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COMPOSITIONS CONTAINING METAL DIALKYL DITHIOPHOSPHATES ARE INHIBITED AGAINST HAZE AND PRECIPITATES BY AMINE SALTS OF MIXED ACID PHOSPHATES

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ABSTRACT OF THE DISCLOSURE

Amine salts of mixed acid phosphates are combined with metal dialkyl dithiophosphates to prevent and control haze and precipitation in compositions containing these dithiophosphate salts.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to new chemical compositions and to lubricating oils containing these compositions. More particularly, this invention relates to a novel class of chemical compositions containing dialkyl dithiophosphates which do not exhibit undesirable precipitation and haze formation.

Description of the Prior Art

Metal dialkyl dithiophosphates are metal salts of dialkyl dithiophosphoric acids and are well known additives for lubricating oil compositions. This class of metal salts is particularly useful as antiwear, corrosion inhibitor, and anti-oxidant additives for lubricating oils used in internal combustion engines.

Compositions containing metal dialkyl dithiophosphates (DDP) frequently suffer from the development of haze or precipitates when small amounts of water, such as 50–500 p.p.m., are present in these compositions. Such small amounts of water typically enter lubricating oil compositions by condensation of atmospheric moisture, see page, etc., and it is difficult to keep these compositions water-free.

The development of haze may be due to the water itself or to a product formed by a reaction of water with DDP. Heat favors the reaction of water with DDP, and the problem of haze formation caused by this reaction is particularly pressing because compositions containing DDP are often kept hot for prolonged periods, for example, during tank car transport. Precipitation can result from interaction of the water with the DDP salt.

Haze and precipitation free lubricating oil compositions are obviously more marketable than hazy compositions.

In the past, barium sulfonate has been used for water dispersion in DDP-containing compositions in an attempt to prevent haze formation. This technique only works, however, if the composition is not heated for prolonged periods. Accordingly, the use of barium sulfonate does not provide an entirely satisfactory solution, and continuing search goes on for an additive composition containing DDP which avoids haze formation and precipitation problems.

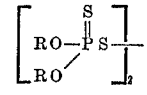
SUMMARY OF THE INVENTION

It has now been discovered that certain amine salts of acid phosphates can be added to compositions containing metal dithiophosphates to prevent precipitation and haze formation in these compositions. Such amine salts are effective in preventing haze formation even through the composition is heated to temperatures which normally promote the formation of haze and precipitates. The compositions of the present invention, therefore, can be pumped at elevated temperatures without haze formation.

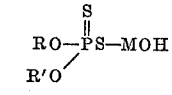
The amine salts of the present invention are also effective in correcting and clearing compositions in which haze has already developed. The haze free compositions are prepared by forming a mixture of the amine salts and DDP, and heating the mixture for about at least 6 hours or more at a temperature of about at least 140° F.

DETAILED DESCRIPTION

In accordance with the invention, the metal dialkyl dithiophosphates used in the present invention have the general formula:



wherein R and R′ are the same or different hydrocarbyl groups having from 3 to 12 carbon atoms and M is zinc, cadmium, barium, nickel or magnesium. Preferably, R and R′ are identical groups having from 3–8 carbon atoms and M is zinc. It is understood that DDP salts may also contain minor amounts of monohydroxide salts of the general formula:



where R, R′ and M are as just defined.

The metal dialkyl dithiophosphates can be obtained commercially or can be prepared by conventional methods well known in the art. For example, metal dialkyl dithiophosphate can be prepared by reacting phosphorus pentasulfide with an aliphatic alcohol, a mixture of aliphatic alcohols, or phenols containing the desired range of hydrocarbyl groups in a molar ratio of approximately 4 moles of alcohol for each mole of phosphorus pentasulfide. This forms the corresponding dialkyl dithiophosphoric acids, and these acids are neutralized with an oxide, hydroxide or carbonate of a polyvalent metal, or alternatively with a reactive polyvalent metal salt to form the metal dialkyl dithiophosphate.

The present invention employs polyvalent metal salts of dialkyl dithiophosphoric acids prepared from alcohols having from about 3 to about 12 carbon atoms. The dialkyl dithiophosphoric acids whose salts are used in this invention include those made from a simple aliphatic alcohol such as isopropyl, normal butyl, normal decyl, etc. They also include those made from mixed aliphatic alcohols including the C_5 or C_8 alcohols obtained by reaction of olefins with carbon monoxide and hydrogen, and subsequent hydrogenation of the resultant aldehydes. These alcohols are known as "Oxo" alcohols. Dithiophosphoric acids obtained from mixtures of isopropyl

alcohol and methyl isobutyl carbinol, primary amyl alcohol and isobutanol, mixed anyl alcohols and technical lauryl alcohol, mixtures of isopropyl alcohol and C_8 Oxo alcohol, and the like can also be used. Mixed acids obtained by individual reaction of selected alcohols with P_2S_5 can also be employed in the preparation of the metal salts.

