through filtering clay contained on a heated Buchner funnel. The filtrate contained 7.67% zinc and 4.82% phosphorus.

Example 18

COMPLEX ZINC ACETATE SALT OF NONYL ALCOHOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:

	Grams
Nonyl alcohol-P_2O_5 (3:1) product (Ex. 16)	400
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	800
$HC_2H_3O_2$ (99.5%) (1 equivalent on basis of N. N.)	138
ZnO (2 equivalents + 5%)	186

Procedure.—The nonyl alcohol-phosphorus pentoxide (3:1) product and one-half (400 grams) the final oil charge were placed in a 3-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer. The acetic acid was added with agitation immediately followed by the gradual addition of the zinc oxide which caused a temperature rise. The reaction mixture was heated gradually and aqueous acetic acid was removed from the mixture by distillation. The reaction mixture was diluted with the second portion (400 grams) of mineral oil at 105° C. to reduce the viscosity and was then heated to 165° C. and held at that temperature for one hour under diminished pressure. The reaction product was cooled and filtered through filtering clay contained on a heated Buchner funnel. The product contained 10.6% zinc and 3.16% phosphorus.

Example 19

DI-TERT-AMYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:

	Grams
Di-tert-amylphenol	2000
P_2O_5	405

Procedure.—The di-tert-amylphenol was placed in a 5-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer. After heating to 100° C., phosphorus pentoxide was gradually added over a six-hour period. The reaction mixture was then held between 90° C. and 100° C. for eight hours to insure complete reaction. The reaction product was filtered through filtering clay contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 7.40% phosphorus and had an N. N. of 183.

Example 20

COMPLEX ZINC ACETATE SALT OF DI-TERT-AMYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:

	Grams
Di-tert-amylphenol-P_2O_5 (3:1) product (Ex. 19)	600
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	450
Zinc oxide	159
Acetic acid (glacial)	236

Procedure.—The di-tert-amylphenol-phosphorus pentoxide (3:1) product and mineral oil were mixed in a 2-liter, 4-necked, round-bottom flask equipped with a condenser, thermometer and mechanically driven stirrer. Acetic acid was added followed by zinc oxide at room temperature and the reaction mixture was heated to 155° C., during the course of which an aqueous acid distillate was collected, with the aid of an N_2 flush. The reaction mixture was then held at 155° C. to 165° C. under diminished pressure for one hour. Upon cooling to 100° C., the reaction product was filtered through filtering clay

contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 10.7% zinc and 3.71% phosphorus.

Example 21

NORMAL CADMIUM SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Octylphenol-P_2O_5 (3:1) product (Ex. 5)	200
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	400
$Cd(C_2H_3O_2)_2.2H_2O$	100

Procedure.—The octylphenol-phosphorus pentoxide (3:1) product and the mineral oil were added to a 2-liter, 4-necked, round-bottom flask equipped with a condenser, thermometer and mechanically driven stirrer and heated to 40° C. The cadmium acetate dihydrate was added and dilute acetic acid was removed by distillation with the aid of a nitrogen flush by heating to 140° C. The reaction mixture was maintained at this temperature under diminished pressure for one-half hour. After cooling to 100° C., the product was filtered through filtering clay contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 7.1% cadmium and 2.65% phosphorus.

Example 22

COMPLEX CADMIUM ACETATE SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Octylphenol-P_2O_5 (3:1) product (Ex. 5)	100
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	100
$Cd(C_2H_3O_2)_2.2H_2O$	101

Procedure.—The octylphenol - phosphorus pentoxide (3:1) product and mineral oil were added to a 1-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and were heated to 70° C. The cadmium acetate dihydrate was added at 70° C. and the reaction mixture heated. Aqueous acetic acid recovery by distillation was complete at 150° C. The reaction mixture was then heated to and held at 165° C. for 1½ hours with nitrogen flush, ½ hour of which was under diminished pressure. The reaction product was cooled and filtered through filtering clay contained on a heated Buchner funnel. The product contained 16.4% cadmium and 3.32% phosphorus.

Example 23

NORMAL MAGNESIUM SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Octylphenol-P_2O_5 (3:1) product (Ex. 5)	200
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	400
$MgCO_3$	33.3

Procedure.—The octylphenol - phosphorus pentoxide (3.1) product and the mineral oil were added to a 2-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and the magnesium carbonate was added at 80° C. The reaction mixture was then heated to and held at 165° C. for one hour and then filtered through filtering clay contained on a heated Buchner funnel. The fluid, amber-colored product contained 1.15% magnesium and 2.44% phosphorus.

