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## LUBRICATING OIL CONTAINING ZINC CARBOXYLATE-COORDINATED ZINC DITHIOPHOSPHATES

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The invention relates to improved lubricating oil compositions. More specifically, it relates to lubricating oil compositions which are substantially non-corrosive to silver.

As is well known, in certain types of diesel engines, such as those used by railroads, silver bushings are used as the bearing surfaces with steel wrist pins. As is also known, a serious problem encountered in the lubrication of these engines is that of inhibiting corrosion of the silver bearing surfaces. Thus, well-known commercial antioxidants and bearing corrosion inhibitors, although highly satisfactory for use in lubricating oils for other types of engines, are not suitable for use in oils designed for the lubrication of engines containing silver bearings. For example, zinc salts of dithiophosphoric acids are widely used as antioxidants and bearing corrosion inhibitors in engine oils. However, experience has shown that when oils containing these salts are used in engines containing silver bearings, such as railroad diesels, rather than inhibiting corrosion, they actually attack and corrode the silver bearing surfaces. A means of overcoming this deficiency in these otherwise highly useful additives has been extensively sought by the art. The present invention provides such a means.

In accordance with the present invention, it has now been found that the corrosiveness towards silver of certain zinc dithiophosphate salts can be overcome by reacting these salts with zinc carboxylates. More specifically, it has been found that two types of zinc dithiophosphate salts, viz., (1) normal zinc bis(aryl)dithiophosphates and (2) normal zinc bis(alkyl)dithiophosphates prepared from so-called neo- or hindered-type alcohols, i.e., alcohols in which the carbon atom adjacent to the carbon atom attached to the hydroxyl group is completely substituted with alkyl groups, when reacted with zinc carboxylate salts, as hereinafter described, are made non-corrosive to silver. Conversely, it has been found that zinc bis(alkyl)dithiophosphates, other than those derived from neo-type alcohols, are not made non-corrosive to silver by reaction thereof with zinc carboxylates. Although the manner in which the zinc dithiophosphate and zinc carboxylate salts are combined in the reaction of the invention is not known with certainty, it is theorized, without wishing to limit the invention in any way, that they are joined by coordinate bonds similar to those existing in complexes of the Werner-type. For convenience, therefore, the product salts are referred to herein as zinc carboxylate-coordinated zinc dithiophosphate salts.

As far as is known, the zinc carboxylate-coordinated zinc dithiophosphate salts contemplated by the invention have not been known heretofore and they are, therefore, believed to be new compositions of matter. Accordingly, it is the primary object of the invention to provide a new class of zinc dithiophosphate salts which are non-corrosive to silver, viz., zinc carboxylate-coordinated zinc dithiophosphate salts. A further object is to provide lubricating oil compositions containing these new coordinated salts. Other and further objects of the invention will be apparent from the following detailed description.

Broadly, in accordance with the invention, the zinc carboxylate-coordinated zinc dithiophosphate salts are produced by (1) forming a reaction mixture of (A) one mol

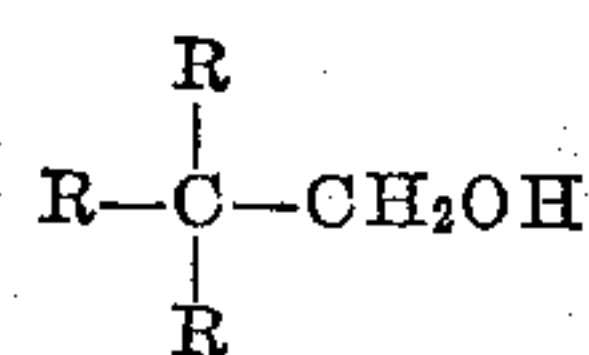
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proportion of zinc dithiophosphate, (B) at least one mol proportion of zinc carboxylate, (C) water and (D) a hydrocarbon solvent and (2) heating the mixture to a temperature sufficient to distill off the water, whereby a solvent solution of the zinc carboxylate-coordinated zinc dithiophosphate salt, containing approximately one mol proportion of each of the reactant salts, is produced. The product mixture is then filtered to remove any unreacted salt. Preferably, a light hydrocarbon solvent, such as xylene, toluene or a petroleum naphtha, is used and the water distilled off as an azeotropic mixture with the solvent. After the water has been completely removed, a lubricating oil may be added to the solvent mixture and the remainder of the solvent distilled off (or the solvent can be removed before the oil is added) whereby a lubricating oil concentrate of the product salt, suitable for blending with the base lubricating oil, is obtained.

