

[54] **MULTIFUNCTIONAL LUBRICATING OIL
ADDITIVE**

[75] Inventor: **Alfred Goldschmidt, El Cerrito,
Calif.**

[73] Assignee: **Chevron Research Company, San
Francisco, Calif.**

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[51] Int. Cl. **C10m 1/48**

[58] Field of Search **252/46.7; 260/326.5 F**

[56] **References Cited**

UNITED STATES PATENTS

2,566,129 8/1951 Hook et al. 252/46.7 X

2,586,656 2/1952 Hook et al. 252/46.7 X
2,736,707 2/1956 Morris 252/46.7 X
3,185,643 5/1965 Lowe et al. 252/32.7 E
3,284,354 11/1966 Tunkel et al. 252/32.7 E
3,324,032 6/1967 O'Halloran 252/46.6
3,756,951 9/1973 Dickert 252/46.7

Primary Examiner—Patrick P. Garvin
Assistant Examiner—Andrew H. Metz
Attorney, Agent, or Firm—G. F. Magdeburger; C. J.
Tonkin; S. R. La Paglia

[57] **ABSTRACT**

The N-substituted, S-aminomethyl dithiophosphates, wherein said substituent is selected from the group consisting of hydrocarbyl, hydrocarbyl-substituted amines, and hydrocarbyl-substituted succinimides, are found to function as extreme pressure agents, oxidation inhibitors and ashless dispersants in lubricating oils.

5 Claims, No Drawings

MULTIFUNCTIONAL LUBRICATING OIL ADDITIVE

CROSS-REFERENCE TO RELATED APPLICATION

The present application is a continuation-in-part of U.S. application Ser. No. 255,605, filed May 22, 1972 and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

Auto manufacturers report a number of cases of extreme oil thickening have occurred in customer service with certain engine models and crankcase oils. These oils, which are excellent for light-duty, stop-and-go service, oxidized and thickened under conditions of sustained high speed, heavy load operations. It is not possible to properly lubricate an engine under conditions of extreme lubricating oil viscosity and as a consequence extensive damage to the engine can occur.

Measurements show that temperatures in excess of 300°F. are not uncommon oil temperatures in engines operating at high speeds under conditions of heavy loads, as in trailer towing. 5°-10°F. can be added to oil temperature by power consuming options such as air conditioning. Further increases in engine operating temperatures are caused by changes in engine design to reduce exhaust emissions. For example, high temperature thermostats, reduced compression ratio, compression spark timing, and lean air-fuel ratios tend to either increase the thermal loads on the engine cooling system or increase the operating temperature. Oil oxidation is promoted and oil thickening is thereby accelerated by lean air-fuel ratios which produce blow-by gases containing high concentrations of oxides of nitrogen. It is believed that the oil thickening problem is related to unusually high engine temperatures and resultant oxidation. The trend toward the operation of passenger cars at higher sustained road speeds and heavier load conditions makes this a potentially serious problem in the formulation of ashless crankcase oils.

Very little is known about the role of oil composition in oxidative oil thickening. It has been established, *Lubrication*, Vol. 57, No. 7, 1971, that certain viscosity increases in crankcase oils under high load conditions are correlated with oil oxidation. The mechanism of oil thickening is a very complex chemical process involving primarily oxidation and nitration of the oil. The cited reference also shows that additional zinc dithiophosphate, which is a commonly used oxidation inhibitor, offers little benefit towards improving the thickening resistance of motor oils, in some types of formulations, within the lubricant performance range of commercial interest. It is also believed that the presence of large amounts of ash-containing basic detergent/dispersant, which is needed for low temperature anti-sludge performance, fosters oxidative thickening of the crankcase oils at high temperature.

Consequently, it is necessary to find other oxidation inhibitors and dispersants for lubricating oils which improve the antioxidant properties of the lubricating oils as well as low temperature anti-sludge dispersancy. These additives are preferably ashless. It is found that a formaldehyde of condensation products of formaldehyde and certain dithiophosphoric acid esters with certain high molecular weight amines and imides, which are hereafter described as N-substituted, S-aminomethyl dithiophosphates, form an improved class of antioxidants/dispersants for lubricating oil compositions. The N-substituted, S-aminomethyl dithiophos-

phates were also found to function as extreme pressure agents.