Example 24

COMPLEX MAGNESIUM ACETATE SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Octylphenol-P_2O_5 (3:1) product (Ex. 5)	150
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	300
$Mg(C_2H_3O_2)_2.4H_2O$	122.5

Procedure.—The octylphenol - phosphorus pentoxide (3:1) product and the first portion (150 grams) of mineral oil were placed in a 1-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and were heated to 40° C., whereupon the magnesium acetate tetrahydrate was added. The reaction mixture was heated with recovery of aqueous acetic acid by distillation and the second portion (150 grams) of mineral oil charge was added at 115° C. to reduce the viscosity of the reaction mixture. The reaction mixture was heated to and held at 165° C. for 1¾ hours, the last ½ hour being under diminished pressure. The reaction product was cooled and filtered through filtering clay contained on a heated Buchner funnel to give a product which contained 2.95% magnesium and 2.76% phosphorus.

Example 25

NORMAL COBALTOUS SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Octylphenol-P_2O_5 (3:1) product (Ex. 5)	100
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	200
$Co(C_2H_3O_2)_2.4H_2O$	46.7

Procedure.—The octylphenol - phosphorus pentoxide (3:1) product and the mineral oil were placed in a 1-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and were heated to 50° C. at which time the cobaltous acetate tetrahydrate was added. Aqueous acetic acid was distilled off to a reaction temperature of 165° C. and then the system was held at 165° C. for one hour under diminished pressure. The reaction product was cooled to 100° C. and filtered through filtering clay on a heated Buchner funnel. The filtrate, representing the finished product, contained 3.43% cobalt and 2.48% phosphorus.

Example 26

COMPLEX COBALTOUS ACETATE SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Octylphenol-P_2O_5 (3:1) product (Ex. 5)	100
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	200
$Co(C_2H_3O_2)_2.4H_2O$	93.5

Procedure.—The octylphenol - phosphorus pentoxide (3:1) product and the mineral oil were placed in a 1-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and were heated to 50° C. at which time the cobaltous acetate tetrahydrate was added. Aqueous acetic acid was distilled off to a reaction temperature of 160° C. and then the system was held at 165° C. for one hour under diminished pressure. The reaction mixture was cooled and filtered through filtering clay contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 6.74% cobalt and 2.46% phosphorus.

Example 27

COMPLEX ZINC CAPROATE SALT OF OCTYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
Octylphenol-P_2O_5 (3:1) product (Ex. 5)	100
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	100
ZnO	30.4
n-Caproic acid	86.5

Procedure.—The octylphenol - phosphorus pentoxide (3:1) product and the mineral oil were mixed in a 500-ml., 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and heated to 98° C.; whereupon the caproic acid was added followed by the zinc oxide. The reaction mixture was heated to 175° C. with distillation of aqueous caproic acid. The reaction was continued for one hour at 200° C. under diminished pressure. Upon cooling to 100° C. the reaction product was filtered through filtering clay contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 9.46% zinc and 3.13% phosphorus.

Example 28

C_{14} ALKYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
C_{14} alkylphenol [2]	300
P_2O_5	44.4

[2] "Oronite" alkylphenol No. 14, a mixture of monoalkylated phenols, consisting predominantly of para isomers, the alkyl groups of which are branch-chained and contain an average of about 14 carbon atoms.

Procedure.—The C_{14} alkylphenol was placed in a 1-liter, 4-necked, round-bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer and heated to 100° C. Phosphorus pentoxide was added during the course of one hour, the temperature then being raised to 150° C. and held there for four hours. The mixture was cooled and filtered through filtering clay contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 5.43% phosphorus and had an N. N. of 148.