The normal zinc bis(aryl)dithiophosphates to which the invention is applicable are those containing aryl radicals, such as phenyl, naphthyl or the like, which radicals may have one or more (up to 5) alkyl groups of from one up to about 20 carbon atoms substituted thereon. Thus, normal zinc salts, such as the following, are contemplated by the invention:

- Zinc bis(phenyl)dithiophosphate
- Zinc bis(naphthyl)dithiophosphate
- Zinc bis(tolyl)dithiophosphate
- Zinc bis(t-amyphenyl)dithiophosphate
- Zinc bis(didodecylphenyl)dithiophosphate
- Zinc bis(waxphenyl)dithiophosphate

As afore-indicated, the normal zinc salts of bis(alkyl)dithiophosphoric acids which are improved by the invention are those derived from aliphatic alcohols having a neo or hindered carbon atom adjacent to the carbon atom bearing the hydroxyl group. These alcohols conform to the structure



where R is alkyl. These alcohols and consequently the alkyl groups derived therefrom may contain from 5 up to about 20 carbon atoms. Examples of suitable zinc dithiophosphate salts of this type are the following:

- Zinc bis(2,2-dimethyl-1-propyl)dithiophosphate
- Zinc bis(2,2,4-trimethyl-1-pentyl)dithiophosphate
- Zinc bis(2,2-dimethyl-1-decyl)dithiophosphate
- Zinc bis(2,2,4-trimethyl-1-hexadecyl)dithiophosphate

The zinc carboxylates with which the zinc dithiophosphate salts may be coordinated in accordance with the invention may be either aliphatic or aromatic in nature. The aliphatic zinc carboxylates may be of the straight chained, branch-chained or cyclic type and may contain from 1 to about 20 carbon atoms. Examples of these salts are zinc acetate, zinc formate, zinc butyrate, zinc decanoate, zinc stearate, zinc oleate, zinc linoleate and the like. Also, zinc naphthenate salts, derived from petroleum oil naphthenic acids, are also highly suitable. The aromatic carboxylate salts include, for example, zinc benzoate, zinc salicylate and such salts which also have one or more alkyl groups having from 1 to 20 carbon atoms each substituted on the aromatic ring thereof.

The invention will be more fully understood by reference to the following examples and test results illustrating typical preparations of the coordinated zinc dithiophosphate-zinc carboxylate salts and their effectiveness in reducing silver corrosion as compared to the normal zinc dithiophosphate salts.



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## EXAMPLE 1

*Preparation of Normal Zinc Salt of Bis(Nonylphenyl)-Dithiophosphoric Acid*

Into a dry 5-liter, 4-necked flask, equipped with a stirrer, thermometer, broad tube for introducing phosphorus pentasulfide and a distilling receiver hooked to a reflux condenser protected by a calcium chloride tube, there was charged 792 grams (3.6 mols) of nonylphenol, 161.1 grams (1.98 mols) of zinc oxide (i.e., 120% excess in order to insure complete conversion of dithiophosphoric acid to normal salt) and 1500 cc. of xylene. The mixture was dehydrated by refluxing for one and one-half hours. The temperature was then lowered to 130–135° C. and 199.8 grams (0.9 mol) of phosphorus pentasulfide added, portionwise, over a period of one and one-half hours while maintaining the temperature at 130–135° C. The mixture was then heated to reflux and refluxed for one hour (144–145° C.). The mixture was then cooled to approximately 90° C. and 150 cc. of distilled water added over a period of about one-half hour. The temperature was held at 88–93° C. for two hours to form the normal zinc salt of bis(nonylphenyl)dithiophosphate. The mixture was then heated to reflux to azeotrope the water. The product was then cooled to about 100° C. and filtered through "Super-Cel" (a diatomaceous earth filter aid). The xylene was then removed at reduced pressure using a water-bath as a source of heat. The reaction mixture was then diluted with approximately 25%, by weight, of mineral oil (100 S.U.S. @ 100° F.), warmed on a water-bath and filtered through a bed of "Super-Cel." The product oil solution analyzed as follows: zinc=5.0%, sulfur=7.3% and phosphorus=3.9%.

