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LIQUID OIL-SOLUBLE NON-CRYSTALLIZING MIXTURES OF ZINC SALTS OF DIALKYL DITHIOPHOSPHATES

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8 Claims

ABSTRACT OF THE DISCLOSURE

Liquid oil soluble non-crystallizing mixtures of basic or mixed basic and neutral zinc salts of di-C₁-C₁₃ alkyl dithiophosphates having 4-13 different alkyl groups and having an average carbon content of 3.5 to 4.5 containing at least 12% by weight of zinc for use in lubricating oil.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to novel liquid zinc salts of dialkyl dithiophosphates. More specifically, this invention relates to liquid mixtures of basic zinc salts of dialkyl dithiophosphates and liquid mixtures of basic and neutral zinc salts of dialkyl dithiophosphates.

2. Description of the Prior Art

The use of neutral metal dialkyl dithiophosphates as lubricating oil additives is well known in the art. These neutral salts in the form of, for example, zinc dialkyl dithiophosphates are known to improve various properties of lubricating oils for internal combustion engines, diesel engines and spark ignition engines. The zinc dialkyl dithiophosphates in order to be effectively utilized must be oil soluble.

A problem associated with the zinc salts of dialkyl dithiophosphates has been the difficulty of preparing oil concentrates of these salts. It is common practice to prepare and market lubricant additives in a mineral oil solution containing at least 35% active ingredient. In the case of the zinc dialkyl dithiophosphates, the lower molecular weight salts are low in cost but are insufficiently oil soluble to form concentrates in the oil. On the other hand, although the higher molecular weight zinc salts are sufficiently soluble to form oil concentrates, they are relatively expensive. Thus there has been an effort in the past to combine the low molecular weight salts with the high molecular weight salts to strike a balance between oil solubility and cost.

Mixtures of zinc dialkyl dithiophosphates have been suggested as oil soluble compositions formed by reacting mixtures of alcohols, such as in U.S. 2,680,123 and U.S. 3,151,075 and U.S. 3,190,833 with P₂S₅ to form mixed dialkyl dithiophosphoric acids, which are then converted into zinc salts. Since the ultimate aim was still to prepare oil concentrates, these salts were prepared in an inert diluent, most conveniently a mineral oil. Thus the zinc salt was formed directly in the oil, forming the concentrate.

It is an object of this invention to eliminate the necessity of forming concentrates by providing liquid mixtures of zinc dialkyl dithiophosphates which do not crystallize on standing. It is also an object of this invention to provide oil soluble liquid mixtures of zinc dialkyl dithiophosphates. Still another object of this invention is to provide an oil soluble zinc dialkyl dithiophosphate composition in liquid form possessing a high zinc content and a high degree of fluidity. It is another

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object to provide a process for preparing liquid oil soluble mixtures of zinc dialkyl dithiophosphates. Other objects will be apparent as the description proceeds.

SUMMARY OF THE INVENTION

Now it has been found that new corrosion inhibitors for lubricating oils, zinc dialkyl dithiophosphates, containing mixed lower alkyl groups, can be prepared in liquid oil soluble form having a surprising fluidity and providing more effective corrosion inhibition in lubricating oils, due to their high zinc content.

In accordance with the invention, these novel compositions of matter are oil soluble liquid compounds containing at least 12% by weight of zinc which comprise zinc salts selected from the group consisting of

- (a) mixed basic zinc salts of dialkyl dithiophosphates containing 4-13 different alkyl radicals and having an average carbon content of 3.5-4.5 carbon atoms and
- (b) mixtures of said basic zinc salts with mixed neutral zinc salts of dialkyl dithiophosphates containing 4-13 different alkyl radicals and having an average carbon content of 3.5-4.5 carbon atoms and wherein the alkyl radicals of (a) and (b) are primary or secondary radicals of 1-13 carbon atoms and wherein the concentration of said alkyl radicals are
 - (1) a maximum of 30 mole percent of each C₁-C₄ alkyl radical
 - (2) a maximum of 58 mol percent of the combined C₁-C₃ alkyl radicals
 - (3) a maximum of 70 mol percent of each C₄ alkyl radical
 - (4) a maximum of 82 mol percent of the combined C₁-C₄ alkyl radicals
 - (5) a maximum of 25 mol percent of secondary alkyl radicals

and wherein the composition of (b) as to mixed neutral zinc salts is a maximum of 75% by weight of the total mixture of (b). Thus, lubricating oil compositions can be prepared with these novel compositions of matter which permit less oxidative deterioration of said oil.

More specifically, the present invention is concerned with novel compositions of matter comprising zinc compound selected from the group consisting of (1) mixed basic zinc salts represented by the formula



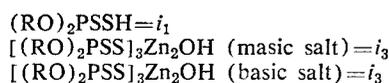
and (2) mixtures of said mixed basic zinc salts and compounds represented by the formula $[(RO)_2PSS]_2Zn$ wherein R is a mixture of 4-13 primary or secondary alkyl radicals of 1-13 carbon atoms having an average carbon content of 3.5-4.5 carbon atoms wherein the concentration of each of the C₁, C₂, C₃ alkyls does not exceed 30 mole percent (the combined concentration of said C₁-C₃ alkyls does not exceed 58 mole percent, the concentration of C₄ alkyl does not exceed 70 mole percent and the combined concentration of C₁-C₄ alkyl does not exceed 82 mole percent, the concentration of secondary alkyls does not exceed 25 mole percent and wherein compounds (1) or (2) contain at least 12% by weight zinc.