Example 29

COMPLEX CALCIUM ACETATE SALT OF C_{14} ALKYLPHENOL-P_2O_5 (3:1) PRODUCT

Reaction mixture:	Grams
C_{14} alkylphenol-P_2O_5 (3:1) product (similar to Ex. 28 with an N. N. of 127)	200
Mineral oil (S. U. V. of 100 sec. at 100° F.; acid-refined Mid-Continent)	400
Calcium acetate monohydrate	80

Procedure.—The C_{14} alkylphenol-phosphorus pentoxide (3:1) product and mineral oil were mixed in a 2-liter, 4-necked, round-bottom flask equipped with a condenser, thermometer and mechanically driven stirrer. Calcium acetate monohydrate was added at 80° C. and the mixture heated to 155° C. during the course of which an aqueous acetic acid distillate was collected with the aid of a nitrogen flush. The reaction mixture was then held at 155° C. to 165° C. under diminished pressure for one hour. Upon cooling to 100° C., the reaction product was filtered through filtering clay contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 2.57% calcium and 1.60% phosphorus.

EVALUATION OF PRODUCTS

To determine the ability of the complex salts of the invention as detergents in lubricating oils, engine tests were conducted on lubricating oil blends of small amounts of various representative complex salt products; and, for purposes of comparison similar tests were also carried out on oil blends of the normal salts and on the lubricating oils per se. The tests used were the Lauson Detergency Test D–4 and the CFR Diesel Detergency Test D–21. The results of these tests are summarized in Tables I and II, respectively. The test procedures were as follows:

LAUSON DETERGENCY TEST D–4

This test determines the effectiveness of the lubricating oil in preventing fouling as measured by the cleanliness of rings, lands, ring grooves and piston skirts. Cleanliness ratings are based on a scale of from 100 to 0, a 100 rating signifying a perfectly clean condition and a 0 rating representing the worst possible deposit condition. Bearing weight loss is also measured as supplemental data.

A single cylinder, 4-cycle, liquid cooled Lauson engine with splash lubrication and having a copper-lead bearing is used. The operating conditions are as follows:

Oil temperature, °F	225
Jacket temperature, °F	275
Speed, R. P. M	1825
Brake load, H. P	1.6

One-half throttle.
13–1 air-fuel ratio.
Oil added every 20 hours (one gallon sample used).

The engine is inspected at the end of 20, 60 and 100 hours, the duration of the test being 100 hours. The fuel used is a controlled "Mobilgas Special" type blend gasoline (40% thermal+30% catalytically cracked+30% straight run+2.5 cc. TEL/gal.)

CFR DIESEL DETERGENCY TEST D–21

This test determines the effectiveness of the lubricating oil in preventing piston deposits and top ring wear.

A single cylinder CFR, 4-cycle, super-charged, diesel engine is used. The operating conditions are as follows:

Oil temperature, °F	175
Jacket temperature, °F	212
Speed, R. P. M	1800
Brake load, H. P	7.5
Oil addition every 8 hours starting at 4 hours (1½ gal. sample used).	
Heat input, B. t. u./min	1260

The duration of the test is 60 hours. The fuel used is a No. 2 fuel oil containing 1% sulfur. The results are reported in terms of piston cleanliness ratings as in the D–4 test.

From the data presented in Table I for the Lauson D–4 test, it will be seen that the complex salts in every instance provided marked improvement in the engine cleanliness rating over that of the corresponding normal salts. Also, the bearing weight loss in most instances is less for the complex salts than for the corresponding normal salts in this test.

The data in Table II clearly show the superiority of the several complex salts tested, as detergents, over the corresponding normal salts in the CFR Diesel D–21 test.

For ready comparison, the metal and phosphorus contents of the various normal and complex salts prepared and tested as described herein are given in Table III. It will be seen that the phosphorus contents of the normal, and corresponding complex salts are practically the same, but that the metal contents of the complex salts are generally at least about twice that of the normal salts.