2. Description of the Prior Art

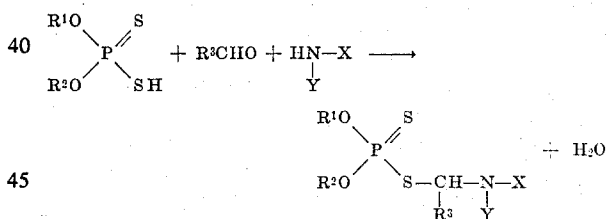
U.S. Pat. No. 2,586,656 describes certain low molecular weight S-aminoalkylidene dithiophosphoric acid triesters which may serve as antioxidant additives in lubricating oil compositions.

SUMMARY OF THE INVENTION

A class of dithiophosphoric acid ester derivatives has been found to possess a surprising lubricating additive trifunctionality, in that they function as effective extreme pressure agents, antioxidants and ashless dispersants when present in 0.5 to 10 percent by weight in lubricating oil compositions. These additives are N-substituted, S-aminomethyl dithiophosphates, wherein said substituent is selected from the group consisting of hydrocarbyl, hydrocarbyl-substituted amine, and hydrocarbyl-substituted succinimide, and said hydrocarbyl-substituents contain at least 40 carbon atoms. They have the additional advantage of being ashless.

DESCRIPTION OF PREFERRED EMBODIMENTS

The dithiophosphates of the present invention are O,O-diester of dithiophosphoric acid. These dithiophosphates are alkyl, aryl, alkaryl or aralkyl diesters of dithiophosphoric acid. The N-substituted, S-aminomethyl dithiophosphates of the present invention are derived from the dithiophosphates by condensing the O,O-diester of dithiophosphoric acid with formaldehyde, or another aldehyde, and a hydrocarbyl-substituted amine, polyamine, or hydrocarbyl-substituted succinimide of a polyamine. The condensation is believed to proceed according to the following reaction:



R^1 and R^2 are alkyl, aryl, alkaryl or aralkyl radicals, or heteroatom-substituted hydrocarbyl radicals, of from low to moderate molecular weight and they may be the same or different. The O,O-diester of dithiophosphoric acid is produced by the reaction of phosphorus pentasulfide with an alcohol, mixture of alcohols, or alkylphenol from which R^1 and R^2 are derived. R^1 and R^2 can be alkyl, aryl, alkaryl or aralkyl groups of from about 1 to about 20 carbon atoms. R^1 and R^2 can also be derived from ether-capped polyoxyalkylene glycols. Preferably, R^1 and R^2 are hydrocarbyl or substituted hydrocarbyl groups of relatively low molecular weight, such as methyl, ethyl, propyl, butyl, amyl, hexyl, cyclohexyl, tetradecyl, dodecyl, decyl, octadecyl, phenyl, naphthyl, methyl phenyl, butyl phenyl, isooctyl, polypropenyl, polyisobutenyl, etc.

The aldehyde which is the preferred condensing agent for the preparation of the products of this invention is formaldehyde, in which case R^3 is hydrogen. However, formaldehyde may be replaced by other aldehydes, for example, benzaldehyde, isobutyraldehyde, butyraldehyde, propionaldehyde, acetaldehyde, vale-

raldehyde, hexaldehyde, etc., in which case R^3 is a hydrocarbyl or substituted hydrocarbyl group.

HNXY represents a substituted primary or secondary amine of relatively high molecular weight (500-10,000). X and Y are radicals of which one may be hydrogen, but at least one is chosen from the group consisting of hydrocarbyl, hydrocarbyl-substituted amine and hydrocarbyl-substituted succinimide of a polyamine. Consequently, the reactant HNXY is a hydrocarbyl-substituted amine or polyamine, or a hydrocarbyl-substituted succinimide of a polyamine.

Hydrocarbyl, as used herein, denotes a monovalent organic radical composed of carbon and hydrogen, except for minor, insubstantial, sometimes adventitious, amounts of other elements such as oxygen, nitrogen, halogen, etc., which may be aliphatic, alicyclic, aromatic, or combinations thereof, e.g., aralkyl. Preferably the hydrocarbyl group will be relatively free of aliphatic unsaturation, i.e., ethylenic and acetylenic, particularly acetylenic unsaturation.

The hydrocarbyl substituent in HNXY contains an average of at least 40 and preferably less than an average of 300 carbon atoms. It is preferably aliphatic, having preferably from zero to two sites of ethylenic unsaturation and most preferably from zero to one such site. Hydrocarbyl groups derived from a polyolefin, itself derived from olefins (normally 1-olefins) or from two to six carbon atoms (ethylene being copolymerized with a higher olefin), or from a higher molecular weight petroleum-derived hydrocarbon, are preferred, and of these, polyisobutene containing from 40 to about 100 carbon atoms is most preferred. Illustrative sources for the high molecular weight hydrocarbyl substituents are petroleum mineral oils such as naphthenic bright stocks, polypropylene, polyisobutylene, poly-1-butene, copolymers of ethylene and propylene, poly-1-pentene, poly-4-methyl-1-pentene, poly-1-hexene, poly-3-methylbutene-1, etc.