Thus according to the invention, oil soluble liquid zinc dialkyl dithiophosphate compositions are provided many of which have pour points of 0° F. or below, and higher zinc content and better viscosity properties than commercially available oil concentrates.

The liquid compositions of this invention are highly stable to crystallization on storage at ambient temperatures. Additionally, since they are prepared as liquids, they do not require the addition of a carrier solvent or oil to render them fluid.

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The zinc dialkyl dithiophosphates of this invention are prepared by reacting mixtures of alcohols with P_2S_5 to produce mixed dialkyl dithiophosphoric acids which are converted to basic or neutral salts according to known procedures. The surprising fluidity of the mixed zinc dialkyl dithiophosphates of this invention depend on the combination and distribution of the alkyl groups present. When three different alcohols are used with P_2S_5 to prepare the mixed basic zinc salt, as many as 126 different basic salts can be in the resultant mixture. In the preparation of neutral zinc salts, three alcohols can produce as many as 21 different neutral salts. As the number of different alcohols increases, the number of different salts present in the mixture rises. When 13 different alcohols are used, 380,926 different basic salts may result and 4,186 neutral salts. When mixtures of basic and neutral salts are prepared, the number of different salts which can be formed equals the number of basic salts that can be formed. The resulting zinc salts are regarded as redistribution mixtures. This may be illustrated as follows: The number of resulting isomers, represented by "i" depending on the number of alcohols, n , that result are shown below:



n	i_1	i_2	i_3
1	1	1	1
2	3	6	18
3	6	21	126
4	10	55	550
5	15	120	1,800
13	91	4,186	380,926

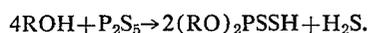
These numbers are based on the assumption that the size of the different alkyl radicals has little or no effect on the reactivity with the P_2S_5 or in the preparation of the zinc salts.

The redistribution mixtures formed are due to random intermolecular exchange of the alkyl radicals. The mixtures formed constitute all possible compounds that may be formed considering the various alcohols in the reactant and the corresponding alkyl groups of these alcohols. The composition of these mixtures depends on the initial amounts of the different alcohols.

In mixture of basic and neutral zinc salts, the amount of neutral salts may vary up to 75% by weight of the entire mixture. The range of weight ratios of mixtures of basic zinc salts to neutral zinc salts, as defined in this invention, are 100-25 weight percent of the basic to 0-75 weight percent of the neutral salts. Preferred ranges are 65-35 weight percent basic salts to 35-65 weight percent neutral salts. Most preferred is 58-62 weight percent basic to 42-38 weight percent of the neutral salts.

The mixed basic and neutral zinc dialkyl dithiophosphates may be prepared by first preparing mixtures of dialkyl dithiophosphoric acids and then treating these acids with water and zinc oxide.

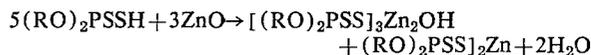
One mole of phosphorus pentasulfide is reacted with about 4 moles of a mixture of alcohols at a temperature sufficient to cause reaction, e.g., 40°-100° C., and held at this temperature until evolution of H_2S ceases. The mixture is cooled and filtered to remove any unreacted P_2S_5 . The reaction proceeds according to the equation



The mixed dialkyl dithiophosphoric acids are dissolved in a suitable solvent, such as n-heptane, benzene, or toluene. Water and then zinc oxide are added and the reaction is held at a temperature sufficient for reaction, e.g., 20°-100° C. The slurry is filtered and the filtrate is vacuum distilled to remove water and solvent to yield an oily liquid product.

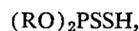
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The principle is illustrated as follows:



Mixture of basic and neutral salts in all proportions may be prepared by this procedure by varying the ratio of zinc oxide and water to the dialkyl dithiophosphoric acids. The temperature of the reaction also plays a part in the composition of the end product.

For example, at equal mole ratios of reactants,



ZnO and H_2O , a 75:25 ratio of basic to neutral zinc salts is obtained when the reaction mass is refluxed in benzene. With the same mole ratio of reactants, a 36:64 ratio of basic to neutral zinc salts is obtained in a higher boiling solvent, toluene. This is illustrated in Table II.

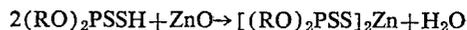
TABLE II.—EFFECT OF RATIO OF REACTANTS ON PRODUCT COMPOSITION

	Mole ratio				
	1	1	1	1	1
Reactants:					
(RO) ₂ PSSH*	1	1	1	1	1
ZnO	1	0.67	0.67	1	1
Water	2.8	2.8	1	1	1
Benzene	2.2	2.2	2.2	2.2	0
Toluene	0	0	0	0	2.2
Product composition, percent:					
Zn	12.7	12.6	12.2	13.3	12.6
P	11.3	12.1	12.4	12.4	12.5
S	22.2	22.6	22.9	22.1	22.5
[(RO) ₂ PSS] ₃ Zn ₂ OH	50	37	28	75	36

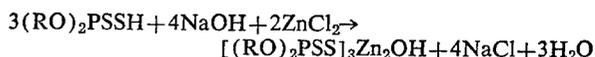
*Where R is a mixture of 12 alkyl radicals having 1 to 6 carbon atoms, the average value of R being 3.9.