The metals employed in making the salts are those of Group II of the Periodic Table including zinc, cadmium, barium and magnesium. Nickel can also be used. Zinc salts are particularly preferred.

In accordance with the present invention the metal DDP salt is mixed with an amine salt of a dihydrocarbyl acid phosphate having the general formula:

$$\left[\begin{matrix}O\\ \|\\ (R^5O)_2PO-\end{matrix}\right]_x^{+}NHR^1,\ R^2,\ R^3$$

wherein x is 1 or 2, R^5 is a C_8 to C_{13} hydrocarbyl group, R^2 and R^3 each are a hydrogen atom or C_3 to C_{12} hydrocarbyl group, and R^1 is selected from the group consisting of:

(a) C_8 to C_{18} hydrocarbyl groups or mixtures thereof,
(b) amino hydrocarbyl groups of the formula

$$\text{-}(CH_2)_n NHR^4$$

where x is 1 or $\text{-}(CH_2)_n N^+H_2R_4$ when x is 2, wherein n is 2 or 3 and R^4 is (a) above; and
(c) alkylene polyamino groups of the formula

$$\text{-}(CH_2CH_2NH)_m H$$

wherein m is an integer between 2 and 4.

Preferably, R^2 and R^3 are each hydrogen atoms or C_3 to C_4 alkyl groups, and R^1 is (b) wherein R^4 is a substantially linear C_{12} to C_{18} aliphatic group. Examples of said amine phosphates include a commercial amine phosphate consisting of an 80% solution of amine salt of mixed alkyl acid phosphates in kerosine. In this preferred amine, R^5 is the hydrocarbyl portion of a C_8 Oxo alcohol, R^2 and R^3 are H, and R^1 is

$$-CH_2CH_2CH_2\overset{+}{N}H_2C_{18}H_{37}$$

Other amine phosphate salts generally suitable for use in the present invention include compounds of the structures:

$$(C_{13}H_{27}O)_2PO_2NH_3(CH_2)_3CH_3,$$

$$(C_8H_{17}O)_2PO_2NH_2CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}H(CH_2)_3CH_3 \text{ and}$$

$$(C_8H_{17}O)_2PO_2NH_3\text{-}\left(CH_2CH_2NH\right)_4\text{-}H$$

The additives of the present invention are prepared by forming a mixture of the metal dialkyl dithiophosphate and the amine salt of the dihydrocarbyl acid phosphate and heating the mixture for about at least 6 hours at a temperature of about at least 140° F. Preferably, the mixture is heated at temperatures from about 140° F. to about 180° F. for about 6 to about 24 hours.

The additives of the present invention contain about 0.005 to 0.5 parts by weight of the amine salt per part of dithiophosphate salt. When used as additives, the composition is incorporated in lubricating oils in concentrations from about 0.5 to 50 weight percent active ingredient, preferably 1 to about 5 weight percent. The final oil compositions formed to include the additives of this invention have a dithiophosphate content of about 0.1 to 1.0% by weight, preferably about .2 to 6% by weight, and an amine salt content of 0.0005 to 0.5% by weight, preferably about .001 to 0.3% by weight. The concentration will vary with the particular metal dialkyl dithiophosphate salt used, the particular base stock employed, and the function of the additive; i.e. whether it is to be simply an anti-oxidant or whether it is also to serve as a corrosion inhibitor, wear reducing or extreme pressure agent.

The additives of this invention can be added to any conventional type lubricating oil including animal and vegetable oils as well as mineral lubricating oils and synthetic oils. The mineral lubricating oils can be of any preferred type, including those derived from the ordinary paraffinic, naphthenic, asphaltic, or mixed base mineral crude oils by suitable refining methods. Suitable synthetic oils include synthetic hydrocarbon lubricating oils, as well as dibasic acid esters such as di-2-ethyl hexyl sebacate, carbonate esters, phosphate esters, halogenated hydrocarbons, polysilicones, polyglycols, glycol esters such as C_{13} oxo acid diesters of tetraethylene glycol, and complex esters, as for example, the complex ester formed by the reaction of 1 mole of sebacic acid with 2 moles of tetraethylene glycol and 2 moles of 2-ethyl hexanoic acid.