TABLE I

Example No.	Product	Percent Additive	Percent Additive, Oil Free Basis	Lauson D-4 Piston Detergency Test (S. A. E. 20 Base oil) [1] Piston Cleanliness 20 Hours	60 Hours	100 Hours	Final Values at 100 Hours N. N.	K. V. @ 210° F.	Bearing Weight Loss (CU-PB) Top, G.	Bottom, G.
		None		69	68	58	2.8	12.14	.290	.308
2	Normal Zinc Salt of Wax-Phenol (3-14)—P_2O_5 (3:1) Product.	4.0	1.0	84	76	73	2.7	11.6	.313	.299
4	Complex Zinc Acetate Salt of Wax-Phenol (3-14)—P_2O_5 (3:1) Product.	2.8	1.0	91	83	79	2.5	11.21	.113	.075
6	Normal Zinc Salt of Octylphenol—P_2O_5 (3:1) Product.	2.8	1.0	78	69	63	2.3	10.48	.067	.063
7	Complex Zinc Acetate Salt of Octylphenol—P_2O_5 (3:1) Product.	2.4	1.0	89	80	72	2.8	10.50	.042	.032
10	do	1.7	1.0	81	74	72	4.6	13.55	.067	.056
11	do	1.7	1.0	90	83	78	3.1	9.91	.031	.033
13	Normal Zinc Salt of Di-Secondary Amylphenol—P_2O_5 (3:1) Product (made with zinc carbonate).	2.8	1.0	66	63	56	2.8	10.56	.064	.065
14	Normal Zinc Salt of Di-Secondary Amylphenol—P_2O_5 (3:1) Product (made with zinc acetate).	2.8	1.0	77	69	65	2.7	11.02	.091	.067
15	Complex Zinc Acetate Salt of Di-Secondary Amylphenol—P_2O_5 (3:1) Product.	2.8	1.0	90	78	78	3.3	10.34	.035	.037
17	Normal Zinc Salt of Nonyl Alcohol—P_2O_5 (3:1) Product.	1.9	1.0	84	74	65	4.3	11.81	.180	.142
18	Complex Zinc Acetate Salt of Nonyl Alcohol—P_2O_5 (3:1) Product.	2.2	1.0	90	80	76	3.3	10.19	.023	.025
20	Complex Zinc Acetate Salt of Di-Tert-Amylphenol—P_2O_5 (3:1) Product.	1.55	1.0	79	73	71	2.9	10.32	.052	.024
21	Normal Cadmium Salt of Octylphenol—P_2O_5 (3:1) Product.	2.6	1.0	79	69	69	2.1	10.30	.036	.033
22	Complex Cadmium Acetate Salt of Octylphenol—P_2O_5 (3:1) Product.	1.6	1.0	81	79	73	2.5	11.05	.145	.128
23	Normal Magnesium Salt of Octylphenol—P_2O_5 (3:1) Product.	3.0	1.0	79	70	68	2.3	10.88	.239	.108
24	Complex Magnesium Acetate Salt of Octylphenol—P_2O_5 (3:1) Product.	2.5	1.0	83	79	74	2.7	11.67	.273	.232
25	Normal Cobaltous Salt of Octylphenol—P_2O_5 (3:1) Product.	2.6	1.0	76	69	68			.022	.018
26	Complex Cobaltous Acetate Salt of Octylphenol—P_2O_5 (3:1) Product.	2.4	1.0	86	83	80	3.0	11.04	.036	.036
27	Complex Zinc Caproate Salt of Octylphenol—P_2O_5 (3:1) Product.	1.6	1.0	82	75	71	3.4	12.50	.209	.112
29	Complex Calcium Acetate Salt of C_{14} Alkylphenol—P_2O_5 (3:1) Product.	2.6	1.0	88	86	83	2.9	11.22	.469	.302

[1] S. A. E. 20 Grade Solvent-Refined Penna. Oil:
K. V. @ 100° F. 66.99
K. V. @ 210° F. 8.69
N. N ..... Nil

TABLE II

Example No.	Product	CFR Comet Diesel D-21 Test (High Sulfur Fuel—SAE 30 Base Oil) [1] Percent Additive	Percent Additive, Oil-Free Basis	Cleanliness Rating @ 60 Hours
		None		44
6	Normal Zinc Salt of Octylphenol-P_2O_5 (3:1) Product	18.2	6.5	78
7	Complex Zinc Acetate Salt of Octylphenol-P_2O_5 (3:1) Product.	8.5	3.6	95
10	Normal Zinc Salt of Di-Secondary Amylphenol-P_2O_5 (3:1) Product (made with zinc acetate).	11.0	4.0	87
11	Complex Zinc Acetate Salt of Di-Secondary Amylphenol-P_2O_5 (3:1) Product.	11.0	4.0	92

[1] S. A. E. 30 Grade Acid-Refined Coastal Oil:
K. V. @ 100° F. 132.7
K. V. @ 210° F. 9.82
N. N 0.1

The amount of the complex metal salt to be incorporated into the lubricating oil generally will be within the range of from about 0.1 to about 10 weight percent, the usual amount being from about 0.5 to about 5 weight percent, i. e., on an oil-free basis.