Various mixtures of basic and neutral salts may also be obtained by combining mixtures of the basic salts with mixtures of the neutral salts to obtain any desired proportion.

Mixed neutral zinc dialkyl dithiophosphates may be prepared by a convenient method involving reacting the mixed dialkyl dithiophosphoric acids with zinc oxide in an organic solvent, such as toluene, xylene, n-heptane or neutral oil. The reaction is illustrated as follows



Mixed basic zinc salts are prepared by a procedure wherein the mixed dialkyl dithiophosphoric acids are dissolved in an aqueous alkali metal solution and an aqueous solution of a zinc salt such as $ZnCl_2$ is added. The layers are separated, the bottom oily layer is washed and the basic zinc salts of the mixed dialkyl dithiophosphates are recovered. The reaction proceeds as follows:



The reaction may be carried out in various ways. For example, the alcohols may be added to the P_2S_5 and optionally mixed with a hydrocarbon solvent. The alcohols and the P_2S_5 may be placed into reactor together or the P_2S_5 may be added to the alcohol mixture in the reactor.

The alcohols useful in the preparation of the mixed basic zinc salts and the mixtures of the mixed basic and mixed neutral zinc salts of dialkyl dithiophosphates of the invention are primary and secondary aliphatic alcohols having 1 to 13 carbon atoms. Representative examples of such alcohols include methanol, ethanol, propanol, isopropanol, n-butanol, isobutanol, 2-butanol, 1-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2,2-dimethylpropanol, 2-pentanol, 3-pentanol, 3-methyl-2-butanol, 1-hexa-

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nol, 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, 2-ethyl-1-butanol, 4-methyl-1-pentanol, 3-methyl-1-pentanol, n-heptanol, 2-heptanol, 3-heptanol, 4-heptanol, 1,5-dimethyl-3-pentanol, 1,1-diethyl-1-propanol, 2,5-dimethyl-2-pentanol, n-octanol, isooctanol, and isooctanol obtained from the OXO process, 1-decanol, 1-tridecyl alcohol and iso-tridecyl alcohol obtained from the OXO process.

To prepare the mixtures of the invention, it is preferred to premix the alcohols before reacting with P_2S_5 . To obtain the specific mixtures of the invention, a mixture of at least 4 and at most 13 different alcohols are used, preferably 5 to 11.

The alcohol mixture may be composed entirely of primary alcohols or mixtures of primary and secondary alcohols. In the latter case, the concentration of the secondary alcohols in the total alcohol mixture should not exceed 25 mole percent. The alcohol mixture should not contain more than 30 mole percent of each of C_1 , C_2 and C_3 alcohols, and also the combined concentration of these C_2 - C_3 alcohols should not exceed 58 mol percent. The concentration of the C_4 alcohols should not exceed 70 mole percent, and the combined concentration of C_1 - C_4 alcohols should not exceed 82 mole percent.

The mixture of the basic zinc salts and mixtures of basic and neutral zinc salts of dialkyl dithiophosphates thus obtained have an average carbon content of 3.5 to 4.5. A preferred carbon content is 3.9 to 4.2. Zinc salts having an average carbon content of less than about 3.5 tend to have less solubility in lubricating oil and may crystallize on standing, while the salts having a carbon content of more than 4.5 have a lower proportion of zinc to carbon and thus present a higher treating cost to the refiner.

The preferred oil soluble mixed basic zinc dialkyl dithiophosphates of this invention include (a) those prepared from 5 different alcohols consisting of methanol, iso-butanol and mixed primary hexanols (b) those prepared from 5 different alcohols consisting of methanol, iso-butanol and mixed oxo-tridecyl alcohols containing at least 3 isomers. The preferred oil soluble mixed neutral-basic zinc dialkyl dithiophosphates of this invention are mixed 50:50 weight percent basic and neutral zinc salts prepared from 12 different alcohols consisting of C_1 , C_2 , C_3 , C_4 , C_5 and C_6 primary alcohols.

The following examples further illustrate the invention. All references are to percent by weight unless otherwise indicated.

EXAMPLE 1

Preparation of a Mixture of Dialkyl Dithiophosphoric Acids

Into a 2-liter round bottomed, 4-necked flask equipped with agitation and a reflux condenser connected to a caustic trap, were charged 307.3 grams of mixed alcohols [consisting of 15.8 grams methanol, 39.9 grams ethanol, 49.6 grams n-propanol and 202 grams mixed primary hexanols consisting of 2-methyl-1-pentanol (21.6 wt. percent), 4-methyl-1-pentanol (17.2 wt. percent), 3-methyl-1-pentanol (22 wt. percent) and 1-hexanol (38.4 wt. percent)]. P_2S_5 (222 grams) was added slowly over a 2 hour period at 60-70° C. The temperature was raised to 95° C. and held at this temperature for 2.5 hours. The mixture was cooled to 30° C., filtered to remove unreacted P_2S_5 . There was obtained 466 grams (98% yield) of mixed dialkyl dithiophosphoric acids having a total acid number of 4.09.