## EXAMPLE 2

*Preparation of Zinc Acetate Coordinated-Zinc Bis(Nonylphenyl)Dithiophosphate*

Into a 5-liter, 4-necked flask equipped with a stirrer, thermometer and distilling receiver connected to a reflux condenser protected by a calcium chloride tube, there was charged 792 grams (3.6 mols) of nonylphenol, 161.1 grams (1.98 mols) of zinc oxide and 1500 cc. of xylene. The mixture was refluxed to dehydrate the apparatus and its contents. The temperature was reduced to 130° C. and 199.8 grams (0.9 mol) of  $P_2S_5$  was added over a period of one and one-quarter hours keeping the temperature at 130–135° C. The temperature was raised to reflux and the mixture refluxed for one hour (144–147° C.). The temperature was reduced to approximately 90° C. and 150 cc. of distilled water was added from the dropping funnel over a period of about 15 minutes. The temperature was maintained at 90–95° C. for two hours in order to form the normal zinc salt of bis(nonylphenyl)-dithiophosphoric acid.

197.6 grams (0.9 mol) of  $Zn(C_2H_3O_2)_2 \cdot 2H_2O$  dissolved in 350 cc. of hot distilled water was next added to the reaction mixture. The temperature was then raised to azeotrope the water, the final temperature being about 146° C. A total of 525 cc. of water was azeotroped. The product was then filtered through a bed of "Super-Cel."

An amount of paraffinic mineral oil (100 S.U.S. @ 100° F.) was then added to provide a xylene-free salt product containing about 25%, by weight, of oil. The xylene was removed at reduced pressure using a water-bath as a source of heat. The product analyzed as follows: zinc=8.85%, sulfur=5.73% and phosphorus=3.24%.

## EXAMPLE 3

*Preparation of Zinc Bis(2,2,4-Trimethyl-1-Pentyl)Dithiophosphate*

Into a 2-liter, 4-necked flask equipped with a stirrer, thermometer, reflux condenser protected by a calcium chloride tube and a broad, closeable tube for periodically introducing  $P_2S_5$  was weighed 676 grams (5.2 mols) of

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2,2,4-trimethyl-1-pentanol. The  $P_2S_5$ , 288.6 grams (1.3 mols), was added over a 38-minute period at a reaction temperature of 68–78° C. The mixture was then stirred and heated for four hours at a temperature of 89–93° C. The whole was then filtered into a dropping funnel to remove unreacted  $P_2S_5$ .

In another 2-liter, 4-necked flask, equipped with a stirrer, thermometer, reflux condenser and the above-mentioned dropping funnel protected by a calcium chloride tube, were placed in turn 158.8 grams (1.95 mols) of zinc oxide and 465 cc. of distilled water. The dithiophosphoric acid was added from the dropping funnel over a period of two and three-quarter hours at a reaction temperature of 60–67° C. During this period 150 cc. of benzene was added to thin the mixture. The mixture was then held at this temperature for one and one-half hours. The temperature was then raised to a maximum of 110° C. to azeotrope the water, 200 cc. more of benzene being added to reduce the reflux temperature. The mixture was then filtered through "Super-Cel." The benzene was removed at reduced pressure using a boiling water-bath as a source of heat. The product was a pale, viscous liquid. It analyzed as follows: zinc=8.9%, sulfur=15.7% and phosphorus=7.7%.