The hydrocarbyl-substituted amines are derived from lower molecular weight amines (LMW amine), preferably alkylene polyamines and polyalkylene polyamines, by, for example, the reaction of a halogenated hydrocarbon with the LMW amine. Examples of such LMW amines include ethylenediamine, methylamine, 2-aminoethyl piperazine, decylamine, diethylene-triamine, octadecylamine, di(trimethylene) triamine, ethylene dipiperazine, dipropylenetriamine, piperazine, triethylenetetramine, tripropylenetetramine, tetraethylenepentamine, pentaethylenehexamine, etc. The LMW amines encompass substituted and alkyl-substituted amines, e.g., N-methylethylenediamine, hydroxyethyl piperazine, N,N'-dimethylethylenediamine, N,N-dimethylpropylenediamine, N,N-dimethyldiamino propane, N-hydroxyethyl ethylenediamine, etc. Amines having up to about 12 amino nitrogens and up to about 36 carbon atoms are especially preferred LMW amines. The hydrocarbyl-substituted amines are prepared, in general, by the reaction of halogenated hydrocarbon with the LMW amine. Details of such preparations and further description of certain hydrocarbyl amines can be found in Hotten and Anderson U.S. Pat. No. 3,565,804.

In preparing the compositions of this invention, rarely will a single compound be employed. With both the polymers and the petroleum-derived hydrocarbyl groups, the composition is a mixture of materials having various structures and molecular weights. There-

fore, in referring to molecular weight, average molecular weights are intended. Furthermore, when speaking of a particular hydrocarbyl group, it is intended that the group include the mixture that is normally contained with materials which are commercially available; that is, polyolefins are known to have a range of molecular weights. Furthermore, depending on the method of preparation, the end group of the polymer may vary and may be terminated, not only with an isobutene group, but also with a 1- or 2-butene group. In addition, alkylene polyamines which are commercially available are frequently mixtures of various alkylene polyamines and branched chain isomers having one or two species dominating. Thus, in commercially available tetraethylene pentamine, there will also be small amounts of pentaethylene hexamine and triethylene tetramine. In referring to hydrocarbyl-substituted tetraethylene pentamine, which is the preferred amine, it is intended not only to include the pure compound, but those mixtures which are obtained with commercially available alkylene polyamines. Finally, as indicated, in preparing the compounds of this invention, where the various nitrogen atoms of the alkylene polyamine are not equivalent, the product will be a mixture of the various possible isomers.

The hydrocarbyl-substituted succinimides which find use as nitrogen substituents in the N-substituted, S-aminomethyl dithiophosphate are prepared by first making a monohydrocarbyl succinic acid or anhydride derivative and then reacting the resultant anhydride or acid with a polyamine. These compounds are described in more detail in numerous references in the art. See, for example, U.S. Pat. No. 3,219,666, as well as U.S. Pat. Nos. 3,018,250; 3,087,936; 3,172,892; 3,630,902; and 3,202,678.

The mono-hydrocarbyl succinic acids or anhydrides are prepared by forming the adduct of maleic anhydride with a suitable olefin polymer, chlorinated hydrocarbon, etc. This reaction proceeds upon mixing and heating of the components at temperatures in the range of from about 100°-200°C. The preparation of these mono-hydrocarbyl succinimides is then effected by the reaction of, for example, mono-hydrocarbyl succinic anhydride with such LMW primary amines or polyamines containing a primary amino nitrogen atom as ethylamine, propylamine, butylamine, tetraethylene pentamine, triethylene tetramine.

The preparation of certain of the hydrocarbyl-substituted succinimides of use in the present invention has been described in U.S. Pat. No. 3,018,291 and the other cited U.S. Patents. In the preparation of these succinimides, LMW polyalkylene polyamines having up to about 12 amino nitrogens are especially preferred. It is understood that the reaction products comprise amides, amine salts, and amidines, as well as the principal imide.

The preferred succinimides are polyisobutenyl succinimides prepared by reaction of a substituted succinic acid or anhydride derived from a polybutene having at least 40 carbon atoms and tetraethylene pentamine or triethylene tetramine. The succinic acid or anhydride and the polyamine are preferably reacted in approximately equal molar ratio to obtain the succinimide product.