EXAMPLE 2

Preparation of a Mixture of Basic Zinc Dialkyl Dithiophosphates

In a 2-liter, round bottomed, 4-necked flask, equipped with agitation and a reflux condenser, was dissolved 48

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grams NaOH in 150 grams water. 220 Grams of the dialkyl dithiophosphoric acid product obtained in Example 1 was added, keeping the temperature below 60° C. An aqueous solution containing 81.7 grams of $ZnCl_2$ in 80 grams water was added dropwise with agitation at 60° C. over a period of 15 minutes, then cooled. An oily yellow product was obtained. The top aqueous layer was separated and the bottom layer was washed twice with hot water, dissolved in n-heptane, filtered and the n-heptane removed by vacuum distillation. An oily liquid, 235.6 grams, was obtained. The neutral equivalent, as determined with perchloric acid in acetonitrile, was 927. Calculated neutral equivalent for 100% basic salt is 870, indicating a 94% yield of basic salt.

Analysis of product: 13.7% Zn, 10.8% P, and 21.0% S.

EXAMPLE 3

Preparation of a Mixture of Basic and Neutral Zinc Dialkyl Dithiophosphates

220 Grams of the dialkyl dithiophosphoric acid product obtained in Example 1 was dissolved in 120 grams heptane and 16 grams water, and charged into a 2-liter, round bottomed, 4-necked flask equipped with agitation and a reflux condenser. To this was added slowly, with agitation, 73 grams ZnO in small portions, keeping the temperature below 60° C. The reaction mass was held at 60° C. for about one hour. The slurry was filtered hot with the aid of a filtering aid, and the filtrate containing heptane and water was distilled under vacuum. The resulting product, 245.8 grams (95% yield) was an oily liquid. Analysis: 13.0% Zn, 11.3% P, 21.6% S. The neutral equivalent was 1420, determined with perchloric acid in acetonitrile. This indicated the product was a mixture of 60.6% by weight of the basic zinc salts and 39.4% by weight of the neutral zinc salts.

EXAMPLE 4

Preparation of a Mixture of Neutral Zinc Dialkyl Dithiophosphates

A 295.9 grams mixture of alcohols (16.2 grams methanol, 24.7 grams ethanol, 30.6 grams n-propanol, 37.7 grams n-butanol, 37.7 grams i-butanol, 44.8 grams mixed C_5 primary alcohols, 52.1 grams 2-methylpentanol-1 and 52.1 grams 2-ethylbutanol-1) was charged into a 2-liter, round bottomed, 4-necked flask equipped with agitator and reflux condenser. The mixture was heated to 65-70° C. and 222 grams of P_2S_5 was added over a 2-hour period. The reaction mass was refluxed at 85° C. for 2 hours, cooled and filtered. The dialkyl dithiophosphoric acid mixture, 464.3 grams, obtained had an acid normality of 4.19.

225 Grams of the above obtained dialkyl dithiophosphoric acids (0.9 mole) and 177 ml. benzene were charged into a 2-liter, round bottomed flask equipped with agitator and reflux condenser. To this mixture 36.5 grams (0.45 mole) ZnO was added slowly, keeping the temperature at about 63° C. The water was distilled into a Dean-Stark trap, the reaction mass was filtered and benzene removed by distillation. Mixed neutral zinc salts of dialkyl dithiophosphates, 249.7 grams, were obtained, containing 10.7% Zn.

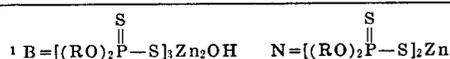
EXAMPLES 5-25

The procedure of the example indicated in Table III was followed and a summary of the results illustrating various mixed basic zinc salt and mixed basic and neutral zinc salt compositions of this invention are presented in said table.