As indicated hereinbefore, the products of the invention may be made up in the form of oil "concentrates." These concentrates will contain, as a rule, amounts of additives ranging from upwards of about 10 weight percent of the complex metal salt to the highest soluble concentration of the salt in oil.

The compounds of this invention may be used in lubricating oil compositions containing other additives designed to improve the oil in different respects, e. g., E. P. agents, pour point depressants. V. I. improvers, defoamants, etc. The additives of the invention may also be used in oil in combination with other antioxidants and/or detergents.

While the preparation and utility of certain specific representative compounds have been described in detail herein, it is not intended that the invention be limited in any way thereby, but include such variations in procedures and such products as come within the spirit and scope of the accompanying claims.

TABLE III

Example No.	Product	Theoretical Percent Metal For Normal Salt	Actual Percent Metal	Percent Metal Equivalents in Excess of Theory	Percent Phosphorus	
					Theory	Actual
4	Complex Zinc Acetate Salt of Wax-Phenol (3-14)-P_2O_5 (3:1) Product.	Zn—1.10	Zn—2.64	140	0.83	0.75
7	Complex Zinc Acetate Salt of Octylphenol-P_2O_5 (3:1) Product.	Zn—3.84	Zn—8.35	118	2.24	2.73
15	Complex Zinc Acetate Salt of Di-Sec-amylphenol-P_2O_5 (3:1) Product.	Zn—3.09	Zn—6.44	108	2.60	2.45
18	Complex Zinc Acetate Salt of Nonyl Alcohol-P_2O_5 (3:1) Product.	Zn—5.56	Zn—10.60	91	2.84	3.16
20	Complex Zinc Acetate Salt of Di-Tert-amylphenol-P_2O_5 (3:1) Product.	Zn—5.75	Zn—10.7	86	3.50	3.71
22	Complex Cadmium Acetate Salt of Octylphenol-P_2O_5 (3:1) Product.	Cd—9.65	Cd—16.4	70	3.01	3.32
24	Complex Magnesium Acetate Salt of Octylphenol-P_2O_5 (3:1) Product.	Mg—1.52	Mg—2.95	94	2.60	2.76
26	Complex Cobalt Acetate Salt of Octylphenol-P_2O_5 (3:1) Product.	Co—3.54	Co—6.74	90	2.30	2.46
27	Complex Zinc Caproate Salt of Octylphenol-P_2O_5 (3:1) Product.	Zn—5.75	Zn—9.64	64	3.00	3.13
29	Complex Calcium Acetate Salt of C_{14} Alkylphenol-P_2O_5 (3:1) Product.	Ca—1.50	Ca—2.57	71	1.50	1.60

What is claimed is:

1. A mineral lubricating oil containing a minor proportion, sufficient to improve the detergent character of said oil, of a complex metal salt of a partial ester of phosphoric acid having a metal content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of an organic hydroxy-aromatic compound that has an alkyl substituent having at least 8 carbon atoms in place of a nuclear hydrogen atom thereof and a primary, aliphatic alcohol having at least 8 carbon atoms per molecule, to form an acidic, partial ester of phosphoric acid, and (2) reacting said acidic, partial ester of phosphoric acid with a metal salt reagent, the metal constituent of which is selected from the group consisting of zinc, cadmium, magnesium, cobalt, barium, calcium and strontium, in an amount sufficient to furnish at least about two equivalents of metal per equivalent of acid-hydrogen content in said acidic, partial ester of phosphoric acid, and in which at least about one of said equivalents of metal is furnished by a metal carboxylate selected from the group consisting of metal acetates and metal caproates.

2. A mineral lubricating oil containing a minor proportion, sufficient to improve the detergent character of said oil, of a complex salt of a partial ester of phosphoric acid having a metal content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of a hydroxyaromatic compound having an alkyl substituent of at least 8 carbon atoms in place of a nuclear hydrogen atom thereof, to form an acidic partial ester of phosphoric acid, (2) reacting said partial ester with an amount of a zinc salt reagent sufficient to provide at least about one equivalent of zinc per equivalent of acid-hydrogen content in said partial ester, and (3) reacting the product obtained in step 2 with zinc acetate in an amount sufficient to provide at least one equivalent of zinc per equivalent of acid-hydrogen in said partial ester.