While the lubricant compositions herein described are primarily used as internal combustion engine crankcase lubricants, they may also be employed in other oil compositions, including turbine oils, various industrial oils, gear oils, hydraulic fluids, transmission fluids and the like.

It is within the contemplation of this invention to prepare easily handled liquid additive concentrates in which the concentration of additive is greater than would normally be employed in a finished lubricant. These concentrates may contain in the range of from 10 to 75% of additive (metal DDP plus amine phosphate salt) on an active ingredient basis, the balance being a petroleum fraction such as mineral oil, kerosene, etc. Such concentrates are convenient for handling the additive in the ultimate blending operation into a finished lubricating oil composition. The additive concentrates can be made up simply by combining the metal DDP and amine phosphate salt of the present invention in a suitable mineral oil medium.

The additive package can also include effective amounts of other additives that are intended for use in a finished lubricant. These additional additives can each be present in amounts up to about 20% by weight of the finished lubricating oil composition. Such additives include, for example, detergents and dispersants of the ash-containing or ashless type, oxidation inhibiting agents, viscosity index improving agents, pour point depressants, extreme pressure agents, color stabilizers and anti-foam agents.

Suitable additives of these types are known in the art. For example, crankcase lubricating oils can contain polymers such as polyisobutylene, polymethacrylates, copolymers of alkyl fumarates with vinyl acetate and various other long chain polymers usually having molecular weight of about 5,000 to 100,000 as viscosity index improvers and pour point depressants. Oxidation inhibitors frequently used in such compositions include, for example, phenyl α-naphthylamine, and detergent additives include metal salts of alkyl phenol sulfides and complexes of various P_2S_5 treated hydrocarbons neutralized with metal bases or metal salts of other materials such as phenols, sulfonates, carbonates and the like.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples will serve to illustrate methods of preparing the compositions of this invention and include preferred embodiments of said invention.

EXAMPLE 1

An oil blend is prepared by blending the following ingredients at 140° F.; (1) 93.75 volume percent of a composition comprising 18 to 22 volume percent of polyisobutylene having a molecular weight of about 18,000 and 78 to 82 volume percent of Solvent 150 Neutral; (2) 3.00 volume percent of an oil composition consisting of 26 weight percent of a hydrocarbon lubricating oil and 74 weight percent of a zinc dialkyl dithiophosphate prepared

from a mixture of acids derived from 65% isobutyl alcohol and 35% primary amyl alcohol; (3) 3.00 volume percent of Solvent 150 Neutral (S–150–N); and (4) 0.25 volume percent of an 80 weight percent solution of an amine salt of mixed alkyl acid phosphates in kerosine. This amine salt was one wherein the alkyl phosphate group (R^5) were derived from a C_8 Oxo alcohol, R^2 and R^3 are hydrogen atoms and R^1 is

$$CH_2CH_2CH_2N^+H_2C_{18}H_{37}$$

This particular solution of amine salt was used in all the following examples.

The Solvent 150 Neutral is a diluent oil sold by Humble Oil Refining Co., Inc. and has an aniline pt. of 64° F., a minimum flash point of 151° F., and a specific gravity at 60° F. of 0.891. The weight percent of each ingredient in the oil blend is shown in Table 1.

TABLE 1

	Ingredients	Vol. percent	Specific gravity	Wt. in gms.	Wt. percent
1	Polyisobutylene in S–150–N	93.75	.8892	279.21	93.07
2	Zn dialkyl dithiophosphate in oil.	3.00	1.1265	11.31	3.77
3	S–150–N	3.00	.8681	8.70	2.90
4	Amine phosphate salt in kerosine.	0.25	.9128	.78	.26
Total		100.00		300.00	100.00

The oil blend is heated at 140° F. for 6 hours. The resulting composition is a clear, yellow liquid and has the following properties:

Specific Gravity	.8877
Density	7.392
Gravity API	27.9
Viscosity at 210° F., c./s.	523
Flash Point ° F. (Cleveland Open Cup)	390
Color ASTM	2.0
Zinc Content, wt. percent	0.35
Phosphorus Content, wt. percent	0.33
Coefficient of Thermal Expansion	0.00043
Barium Content, wt. percent	.04

This oil blend is tested for haze formation by adding 500 p.p.m. of water to it. The water and oil blend are mixed in a General Electric Mixer Model 5BA60V222 that is operated at maximum r.p.m. for two minutes at room temperature.

The mixture is stored for 3 days at 180° F., and then cooled to room temperature. The mixture retains its clear yellow color and no haze formation is observed.