TABLE III

Compositions and properties of liquid oil soluble zinc dialkyldithio phosphates

Ex. No.	Structure, ¹ wt. ratio	Preparative process	Av. carbon content	Mole percent						ASTM D97 pour point (° F.)	ASTM D445 Viscosity, cs.		Analysis, percent		
				Secondary alkyls	C ₁	C ₂	C ₃	C ₄	Higher alkyl ^{a b}		210° F.	100° F.	Zn	P	S
2	100B	Ex. 2	4.0	0	12	20	20	0	48-(C ₆)	-5	43.22	769	13.1	10.2	21.0
3	61B+39N	Ex. 3	4.0	0	12	20	20	0	48-(C ₆)	-20	23.9	376	13.0	11.3	21.6
4	100B	Ex. 2	4.5	25	0	0	25	25	25-(C ₃); 25-(C ₆)	-10	35.1	615	13.0	11.0	20.1
5	100B	Ex. 2	3.5	18.8	12.5	12.5	25	25	37.5-(C ₆)	0	33.4	769	13.7	11.9	21.2
6	100B	Ex. 2	4.2	0	6.3	6.3	18.8	25	18.8-(C ₃); 25-(C ₆)	-5	41.2	777	13.1	10.8	22.0
7	100B	Ex. 2	3.9	0	12.5	12.5	12.5	25	12.5-(C ₃); 25-(C ₆)	0	44.6	1,031	13.7	11.3	22.6
8	60B+40N	Ex. 3	3.9	0	12.5	12.5	12.5	25	12.5-(C ₃); 25-(C ₆)	-5	32.3	720	13.3	11.4	22.0
9	100B	Ex. 2	3.9	12.5	0	12.5	25	25	12.5-(C ₃); 25-(C ₆)	-5	43.8	995	13.7	11.3	21.5
10	50B+50N	Ex. 3	3.9	12.5	0	12.5	25	25	12.5-(C ₃); 25-(C ₆)	-10	23.9	534	12.6	11.8	22.5
11	100B	Ex. 2	3.9	0	6.3	6.3	25	31.2	18.8-(C ₃); 12.5-(C ₆)	-5	35.6	657	13.2	11.3	21.7
12	24B+76N	Ex. 3	3.9	0	6.3	6.3	25	31.2	18.8-(C ₃); 12.5-(C ₆)	-20	21.1	340	12.8	11.6	22.2
13	160B	Ex. 2	4.25	0	0	0	25	37.5	25-(C ₃); 12.5-(C ₆)	-15	36.5	621	12.9	11.0	21.7
14	100B	Ex. 2	4.0	12.5	0	12.5	25	25	25-(C ₃); 12.5-(C ₆)	-10	36.2	546	13.3	10.7	21.0
15	45B+55N	Ex. 3	4.0	12.5	0	12.5	25	25	25-(C ₃); 12.5-(C ₆)	-10	22.2	375	12.5	11.2	21.8
16	50B+50N	Ex. 3	3.9	0	12.5	12.5	12.5	25	12.5-(C ₃); 25-(C ₆)	-10	22.2	372	12.9	11.3	21.7
17	100B	Ex. 2	4.5	0	0	0	16.7	33.3	33.3-(C ₃); 16.7-(C ₆)	-30	24.23	307	12.5	10.6	20.7
18	75B+25N	Ex. 3	3.9	0	12.5	12.5	12.5	25	12.5-(C ₃); 25-(C ₆)	-5	30.34	598	13.3	12.4	22.1
19	100B	Ex. 2	4.4	0	4	0	0	60	35-(C ₆)	+5	54.9	1,275	13.1	10.2	21.0
20	100B	Ex. 2	4.0	0	10	0	0	60	15-(C ₃); 15-(C ₆)	-10	44.7	858	13.5	11.7	22.8
21	51B+49N	Ex. 3	3.9	18.8	12.5	12.5	12.5	25	12.5-(C ₃); 25-(C ₆)	0	26.3	580	13.2	11.6	22.2
22	100B	Ex. 2	4.0	0	12	0	0	70	18-(C ₆)	+40	10.3	4,813	13.9	10.8	22.0
23	100B	Ex. 2	4.3	0	20	0	0	70	10-(C ₁₃)	+30	80.0	4,235	12.6	12.4	21.4
24	100B	Ex. 2	4.5	0	0	0	0	50	50-(C ₃)	-5	55.7	1,324	13.1	11.1	21.3
25	35B+65N	Ex. 3	4.5	0	0	0	0	50	50-(C ₃)	-20	22.4	416	12.2	12.2	21.5

^a C₃ Composition, wt. percent.^b C₆ Composition, wt. percent.

EXAMPLE 26

Preparation of Mixed Basic Zinc Dialkyl Dithiophosphates

P₂S₅ (222 grams, 1.0 mole) was added to a mixture of alcohols consisting of methanol (26.4 grams, 0.8 mole), isobutanol (183.2 grams, 2.4 mole) and mixed C₆, C₇, C₈, C₉, C₁₀ and C₁₁ alkyl alcohols (110.2 grams, 0.8 mole), 10% of which are branched or secondary, in a 2-liter, round bottomed, 4-necked flask equipped with stirrer and reflux condenser, over a period of 30 minutes as the temperature rose from 40° C. to 74° C. Stirring was continued until evolution of gas ceased. The reaction mixture was cooled to ambient temperature and filtered to remove unreacted P₂S₅. There was obtained 490 grams (sp. g. 1.041) of mixed dialkyl dithiophosphoric acids having a total acid number 3.75 (94.1% yield).

73.8 Grams of sodium hydroxide added as an aqueous solution (378 ml.) was added to the mixed dialkyl dithiophosphoric acids over a period of 10 minutes at ambient temperature. To this mixture 163.9 grams of zinc chloride added as an aqueous solution (267 ml.) and 23.8 grams sodium hydroxide added as an aqueous solution (124 ml.) were added dropwise simultaneously. The resulting organic phase was separated from the aqueous phase and filtered. The light yellow, liquid organic phase obtained (396.2 grams) was the basic zinc salt of mixed C₁, C₄, C₆₋₁₁ dialkyl dithiophosphates. Elemental analysis showed: P=10.7%; C=36.6%; H=6.7%; S=21.0% and Zn=13.4%. The pour point was 20° F.