Method of Preparation

Typically, one mol of substituted amine is diluted

with benzene, approximately 0.9–1.1 mols of CH_2O are added, and stirred for about one hour at 120°–150°F. Approximately 1 mol of dithiophosphoric acid is then added, and the mixture is heated for 3–5 hours at 170°–190°F. The product is then stripped of solvent and analyzed.

Example 1

650 g. of polyisobutenyl ethylene diamine (80 percent concentrate in a 100 SSU at 100°F. neutral oil), wherein the number average molecular weight of the polyisobutenyl was 1,400 (average carbon number of 100), was diluted with 300 ml of benzene. 37 g. of a 37 percent aqueous CH_2O solution was added, whereupon the temperature rose from 75° to 87°F. The mixture was stirred one-half hour and 120 g. of di(isooctyl)dithiophosphoric acid was added in 100 ml. of benzene. The temperature rose to 107°F, whereupon heat was applied and the mixture was stirred for 5 hours at 170°–180°F. 150 g. of a 100 SSU at 100°F. neutral petroleum oil was added, and the product stripped of solvent at 220°F for 3 minutes. Percent phosphorus, 1.04.

Example 2

700 g. of polyisobutenyl succinimide of ethylene diamine (as 50 percent concentrate in 100 SSU at 100°F. neutral petroleum oil), wherein the number average molecular weight of the polyisobutenyl was 950, was diluted with 200 ml of benzene. 10.5 g. of paraformaldehyde was added and the mixture was stirred for 1 hour at 120°–130°F. 120 g. of di(isooctyl)dithiophosphoric acid was added in 50 ml. of benzene. The mixture was heated for four hours at 185°F and stripped at 210°F for 4 minutes. Percent phosphorus, 1.1 percent.

Example 3

830 g. of a 50 percent concentrate of polyisobutenyl succinimide of tetraethylene pentamine, wherein the number average molecular weight of the polyisobutenyl was 950, was diluted with 250 ml. of benzene. 8.5 grams of paraformaldehyde was added and the mixture was stirred for one hour at 130°F. 9.6 g. of a di(isooctyl)dithiophosphoric acid in 50 ml. of benzene was then added and the mixture was heated for five hours at 190°F. The product was stripped at 210°F for 5 minutes. Percent phosphorus, 0.88 percent.

Example 4

Analogous to Example 3, using a bis(polypropenyl phenol) dithiophosphoric acid.

Lubricant Composition

The lubricating oils which comprise the basis for the composition of this invention are those oily or greasy materials employed in lubrication. Examples of these materials are natural and synthetic oils and greases made from these oils, and synthetic oils. Synthetic oils include alkylene polymers, such as polymers of propylene, butylene, etc., and mixtures thereof; alkylene oxide-type polymers, e.g., alkylene oxide polymers prepared by polymerization of alkylene oxide in the presence of water or alcohols, such as propylene oxide polymer, ethylene oxide polymer; carboxylic acid esters, such as those which are prepared by esterifying carboxylic acid, e.g., adipic acid, suberic acid, fumaric acid, etc. with alcohols such as butyl alcohol, hexyl alcohol, pentaerythritol, etc.; polymers of silicon; alkyl-

biphenyl ethers and other ethers, etc. The base oils can be used individually or in combinations wherever miscible or whenever made so by use of mutual solvents. Oils of lubricating viscosity generally have viscosities of 35–50,000 SUS at 100°F.

The lubricating compositions of the present invention contain a major amount of an oil of lubricating viscosity and will also contain a functional amount, from 0.1 to 10 percent by weight, of the N-substituted, S-aminomethyl dithiophosphate of the present invention. In concentrates, the weight percent of this additive will usually range from about 20 to 60 percent by weight.

In addition to the N-substituted, S-aminomethyl dithiophosphate, these lubricating compositions can also contain other lubricating oil and grease additives such as oiliness agents, extreme pressure agents, rust inhibitors, other oxidation inhibitors, corrosion inhibitors, viscosity index improving agents, dyes, detergents, dispersants, etc. Usually, for oils to be used in an internal combustion engine, the total amount of these additives will range from about 0.1–20 percent by weight, and more usually from about 0.5–10 weight percent. The individual additives may vary in amounts from about 0.01–10 weight percent of the total composition. In concentrates, the weight percent of these additives will usually range from about 20–60 weight percent.

Evaluation

The Falex test results are given in Table I. The Falex test is a test for extreme pressure properties. In this test stationary vee-blocks are pressed on either side of a rotating pin by a nutcracker arrangement of lever arms. Test specimens are immersed in a tank of test lubricant which is at a known temperature. Loading is automatically increased until seizure occurs. This failure point is indicated by shearing of the pin holding the vertical shaft. The load at shear in pounds is taken as a quantitative measure of the extreme pressure property of the oil composition. Mineral oils may fail at 600–900 pounds. Oils with EP additives will fail at 1,000–2,000 pounds. The wear is determined by conducting the test at constant load and measuring the pin weight loss in milligrams.