## EXAMPLE 4

*Preparation of Zinc Acetate-Coordinated Salt of Example 3*

Into a 2-liter, 4-necked flask equipped with a stirrer, thermometer, a distilling receiver hooked to a reflux condenser and a dropping funnel protected by a calcium chloride tube, were placed in turn 102 grams (1.26 mols) of zinc oxide and 300 cc. of distilled water. To the stirred mixture was added 593 grams (1.68 mols) of the dithiophosphoric acid prepared as described in the first part of Example 3. The acid was added in about two hours at a reaction temperature of 60–67° C. During the acid addition 100 cc. of benzene was added to thin the mixture. The mixture was stirred for an additional one and one-half hours at 62–63° C. 184 grams (0.84 mol) of zinc acetate dihydrate dissolved in 326 cc. of hot distilled water was then added. The temperature was then raised to azeotrope the water, 129 cc. of benzene being added to reduce the temperature during azeotroping (84–106° C.). The whole was then filtered through "Super-Cel." The benzene was then removed at reduced pressure using a boiling water-bath as a source of heat. The product was a pale, viscous liquid. It analyzed as follows: zinc=15.1%, sulfur=12.7% and phosphorus=6.6%.

## EXAMPLE 5

This was a commercial additive-normal zinc bis(4-methyl-2-pentyl)dithiophosphate containing 15%, by weight, of dilution oil. It showed the following analysis: zinc=9.5%, sulfur=17.4% and phosphorus=8.6%.

## EXAMPLE 6

*Preparation of Zinc Acetate-Coordinated Salt of Example 5*

Into a 2-liter, 4-necked flask, equipped with a stirrer, thermometer and a distillate receiver hooked to a reflux condenser was weighed 180 grams of the additive of Example 5 [equivalent to 164.8 grams (0.25 mol) of zinc bis(4-methyl-2-pentyl)dithiophosphate on an oil-free basis]. This material was diluted with 400 cc. of toluene 65.9 grams (0.30 mol) of zinc acetate dihydrate, dissolved in 227 cc. of warm distilled water, was then added. The mixture was stirred and heated to azeotrope the water. The maximum azeotroping temperature was 116° C. The product was then filtered through a bed of "Super-Cel." The product was then removed at reduced pressure using a boiling water-bath as a source of heat. The product was a fairly fluid, dark amber-colored liquid. It has the following analysis: zinc=12.8%, sulfur=16.6% and phosphorus=7.6%.



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## EXAMPLE 7

*Preparation of Zinc Acetate-Coordinated Salt of Zinc Bis(n-Octyl)Dithiophosphate*

Into a dry 500 cc. 4-necked flask equipped with a thermometer, stirrer, reflux condenser protected by a calcium chloride tube and a broad, closeable tube for introducing  $P_2S_5$  was weighed 78.0 grams (0.6 mol) of n-octyl alcohol. The  $P_2S_5$ , 33.3 grams (0.15 mol) was then added in small increments to the alcohol held at 60–70° C. The temperature was then raised to 90° C. and held there for four hours. The product was then filtered into a dry dropping funnel.

Into a one-liter, 4-necked flask equipped with a stirrer, thermometer, dropping funnel containing the above-prepared dithiophosphoric acid and a distilling receiver hooked to a reflux condenser was weighed 18.3 grams (0.225 mol) of zinc oxide. 54 cc. of water was then added. The acid was added slowly to the stirred slurry of zinc oxide and water and the whole heated to 60–65° C. The thick mixture was thinned with 250 cc. of benzene. The temperature was then raised to 75° C. and held there for two hours. Zinc acetate dihydrate, 36.3 grams (0.16 mol), dissolved in 100 cc. of distilled water, was then added. The mixture was then refluxed to azeotrope the water. The product was then filtered through "Super-Cel." The benzene was then removed at reduced pressure using a water-bath as a source of heat. The product was a fairly fluid, colorless liquid. It analyzed as follows: zinc=15.4%, sulfur=11.7% and phosphorus=6.3%.