EXAMPLE 27

Mixture of Basic Zinc Salts—Physical mixture of 3 salts

A mixture of three basic zinc salts was prepared by mixing 7.42 grams basic zinc salt of dimethyldithiophosphate, 61.0 grams basic zinc salt of di-isobutyldithiophosphate and 18.7 grams basic zinc salt of di-n-hexyldithiophosphate with 300 ml. n-heptane at room temperature. The solvent was removed by vacuum distillation. The resulting mixture was an opaque liquid mass in which the basic zinc salt of dimethyldithiophosphate settled out as a solid phase.

It can be seen from No. 5 Table V, that mixed basic zinc salts prepared from methanol, iso-butanol and primary hexanols, but falling outside the limits of the invention also crystallize.

In contrast to these mixtures, Nos. 15 and 16 of Table IV, also prepared from ethanol, iso-butanol and primary hexanols, but falling within the limits of the invention, do not crystallize.

It can be seen from the above Table III that the mixtures of basic salts containing an average carbon chain length of 3.5–4.5, prepared from C₁–C₈ alkanols are liquid, have low pour points and good viscosity properties. They are high in zinc content.

Although No. 22 has a pour point higher than those of the other mixed salts, it does not influence the pour point of the oil in which it is dissolved. For instance, when 10 wt. percent of No. 22 is introduced into a formulation additive composition containing only 5% neutral oil, 120 SUS at 100° F., the pour point of the concentrate drops to 5° F. The same additive composition containing 12.9 wt. percent of a commercial concentrate containing mixed neutral salts having 10.4 wt. percent zinc has a pour point of 20° F., as shown below:

Additive composition ¹ contg.	No. 22 ^a	Commercial additive B ^{2 b}
Visc. SUS at 210° F.	797	752
Pour point, ° F.	5	20
Total base number	92.7	89.8
Percent N (calc.)	0.74	0.71
Percent Mg	1.76	1.71
Percent Zn	1.39	1.34
Percent P	1.08	1.25
Percent S	2.70	3.15

¹ Contains 68 wt. percent of a nitrogen containing ashless detergent, 27 wt. percent of an overbased (300 base No.) Mg sulfonate and 5 wt. percent of a neutral oil SUS 120 at 100° F.

² Commercial additive B from Col 7.

^a Composition contains 10 wt. percent of mixed salts No. 22.

^b Composition contains 12.9 wt. percent of an oil concentrate of commercial additive B.

A composition comparison is shown in Table IV of typical liquid mixtures of the invention with commercial concentrates of neutral zinc salts. The lower pour points and excellent viscosity data can be readily seen.

TABLE IV

Composition and properties of commercial concentrate additives and liquid mixtures of the invention

Structure.....	Commercial Additive A	Commercial Additive B	No. 4 of Table III	No. 16 of Table III
	Neutral	Neutral	Basic	Basic plus neutral (50:50)
Percent Zn.....	8.3	8.5	13.0	12.9
Percent P.....	8.7	8.5	11.0	11.3
Percent S.....	16.4	16.0	20.1	21.7
A.v. carbon content.	4.5	4.25	4.5	3.9
Mole, percent				
secondary alkyl.....	100	0	25	0
Number of alkyls.....	2	4	8	12
Pour point, ° F.....	+10	+10	-10	-10
Viscosity, cs.:				
210° F. ASTM				
D 445.....	8.6	9.7	35.1	22.2
190° F.....	170	136	615	372
V.I. ASTM D 2270.....	-88	27	97	79
Slope ASTM D 341.....	0.927	0.822	0.647	0.703

Commercial Additive A.—Mixture of neutral zinc salts of dialkyl-dithiophosphates containing isopropyl and 4-methyl-2-pentyl radicals.
Commercial Additive B.—Mixture of neutral zinc salts of dialkyl-dithiophosphates containing mixed amyl and isobutyl radicals.

Table V shows mixtures of basic and neutral salts are crystalline or crystallize on standing. The compositions show that they do not meet all the parameters specified for liquid mixtures.

TABLE V
Crystalline mixtures

Composition No.....	B=[(RO) ₂ PSS] ₂ Zn ₂ OH B					N=[(RO) ₂ PSS] ₂ Zn B+N					
	1	2	3	4	5	6	7	8	9	10, + + 11	
Ave. C content.....	3.76	4.0	4.1	4.25	4.0	4.27	5.0	4.1	4.1	4.24	4.1
No. of alkyls.....	10	5	7	4	6	5	7	7	7	4	6
Percent B.....	100	100	100	100	100	100	3	7	5	36	31
Mole percent:											
C ₁	0	0	0	0	8	17	0	0	0	0	0
C ₂	12.5	0	0	0	0	0	0	0	0	0	0
n-C ₃	37.5	33.3	10	0	0	0	50	25	10	0	0
i-C ₃	0	0	0	0	0	0	0	0	0	0	0
n-C ₄	12.5	16.7	30	37.5	0	0	12.5	25	30	37.5	0
i-C ₄	12.5	16.7	50	37.5	80	70	12.5	37.5	50	37.5	80
C ₅ ^a	12.5	33.3	0	25	0	0	0	0	0	25	0
C ₅ ^b	12.5	0	10	0	12	0	25	12.5	10	0	10
C ₁₀ ^c	0	0	0	0	0	13	0	0	0	0	0
C ₁ -C ₃	50	33.3	10	0	8	17	50	25	10	0	10
C ₄	25	33.3	80	75	80	70	25	62.5	80	75	80

^a Composition, wt. percent: 2-Me-1-butanol—39.2; n-Pentanol—60.8.