EXAMPLE 2

The procedure of Example 1 is repeated except that different amounts of the ingredients are mixed together as set forth in Table 2 below:

TABLE 2

	Ingredients	Vol. percent	Specific gravity	Wt. in gms.	Wt. percent
1	Polyisobutylene in S–150–N	95.75	.8892	284.19	94.73
2	Zn dialkyl dithiophosphate in	1.00	1.1265	3.72	1.26
3	S–150–N	3.00	.8681	11.28	3.76
4	Amine phosphate salt in kerosine.	0.25	.9128	.75	.25
Total		100.00		300.00	100.0

The oil blend is heated at 140° F. for 6 hours, and the resulting composition is a clear amber liquid.

Water at a level of 500 p.p.m. is added as in Example 1. The mixture is stored for 3 days at 180° F. and then cooled at room temperature. The mixture retains its amber color and no haze formation is observed.

EXAMPLE 3

The procedure of Example 1 is repeated except that different amounts of the ingredients are mixed together as set forth in Table 3 below.

TABLE 3

	Ingredients	Vol. percent	Specific gravity	Wt. in gms.	Wt. percent
1	Polyisobutylene in S–150–N	95.50	.8892	283.41	94.47
2	Zn dialkyl dithiophosphate in oil.	1.00	1.1265	3.78	.126
3	S–150–N	3.00	.8681	11.28	3.76
4	Amine phosphate salt in kerosine.	0.50	.9128	1.53	.51
Total		100.00		300.00	100.00

The oil blend is heated at 140° F. for 6 hours, and the resulting composition is a clear amber liquid.

Water at a level of 500 p.p.m. is added as in Example 1. The mixture is stored for 3 days at 180° F. and then cooled at room temperature. The mixture retains its amber color and no haze formation is observed.

EXAMPLE 4

The procedure of Example 1 is repeated except that different amounts of the ingredients are mixed together as set forth in Table 4 below.

TABLE 4

	Ingredients	Vol. percent	Specific gravity	Wt. in gms.	Wt. percent
1	Polyisobutylene in S–150–N	93.75	.8892	279.15	93.05
2	Zn dialkyl dithiophosphate in oil.	3.00	1.1265	11.31	3.77
3	S–150–N	2.75	.8681	8.01	2.67
4	Amine phosphate salt in kerosine.	0.50	.9128	1.53	.51
Total		100.00		300.00	100.00

The oil blend is heated at 140° F. for 6 hours, and the resulting composition is a clear amber liquid.

Water at a level of 500 p.p.m. is added as in Example 1. The mixture is stored for 3 days at 180° F. and then cooled at room temperature. The mixture retains its amber color and no haze formation is observed.

EXAMPLE 5

Two oil blends are prepared by following the procedure of Example 1 except that different amounts of the ingredients are mixed together as set forth in Table 5 below.

TABLE 5

	Ingredients	Volume percent Comp. A	Comp. B
1	Polyisobutylene in S-150-N	93.75	93.75
2	Zn dialkyl dithiophosphate in oil	3.00	3.00
3	S-150-N	3.15	3.00
4	Amine phosphate salt in kerosine	0.10	0.25

The oil blends are heated at 140° F. for 6 hours, and the resulting compositions are clear liquids.

Varying amounts of water from 100 to 500 p.p.m. are added to aliquots of each oil blend. A first set of aliquots for each blend is stored for 3 days at 180° F. and then cooled for observation. A second set of aliquots for each blend is stored at room temperature for 24 hours and observed. The results are set forth below.

P.p.m. H_2O	After 24 hrs. at room temperature Comp. A	Comp. B	After 3 days storage at 180° F. and cooling for observation Comp. A	Comp. B
100	Slight haze	Slight haze	Clear	Clear.
200	Haze	Haze	do	Do.
300	Very hazy	Very hazy	do	Slight haze.
400	do	do	do	Hazy.
500	do	do	do	Do.

EXAMPLE 6

This example demonstrates the advantages of the present invention as compared with the prior art method of adding barium sulfonate to metal dialkyl dithiophosphate. The procedure of Example 1 is repeated except that 3.00 volume percent of a composition containing 45 to 48 weight percent of barium sulfonate sold under the name Bryton Hibase Barium Sulfonate by Bryton Chemical Co., Saddle Brook, N.J., and 55 to 52 weight percent of a petroleum diluent oil is added instead of 3.00 volume percent of the composition containing the amine salt of mixed alkyl acid phosphates.