## EXAMPLE 8

*Preparation of Zinc Naphthenate-Coordinated Salt of Zinc Bis(Mixed Phenol)Dithiophosphate*

Into a one-liter, 4-necked flask, equipped with a stirrer, thermometer and a distilling receiver hooked to a reflux condenser protected by a calcium chloride tube and a broad closeable tube for introducing  $P_2S_5$ , there was placed in turn 63.7 grams (0.6 mol) of a mixture of 40%, by weight, of phenol, 56%, by weight, of cresols and 4%, by weight, of xlenols, 250 milliliters of xylene and 40.5 grams (0.5 mol) of zinc oxide. The mixture was stirred and refluxed at approximately 144° C. to remove all water from the system. The temperature was reduced to approximately 130° C. and 34.3 grams (0.15 mol) of phosphorus pentasulfide was added over a period of 50 minutes at a reaction temperature of 130–135° C. The temperature of the mixture was raised to reflux (141–142° C.) and refluxed for one hour. The temperature was then reduced to approximately 90° C. and 88.0 grams (0.225 mol) of petroleum naphthenic acid was added, followed by 50 milliliters of distilled water. The mixture was stirred and heated for two hours at 90–93° C. The temperature was then raised to azeotrope the water (144° C.). The mixture was then cooled and filtered through "Super-Cel." The filtrate was washed with 150 milliliters of fresh xylene. The xylene was removed from the filtrate at reduced pressure using a water-bath as a source of heat. The product was a very viscous dark-brown liquid. After being fluidized by the addition of 25%, by weight, of mineral oil, (100 S.U.S. @ 100° F.), it showed the following analysis: zinc=9.9%, sulfur=6.3% and phosphorus=3.3%.

## SILVER CORROSION TEST

The non-corrosiveness towards silver of the zinc carboxylate-coordinated zinc dithiophosphate salts of the invention as compared to the uncoordinated zinc dithiophosphate salts is illustrated by the following series of tests conducted on the additives of the foregoing Examples 1–8.

The test method used was that developed by the Electro-Motive Division of General Motors Corporation, designated EMD Method No. L.O. 201–47, for determining the corrosivity towards silver of a heavy duty lubricating oil. In brief, the procedure consists in heating in an

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oil bath held at 325° F.±2° F., 300 milliliters of lubricating oil contained in a 600-milliliter beaker. The oil is stirred at 300 r.p.m. When the test oil is up to temperature, a weighed section of a silver-plated wrist-pin bushing (approximate size 3" x 1" x 1/4"—lead flashing removed from surface prior to test) is suspended in the oil so that it is immersed to approximately 75% of its surface area. At the end of 72 hours the bushing section is removed from the oil, washed with carbon tetrachloride and dried. The corrosion layer is then electrolytically removed after which the bushing is washed with water and alcohol and dried by wiping with a cloth and placing it in an oven held at 105° F. for 10 minutes. After cooling in a desiccator, it is reweighed. If the weight loss is no greater than 5 milligrams, the oil is considered to have passed the test.

The lubricating oil used in the tests was a Mid-Continent solvent-refined, all paraffin distillate having an S.U.V. of 77 seconds at 210° F. In order to provide a proper comparison between the additives, the percentage of additive used in the oil in each instance was adjusted to give the same percentage of zinc bound to sulfur (excludes the zinc bound to zinc carboxylate coordinating agent) as contained in 0.44% and 0.89%, by weight, respectively, of the normal zinc bis(4-methyl-2-pentyl)dithiophosphate additive (Example 5). The test results are shown in Table I.

Table I

Additive Used	Silver Corrosion @ 325° F.	
	Wt., Percent	Silver Loss, Mg.
None		1.5
Zinc bis(nonylphenyl)dithiophosphate (Example 1)	1.04	19.8
Do	2.07	43.1
Zinc acetate-coordinated salt of Example 1 (Example 2)	0.95	0.8
Do	1.90	1.3
Zinc bis(2,2,4-trimethyl-1-pentyl)dithiophosphate (Example 3)	0.47	18.1
Do	0.94	48.1
Zinc acetate-coordinated salt of Example 3 (Example 4)	0.62	1.8
Do	1.24	2.1
Zinc bis(4-methyl-2-pentyl)dithiophosphate (Example 5)	0.44	19.1
Do	0.89	38.8
Zinc acetate-coordinated salt of Example 5 (Example 6)	0.48	25.2
Do	0.96	65.4
Zinc acetate-coordinated salt of zinc bis(n-octyl)dithiophosphate (Example 7)	0.55	9.1
Do	1.10	36.2
Zinc naphthenate-coordinated salt of zinc bis(mixed phenol)dithiophosphate (Example 8)	0.85	1.8
Do	1.69	3.6