^b Composition, wt. percent: 2-Me-1-pentanol—21.6; 4-Me-1-pentanol—17.2; 3-Me-1-pentanol—22.0; 1-hexanol—38.4.

^c Composition, wt. percent, structures unknown: Isomer 1—8.9; Isomer 2—55.1; Isomer 3—35.1.

Some of these mixtures formed crystalline mass on standing overnight while others crystallized slowly over a period of several weeks.

Table VI shows that compositions of liquid mixtures of this invention meet all the specified requirements.

TABLE VI
Non-crystallizing mixtures

Composition No.....	B=[(RO) ₂ PSS] ₂ Zn ₂ OH B								N=[(RO) ₂ PSS] ₂ Zn B+N	
	12	13	14	15	16	17	18	19	20	21
Ave. C content.....	3.56	3.85	3.88	4.4	4.2	4.15	4.4	3.56	3.85	3.88
No. of alkyls.....	11	9	11	6	6	5	4	11	9	11
Percent B.....	100	100	100	100	100	100	100	34	50	24
Mole percent:										
C ₁	12.5	0	6.25	4	14	10	12	12.5	0	6.25
C ₂	20	12.5	6.25	0	0	0	0	20	12.5	6.25
n-C ₃	12.5	12.5	25	0	0	0	0	12.5	12.5	25
i-C ₃	0	12.5	0	0	0	0	0	0	12.5	0
n-C ₄	10	12.5	12.5	0	0	20	0	10	12.5	12.5
i-C ₄	10	12.5	18.75	60	55	40	45	10	12.5	18.75
n-C ₅	0	0	0	0	0	15	10	0	0	0
C ₅ ^a	25	12.5	18.75	0	0	0	0	25	12.5	18.75
2-Me-1-butanol.....	0	12.5	0	0	0	0	0	0	12.5	0
3-Me-1-butanol.....	0	12.5	0	0	0	0	0	0	12.5	0
C ₆ ^b	10	0	12.5	36	31	0	0	10	0	12.5
n-C ₆	0	0	0	0	0	15	33	0	0	0
C ₁ -C ₃	45	37.5	37.5	4	14	10	12	45	37.5	37.5
C ₄	20	25	31.25	60	55	60	45	20	25	31.25
Pour pt., ° F.....	-5	-5	-5	5	15	-10	-5	-15	-10	-20
Oil solubility.....	+	+	+	+	+	+	+	+	+	+

* Marginal solubility, i.e. determined by solubility of 1 wt. percent of the zinc salt in a neutral oil.

^a Composition, wt. percent: 2-Me-1-butanol—39.2; n-Pentanol—60.8.

^b Composition, wt. percent: 2-Me-1-pentanol—21.6; 4-Me-1-pentanol—17.2; 3-Me-pentanol—22.0; 1-hexanol—38.4.

The oxidation inhibiting properties of the compositions of the invention were demonstrated with representative mixtures in the MS Sequence IIB and IIIB tests, as specified in ASTM Special Technical Publication No. 315-D,

TABLE VII

MS sequence IIB and IIIB test

	Additive A	Additive B	Ex. No. 4 of Table III	Ex. No. 18 of Table III	Ex. No. 21 of Table III
	Base oil.....	10W40	10W40	10W40	10W40
Wt. percent zinc.....	0.10	0.10	0.10	0.10	0.08
CR ratings:					
Eng. sludge.....	9.8	9.8	9.8	9.8	9.8
Piston varnish.....	9.8	9.8	9.8	9.8	9.8
Rust.....	8.6	8.8	8.6	8.9	8.5
Scuffing: Cams/lifters.....	0/0	0/0	0/0	0/0	0/0
Cam and lifters, wear, in. X10 ⁴ , av./max.....	5/8	19/26	21/57	7/12	10/20
No. scuffed/worn/S+W:					
Valve stem tips.....	3/4/0	2/3/0	2/3/0	3/5/2	3/6/2
Rocker arm pads.....	0/5/1	0/2/0	0/2/0	0/4/1	1/5/0
Rocker arm pivots.....	1/3/1	1/1/0	1/2/1	1/4/1	0/4/2
Rumble, LIB.....	13	20	10	30	23
Cu-Pb bearing wt. loss, mg.: Av. (2 rods).....	582	1620	122	653	534

1968, "Engine Test Sequences for Evaluation of Automatic Lubricants for API Service MS (Most Severe)." A 1967 Oldsmobile, 10.25:1 CR, 425 CID engine was operated continuously for 22 hours under one phase for an additional 58 hours under another phase. These tests are

used for evaluating rusting, deposition, wear and rumble. The test method was designed to relate particularly to short trip service under typical winter conditions in the upper midwestern United States. It is used for motor oil specification acceptance. The results are shown in Table VII above compared with commercial additives A and B.