The oil blend has the following composition:

	Ingredient	Vol. percent	Specific gravity	Wt. in gms.	Wt. percent
1	Polyisobutylene in S-150-N	93.75	.8892	465.10	93.02
2	Zn alkyl dithiophosphate in oil	3.00	1.2165	18.85	3.77
3	S-150-N	3.00	.8681	14.50	2.90
4	Barium sulfonate in oil	.25	1.1172	1.55	.31
	Total	100.00		500.00	100.00

Varying amounts of water from 100 to 500 p.p.m. are added to aliquots of the oil blend. A first set of aliquots is stored at room temperature for 24 hours and observed. A second set of aliquots is stored for 3 days at 180° F. and then cooled for observation. The results are set forth below.

P.p.m. H_2O	After 24 hours at room temperature	After 3 days storage at 180° F. and cooling for observation
100	Clear	Slight haze.
200	do	Hazy.
300	Slight haze	Do.
400	Hazy	Do.
500	do	Do.

The hazy aliquots containing 100 and 200 p.p.m. that have been stored for 3 days at 180° F. and then cooled are cleared up by adding 0.25 volume percent of amine phosphate and heating at 180° F. for 12 hours.

EXAMPLE 7

A number of other control blends are prepared using various combinations of barium sulfonate and a C_{13} Oxo alcohol in an attempt to produce haze free compositions. The C_{13} Oxo alcohol used is a primary alcohol made by treating 1-dodecene with carbon monoxide in the presence of an "Oxo" catalyst, see "Applied Organic Chemistry," by Kilner and Samuel, Interscience Publishing, Inc., New York, 1960, p. 43. The C_{13} Oxo alcohol used has a specific gravity of 0.8400.

TABLE 7

		Comp. C Vol. percent	Comp. C Wt. percent	Comp. D Vol. percent	Comp. D Wt. percent	Comp. E Vol. percent	Comp. E Wt. percent	Comp. F Vol. percent	Comp. F Wt. percent	Comp. G Vol. percent	Comp. G Wt. percent
1	Polyisobutylene in S-150-N	94.00	93.41	93.75	93.10	93.75	93.06	94.00	93.36	94.00	93.90
2	Zn dialkyl dithiophosphate in oil	3.00	3.77	3.00	3.77	3.00	3.77	3.00	3.78	1.0	1.27
3	S-150-N					1.50	1.45	1.50	1.45	3.5	3.42
4	C_{13} oxo	3.00	2.82	3.00	2.82	1.50	1.41	1.50	1.41	1.5	1.41
5	Barium sulfonate in oil			0.25	.31	0.25	.31				

The above table lists the compositions tested.

All of the above blends are tested for haze formation by adding 500 p.p.m. of water, storing them at 180° F. for 3 days, and then cooling to room temperature. All of the blends exhibit significant haze formation showing by comparison the improved results achieved by the composition of the present invention in the preceding examples.

The invention in its broader aspects is not limited to the specific details shown and described and departures may be made from such details without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed is:

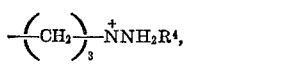
1. An additive composition of improved resistance to haze and precipitate formation which comprises a metal dialkyl dithiophosphate wherein the metal is zinc, barium, cadmium, magnesium or nickel and said alkyl groups contain 3 to 12 carbon atoms; heated to at least about 140° F. for at least about 6 hours with about 0.005 to 0.5 parts by weight, per part of said dithiophosphate, of an amine salt of dihydrocarbyl acid phosphate of the structure

$$\left[(R^5O)_2\overset{\overset{O}{\|}}{P}O^-\right]_x \overset{+}{N}HR^1, R^2, R^3$$

wherein x is 1 or 2, R^5 is a C_8 to C_{13} hydrocarbyl group, R^2 and R^3 each are a hydrogen atom or C_3 to C_{12} hydrocarbyl group, and R^1 is an amino-hydrocarbyl group of

the formula $-(CH_2)_n NHR^4$ when x is 1, or $-(CH_2)_n N^+H_2R^4$ when x is 2, wherein n is 2 or 3 and R^4 is a C_8 to C_{18} hydrocarbyl group.

2. The composition of claim 1, wherein said metal is zinc, the alkyl group of said dithiophosphate has from 5 to 8 carbon atoms, x is 2, R' is



and R^4 is a substantially linear C_{12} to C_{18} aliphatic group.

3. The composition of claim 2, wherein R^2 and R^3 are each hydrogen and R^1 is $-(CH_2)_3N^+H_2C_{18}H_{37}$.

4. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and about 0.5 to 10 weight percent, based on the weight of said composition, of the additive composition of claim 1.

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