Referring to Table I, it is seen that all three of the uncoordinated salts (Examples 1, 3 and 5) are highly corrosive to silver. It is seen, however, that whereas the zinc bis(aryl)dithiophosphates and the zinc bis(alkyl)dithiophosphates derived from hindered-type aliphatic alcohols are made non-corrosive to silver by forming the coordination salts thereof in accordance with the invention (compare Examples 1 and 3 with Examples 2 and 4, respectively; also, note Example 8), the zinc bis(alkyl)dithiophosphate derived from non-hindered type aliphatic alcohols are not made non-corrosive by the formation of the coordination salts thereof. (Compare Examples 5 and 6; also, note Example 7.)

As shown by analysis, the coordinated salts contemplated by the invention contain approximately one mol. of zinc carboxylate per mol. of zinc dithiophosphate. It has been found that if less than approximately one mol. of the zinc carboxylate is combined with the zinc dithiophosphate salt, the resulting coordinated salt will not pass the silver corrosion test. The amount of zinc carboxylate salt used in the reaction with the zinc dithiophos-



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phate salt, therefore, must be at least about one mol per mol of zinc dithiophosphate, the use of a moderate excess over this amount, say, from 10% to about 50%, being preferred in order to insure incorporation of the required one mol proportion thereof in the coordinated salt product.

Also, as brought out herein, the presence of water is essential to the coordination reaction, the minimum required amount being about 0.5 mol per mol of zinc dithiophosphate being reacted with the zinc carboxylate. The reaction is greatly facilitated, however, by the use of much larger amounts, say, from 10 to about 50 mols of water per mol of zinc dithiophosphate being reacted. Actually, the upper limit of the amount of water is not critical and the amount used is, therefore, governed largely by practical considerations.

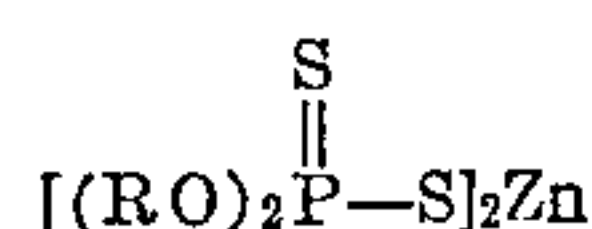
As shown in the examples presented herein, the coordinated salt products of the invention may conveniently be prepared in the form of concentrated oil solutions thereof which solutions are readily blendable with base oils desired to be improved thereby. The concentration of the product salt in these solutions will depend, of course, on the amount of diluent oil used in the process. For commercial purposes this amount can be standardized to provide a specified level of concentration. Expressed on an "oil-free" basis, however, the amount of the coordinated salt to be utilized in lubricating oil will range from about 0.01% to about 10%, by weight, the usual amount being from about 0.5% to about 5%.

The lubricating oil to which the salts of the invention are added may also contain other addition agents designed to improve the characteristics of the oil in various respects, such as detergents, pour point depressants, viscosity index improvers, extreme pressure agents, additional antioxidants, etc.

Although the present invention has been described herein by means of certain specific embodiments and illustrative examples, it is not intended that the scope thereof be limited in any way thereby but only as indicated in the following claims.