3. A mineral lubricating oil containing a minor proportion, sufficient to improve the detergent character of said oil, of a complex zinc salt of a partial ester of phosphoric acid having a zinc content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with about three mols of octylphenol, to form an acidic partial ester of phosphoric acid, (2) reacting said partial ester with an amount of zinc carbonate sufficient to provide at least about one equivalent of zinc per equivalent of acid-hydrogen content in said partial ester, and (3) reacting the product obtained in step 2 with zinc acetate in an amount sufficient to provide at least about one equivalent of zinc per equivalent of acid-hydrogen in said partial ester.

4. A mineral lubricating oil containing a minor proportion, sufficient to improve the detergent character of said oil, of a complex metal salt of a partial ester of phosphoric acid having a metal content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of a hydroxy compound selected from the group consisting of a hydroxyaromatic compound having an alkyl substituent of at least 8 carbon atoms in place of a nuclear hydrogen atom thereof and a primary, aliphatic alcohol having at least 8 carbon atoms, to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with a metal carboxylate selected from the group consisting of metal acetates and metal caproates, and in which the metal constituent is selected from the group consisting of zinc, cadmium, magnesium, cobalt, barium, calcium and strontium, in an amount sufficient to provide at least about two equivalents of metal per equivalent of acid-hydrogen in said partial ester.

5. A mineral lubricating oil containing a minor proportion, sufficient to improve the detergent character of said oil, of a complex zinc salt of a partial ester of phosphoric acid having a zinc content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of a hydroxy compound selected from the group consisting of a hydroxyaromatic compound having an alkyl substituent of at least 8 carbon atoms in place of a nuclear hydrogen atom thereof and a primary, aliphatic alcohol having at least 8 carbon atoms, to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with an amount of zinc acetate to provide at least about two equivalents of zinc per equivalent of acid-hydrogen content in said partial ester.

6. A mineral lubricating oil containing a minor proportion, sufficient to improve the detergent character of said oil, of a complex zinc salt of a partial ester of phosphoric acid having a zinc content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with about three mols of octylphenol to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with an amount of zinc acetate to provide at least about two

equivalents of zinc per equivalent of acid-hydrogen content in said partial ester.

7. A mineral lubricating oil containing a minor proportion, sufficient to improve the detergent character of said oil, of a complex zinc salt of a partial ester of phosphoric acid having a zinc content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with about three mols of nonyl alcohol to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with an amount of zinc acetate to provide at least about two equivalents of zinc per equivalent of acid-hydrogen content in said partial ester.

8. A mineral lubricating oil containing a minor proportion, sufficient to improve the detergent character of said oil, of a complex zinc salt of a partial ester of phosphoric acid having a zinc content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with about three mols of di-secondary amylphenol to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with an amount of zinc acetate to provide at least about two equivalents of zinc per equivalent of acid-hydrogen content in said partial ester.

9. A mineral lubricating oil containing a minor proportion, sufficient to improve the detergent character of said oil, of a complex cobalt salt of a partial ester of phosphoric acid having a cobalt content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of a hydroxy compound selected from the group consisting of a hydroxyaromatic compound having an alkyl substituent of at least 8 carbon atoms in place of a nuclear hydrogen atom thereof and a primary, aliphatic alcohol having at least 8 carbon atoms, to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with an amount of cobalt acetate to provide at least about two equivalents of cobalt per equivalent of acid-hydrogen content in said partial ester.

10. A mineral lubricating oil containing a minor proportion, sufficient to improve the detergent character of said oil, a complex cobalt salt of a partial ester of phosphoric acid having a cobalt content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with about three mols of octylphenol to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with an amount of cobalt acetate to provide at least about two equivalents of cobalt per equivalent of acid-hydrogen content in said partial ester.

11. As a new composition of matter, a complex metal salt of a partial ester of phosphoric acid having a metal content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of an organic hydroxy compound selected from the group consisting of a hydroxyaromatic compound that has an alkyl substituent having at least 8 carbon atoms in place of a nuclear hydrogen atom thereof and a primary, aliphatic alcohol having at least 8 carbon atoms per molecule, to form an acidic, partial ester of phosphoric acid, and (2) reacting said acidic, partial ester of phosphoric acid with a metal salt reagent, the metal constituent of which is selected from the group consisting of zinc, cadmium, magnesium, cobalt, barium, calcium and strontium, in an amount sufficient to furnish at least about two equivalents of metal per equivalent of acid-hydrogen content in said acidic, partial ester of phosphoric acid, and in which at least about one of said equivalents of metal is furnished by a metal carboxylate selected from the group consisting of metal acetates and metal caproates.