The ratings shown above for the liquid mixtures are comparable to those of the commercial additives. An additional test was conducted which demonstrates the superiority of the liquid mixtures of the invention versus oils containing the commonly used concentrates of neutral salts present in the commercial additives.

After the MS Sequence tests were run, the oil drainings were subjected to differential infra-red analysis to determine the extent of breakdown of the lubricating oils. The analyses are reported in Table VIII.

TABLE VIII
Differential infra-red analysis of oil drains

Oil	10W40	10W4C	10W40	10W4C	10W30
Wt. percent Zn	0.10	0.10	0.13	0.10	0.08
Inhibitor	Additive A	Additive B	Ex. 4 of Table III	Ex. 18 of Table III	Ex. 21 of Table III
A/cm. at 5.8 μ					
Test hours:					
0	54	48	52	51	32
22	53	49	52	51	34
24	56	54	56	54	37
52	110	124	60	86	52
80	109	116	70	81	68
A/cm. at 6.3 μ					
0	5	4	8	10	9
22	11	10	13	10	15
24	9	8	9	6	13
52	23	28	11	22	24
80	36	31	18	24	38

Table VIII shows that the lubricating oils containing the additives of the invention undergo oxidative deterioration than those containing the neutral salt commercial additives A & B. Absorption of 5.8 μ indicates the presence of carbonyl radicals. Absorption at 6.3 μ indicates presence of carboxyl radicals. The oil containing additive No. 21 shows about the same amount of carboxyl groups as the additives A and B, however, the concentration of zinc is lower and therefore demonstrates equal inhibition at a lower zinc level. With respect to the presence of carbonyl groups, the additives of the invention show greater inhibition to oxidation.

The liquid zinc salt compositions of the invention are soluble in neutral distillate oils in an amount sufficient to give at least 0.10 wt. percent zinc content in the oil. The salt compositions are contemplated for use in neutral distillate base stock lubricating oils which may also contain some bright stock. They are also useful in automatic transmission oils, which are chiefly lighter neutral oils, and in lubricating base stock for greases which contains neutral distillate oils, bright stock and thickener.

The additives of the invention may be used in conjunction with a variety of other additives commonly used in lubricating oils, such as dispersants, anti-oxidants, pour point depressants, corrosion inhibitors and the like.

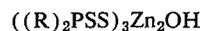
The foregoing detailed description has been given for clarity of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to exact details shown and described for obvious modifications will occur to one skilled in the art.

What is claimed is:

1. An oil soluble non-crystallizing liquid composition containing at least 12% by weight of zinc which comprises zinc salts selected from the group consisting of

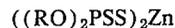
(a) mixed basic zinc salts of dialkyl dithiophosphates

containing 4 to 13 different alkyl radicals and having an average carbon content of 3.5 to 4.5 carbon atoms of the formula



and

(b) mixtures of said basic zinc salts with mixed neutral zinc salts of dialkyl dithiophosphates containing 4 to 13 different alkyl radicals and having an average carbon content of 3.5 to 4.5 carbon atoms of the formula



and wherein the alkyl radicals of (a) and (b) are primary or secondary radicals of 1-13 carbon atoms and wherein the concentration of said alkyl radicals are

- (1) a maximum of 30 mol percent of each C₁-C₃ alkyl radical
- (2) a maximum of 58 mol percent of the combined C₁-C₃ alkyl radicals
- (3) a maximum of 70 mol percent of each C₄ alkyl radical
- (4) a maximum of 82 mol percent of the combined C₁-C₄ alkyl radicals
- (5) a maximum of 25 mol percent of secondary alkyl radicals

and wherein the composition of (b) as to mixed neutral zinc salts is a maximum of 75% by weight of the total mixture of (b).

2. The composition of Claim 1 wherein the mixed salts of (a) and (b) have an average carbon content of 3.9 to 4.2 carbon atoms.

3. The composition of Claim 1 wherein the zinc salts are described by (a).

4. The composition of Claim 1 wherein the zinc salts are described by (b).

5. The composition of Claim 4 wherein (b) is composed of 35-65% by weight of mixed neutral zinc salts and 65-35% by weight of mixed basic zinc salts.

6. An oil composition comprising a major amount of lubricating oil and sufficient weight percent of the oil soluble liquid composition of Claim 1 to have a zinc content of from about 0.01 to 0.25% by weight.

7. An oil composition comprising a major amount of a lubricating oil and sufficient weight percent of the oil soluble liquid composition of Claim 3 to have a zinc content of from about 0.01 to 0.25% by weight.

8. An oil composition comprising a major amount of a lubricating oil and sufficient weight percent of the oil soluble liquid composition of Claim 5 to have a zinc content of from about 0.01 to 0.25% by weight.

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