What is claimed is:

1. As a new composition of matter, a zinc carboxylate-coordinated zinc dithiophosphate salt composed of approximately one mol proportion of zinc carboxylate per mol proportion of zinc dithiophosphate, said coordinated salt being prepared by the method which comprises (1) forming a reaction mixture of one mol proportion of (A) a zinc dithiophosphate salt of the formula



where R is a hydrocarbon radical selected from the group consisting of (a) aryl radicals, (b) alkyl-substituted aryl radicals having from one to 5 alkyl radicals substituted on the aryl nucleus thereof, each of said alkyl radicals having from one up to about 20 carbon atoms and (c) alkyl radicals containing from 5 to about 20 carbon atoms in which the carbon atom adjacent to the carbon atom attached to the oxygen atom in said formula is completely substituted with alkyl groups, (B) at least one mol proportion of a zinc salt of a carboxylic acid selected from the group consisting of (a) aliphatic carboxylic acids having from one to about 20 aliphatic carbon atoms and (b) aryl carboxylic acids and (c) alkyl-substituted aryl carboxylic acids having from one up to 5 alkyl groups substituted on the aryl nucleus thereof, each of said alkyl groups containing from one to about 20 carbon atoms, (C) water and (D) a hydrocarbon solvent; (2) heating the reaction mixture to remove the water therefrom by distillation; and (3) filtering the reaction mixture to obtain a solvent solution of the zinc carboxylate-coordinated zinc dithiophosphate salt.

2. As a new composition of matter, a zinc acetate-coordinated zinc bis(nonylphenyl)dithiophosphate salt composed of approximately one mol proportion of zinc

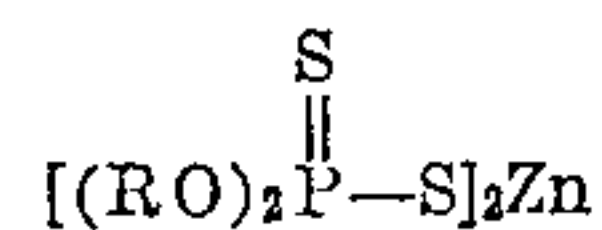
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acetate per mol proportion of zinc bis(nonylphenyl)dithiophosphate, said coordinated salt being prepared by the method which comprises (1) forming a reaction mixture of (A) one mol proportion of normal bis(nonylphenyl)dithiophosphate, (B) at least one mol proportion of zinc acetate, (C) water and (D) a hydrocarbon solvent; (2) heating the reaction mixture to distill off the water and a portion of the hydrocarbon solvent as an azeotropic mixture; (3) filtering the reaction mixture to obtain a solvent solution of the zinc acetate-coordinated zinc bis(nonylphenyl)dithiophosphate; and (4) distilling off the remainder of the solvent.

3. As a new composition of matter, a zinc acetate-coordinated zinc bis(2,2,4-trimethyl-1-pentyl)dithiophosphate salt composed of approximately one mol proportion of zinc acetate per mol proportion of zinc bis(2,2,4-trimethyl-1-pentyl)dithiophosphate, said coordinated salt being prepared by the method which comprises (1) forming a reaction mixture of (A) one mol proportion of normal bis(2,2,4-trimethyl-1-pentyl)dithiophosphate, (B) at least one mol proportion of zinc acetate, (C) water and (D) a hydrocarbon solvent; (2) heating the reaction mixture to distill off the water and a portion of the hydrocarbon solvent as an azeotropic mixture; (3) filtering the reaction mixture to obtain a solvent solution of the zinc acetate-coordinated zinc bis(2,2,4-trimethyl-1-pentyl)dithiophosphate; and (4) distilling off the remainder of the solvent.

4. As a new composition of matter, a zinc naphthenate-coordinated zinc bis(mixed phenols)dithiophosphate salt composed of approximately one mol proportion of zinc naphthenate per mol proportion of zinc bis(mixed phenols)dithiophosphate, said coordinated salt being prepared by the method which comprises (1) forming a reaction mixture of (A) one mol proportion of normal bis(mixed phenols)dithiophosphate, (B) at least one mol proportion of zinc naphthenate, (C) water and (D) a hydrocarbon solvent; (2) heating the reaction mixture to distill off the water and a portion of the hydrocarbon solvent as an azeotropic mixture; (3) filtering the reaction mixture to obtain a solvent solution of the zinc naphthenate-coordinated zinc bis(mixed phenols)dithiophosphate; and (4) distilling off the remainder of the solvent.