12. As a new composition of matter, a complex salt of a partial ester of phosphoric acid having a metal content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of a hydroxyaromatic compound having an alkyl substituent of at least 8 carbon atoms in place of a nuclear hydrogen atom thereof, to form an acidic partial ester of phosphoric acid, (2) reacting said partial ester with an amount of a zinc salt reagent sufficient to provide at least about one equivalent of zinc per equivalent of acid-hydrogen content in said partial ester, and (3) reacting the product obtained in step 2 with zinc acetate in an amount sufficient to provide at least one equivalent of zinc per equivalent of acid-hydrogen in said partial ester.

13. As a new composition of matter, a complex zinc salt of a partial ester of phosphoric acid having a zinc content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with about three mols of octylphenol, to form an acidic partial ester of phosphoric acid, (2) reacting said partial ester with an amount of zinc carbonate sufficient to provide at least about one equivalent of zinc per equivalent of acid-hydrogen content in said partial ester, and (3) reacting the product obtained in step 2 with zinc acetate in an amount sufficient to provide at least about one equivalent of zinc per equivalent of acid-hydrogen in said partial ester.

14. As a new composition of matter, a complex metal salt of a partial ester of phosphoric acid having a metal content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of a hydroxy compound selected from the group consisting of a hydroxyaromatic compound having an alkyl substituent of at least 8 carbon atoms in place of a nuclear hydrogen atom thereof and a primary, aliphatic alcohol having at least 8 carbon atoms, to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with a metal carboxylate selected from the group consisting of metal acetates and metal caproates, and in which the metal constituent is selected from the group consisting of zinc, cadmium, magnesium, cobalt, barium, calcium and strontium, in an amount sufficient to provide at least about two equivalents of metal per equivalent of acid-hydrogen in said partial ester.

15. As a new composition of matter, a complex zinc salt of a partial ester of phosphoric acid having a zinc content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of a hydroxy compound selected from the group consisting of a hydroxyaromatic compound having an alkyl substituent of at least 8 carbon atoms in place of a nuclear hydrogen atom thereof and a primary, aliphatic alcohol having at least 8 carbon atoms, to form an acidic, partial ester of phosphoric acid and (2) reacting said partial ester with an amount of zinc acetate to provide at least about two equivalents of zinc per equivalent of acid-hydrogen content in said partial ester.

16. As a new composition of matter, a complex zinc salt of a partial ester of phosphoric acid having a zinc content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with about three mols of octylphenol to form an acidic, partial ester of phosphoric acid, and (2) re-

acting said partial ester with an amount of zinc acetate to provide at least about two equivalents of zinc per equivalent of acid-hydrogen content in said partial ester.

17. As a new composition of matter, a complex zinc salt of a partial ester of phosphoric acid having a zinc content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with about three mols of nonyl alcohol to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with an amount of zinc acetate to provide at least about two equivalents of zinc per equivalent of acid-hydrogen content in said partial ester.

18. As a new composition of matter, a complex zinc salt of a partial ester of phosphoric acid having a zinc content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with about three mols of di-secondary amylphenol to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with an amount of zinc acetate to provide at least about two equivalents of zinc per equivalent of acid-hydrogen content in said partial ester.

19. As a new composition of matter, a complex cobalt salt of a partial ester of phosphoric acid having a cobalt content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with from about one to about three mols of a hydroxy compound selected from the group consisting of a hydroxyaromatic compound having an alkyl substituent of at least 8 carbon atoms in place of a nuclear hydrogen atom thereof and a primary, aliphatic alcohol having at least 8 carbon atoms, to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with an amount of cobalt acetate to provide at least about two equivalents of cobalt per equivalent of acid-hydrogen content in said partial ester.

20. As a new composition of matter, a complex cobalt salt of a partial ester of phosphoric acid having a cobalt content greater than that which would be equivalent to the acid-hydrogen content of said partial ester, prepared by the steps of (1) reacting one mol of phosphorus pentoxide with about three mols of octylphenol to form an acidic, partial ester of phosphoric acid, and (2) reacting said partial ester with an amount of cobalt acetate to provide at least about two equivalents of cobalt per equivalent of acid-hydrogen content in said partial ester.

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