5. A lubricating oil containing a minor amount, from about 0.01% to about 10%, by weight, of a zinc carboxylate-coordinated zinc dithiophosphate salt composed of approximately one mol proportion of zinc carboxylate per mol proportion of zinc dithiophosphate, said coordinated salt being prepared by the method which comprises (1) forming a reaction mixture of one mol proportion of (A) a zinc dithiophosphate salt of the formula



where R is a hydrocarbon radical selected from the group consisting of (a) aryl radicals, (b) alkyl-substituted aryl radicals having from one to 5 alkyl radicals substituted on the aryl nucleus thereof, each of said alkyl radicals having from one up to about 20 carbon atoms and (c) alkyl radicals containing from 5 to about 20 carbon atoms in which the carbon atom adjacent to the carbon atom attached to the oxygen atom in said formula is completely substituted with alkyl groups, (B) at least one mol proportion of a zinc salt of a carboxylic acid selected from the group consisting of (a) aliphatic carboxylic acids having from one to about 20 aliphatic carbon atoms, (b) aryl carboxylic acids and (c) alkyl-substituted aryl carboxylic acids having from one up to 5 alkyl groups substituted on the aryl nucleus thereof, each of said alkyl groups containing from one to about 20 carbon atoms, (C) water and (D) a hydrocarbon solvent; (2) heating the reaction mixture to distill off the water and a portion of the hydrocarbon solvent as an azeotropic mixture; (3) filtering the reaction mixture to obtain a



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solvent solution of the zinc carboxylate-coordinated zinc dithiophosphate salt; and (4) distilling off the remainder of the solvent.

6. A lubricating oil containing a minor amount, from about 0.01% to about 10%, by weight, of a zinc acetate-coordinated zinc bis(nonylphenyl)dithiophosphate salt composed of approximately one mol proportion of zinc acetate per mol proportion of zinc bis(nonylphenyl)dithiophosphate, said coordinated salt being prepared by the method which comprises (1) forming a reaction mixture of (A) one mol proportion of normal bis(nonylphenyl)dithiophosphate, (B) at least one mol proportion of zinc acetate, (C) water and (D) a hydrocarbon solvent; (2) heating the reaction mixture to distill off the water and a portion of the hydrocarbon solvent as an azeotropic mixture; (3) filtering the reaction mixture to obtain a solvent solution of the zinc acetate-coordinated bis(nonylphenyl)dithiophosphate; and (4) distilling off the remainder of the solvent.

7. A lubricating oil containing a minor amount, from about 0.01% to about 10%, by weight, of a zinc acetate-coordinated zinc bis(2,2,4-trimethyl-1-pentyl)dithiophosphate salt composed of approximately one mol proportion of zinc acetate per mol proportion of zinc bis(2,2,4-trimethyl-1-pentyl)dithiophosphate, said coordinated salt being prepared by the method which comprises (1) forming a reaction mixture of (A) one mol proportion of normal bis(2,2,4-trimethyl-1-pentyl)dithiophosphate, (B) at least one mol proportion of zinc acetate, (C) water and (D) a hydrocarbon solvent; (2) heating the reaction mixture to distill off the water and a portion of the hydrocarbon solvent as an azeotropic mixture; (3) filtering the reaction mixture to obtain a solvent solution of the

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zinc acetate-coordinated zinc bis(2,2,4 - trimethyl-1-pentyl)dithiophosphate; and (4) distilling off the remainder of the solvent.

8. A lubricating oil containing a minor amount, from about 0.01% to about 10%, by weight, of a zinc naphthenate-coordinated zinc bis(mixed phenols)dithiophosphate salt composed of approximately one mol proportion of zinc naphthenate per mol proportion of zinc bis(mixed phenols)dithiophosphate, said coordinated salt being prepared by the method which comprises (1) forming a reaction mixture of (A) one mol proportion of normal bis(mixed phenols)dithiophosphate, (B) at least one mol proportion of zinc naphthenate, (C) water and (D) a hydrocarbon solvent; (2) heating the reaction mixture to distill off the water and a portion of the hydrocarbon solvent as an azeotropic mixture; (3) filtering the reaction mixture to obtain a solvent solution of the zinc naphthenate-coordinated zinc bis(mixed phenols)dithiophosphate; and (4) distilling off the remainder of the solvent.

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