The N-substituted, S-aminomethyl dithiophosphates have also been tested for antiwear properties by means of the well-known 4-Ball Test. In this test, three ½-diameter steel balls are clamped together and immersed in the test lubricant. A fourth ball is then rotated at about 1,800 rpm in contact with the other three balls. A 20–50 kg. load is applied, forcing the rotating ball against the three stationary balls. The test is run for 60–30 minutes and the sizes of the wear scars on the three stationary balls are measured and the average scar size in millimeters reported. The smaller the scar, the greater the anti-wear properties of the test lubricant. These EP properties are reported in Table I and II. Note that reference oils containing well-known EP agents give Falex Shear test results of 850–1,450 pounds. Similar properties are obtained with the additives of the present invention, but the Falex wear is much less with the additives of the present invention. This excellent wear result is confirmed in the 4-Ball test results given in Table II.

TABLE I

Additive ^a	Falex Shear, lbs.	Falex Wear,
1. 0.7% zinc di(isooctyl)dithiophosphate + 5% polyisobutenyl succinimide of tetraethylenepentamine	1450	7.5
2. 1.7% zinc bis(polypropenylphenyl) dithiophosphate + 5% polyisobutenyl succinimide of tetraethylenepentamine	850	31.8
3. 4.5% of the product of Example 1	1300	1.6
4. 4.5% of the product of Example 2	1400	4.6
5. 6.0% of the product of Example 3	1300	1.9
6. 6.3% of the product of Example 4	1000	3.3

^aPercent by weight. All test lubricants contain 15 mM/g P in a 496 SSU at 100°F, neutral petroleum oil.

TABLE II

Additive ^a	4-Ball Wear, mm
1. 5% polyisobutenyl succinimide of tetraethylenepentamine + 1.7% zinc bis(polypropenylphenyl)-dithiophosphate	1.80
2. 6.3% of the product of Example 4	0.45

^aSee footnote a of Table I.

The Oxidator B test is our laboratory designation for a test measuring resistance to oxidation by means of a Dorn-type oxygen absorption apparatus (R.W. Dorn, "Oxidation of White Oils," *Industrial and Engineering Chemistry*, Vol. 28, p. 26, 1936). Normally, the conditions are 1 atmosphere of pure oxygen at 340°F and one reports the hours to absorption of 1,000 ml. of O₂ by 100 grams of oil. In the Oxidator B test a catalyst is used and a reference additive package is included in the oil. The catalyst is a mixture of soluble metal-naphthenates simulating the average metal analysis of used crankcase oils. Thus, the Oxidator B method measures the response to conventional inhibitors in a simulated application. The results are given in Table III where the composition of the present invention is compared to compositions containing other dithiophosphates. Direct comparisons are made in Table III between Additives 1 and 3, 4 and 5, and 6 and 7, which correspond to the zinc containing additive and the corresponding ashless antioxidant of the present invention. These results are uniformly outstanding in favor of the N-substituted, S-aminomethyl dithiophosphates.

TABLE III

Additive ^a	Oxidator B hrs.
1. 5% polyisobutenyl succinimide of tetraethylenepentamine	0.6
2. ^b	2.5
3. 6% of the product of Example 3	5.1
4. 3.5% of polyisobutenyl amine + 0.7% of zinc di(isooctyl) dithio-	

TABLE III-Continued

Additive ^a	Oxidator B hrs.
5. phosphate	3.1
5. 4.5% of the product of Example 1	5.3
6. 3.8% polyisobutenyl succinimide of ethylenediamine + 0.7% of zinc di(isooctyl)dithiophosphate	2.3
7. 4.5% of the product of Example 2	5.4

^aSee footnote ^a of Table I.

^bAdditive 2 of Table I.

15 In a further heat stability test, 6 percent of Example 3 in a 496 SSU at 100°F neutral petroleum oil was heated for 48 hours at 300°F. The product was found to have an undiminished oxidator B rating. When 4.5 percent of the additive of Example 2 in the same base oil was heated for 48 hours at 300°F, it was found that the infrared spectrum remained practically unchanged.

20 Table IV illustrates the detergency of the N-substituted, S-aminomethyl dithiophosphates. The data refers to a severe Caterpillar diesel engine test, run for 12 hours at 1,200 rpm, 280 brake means effective pressure in psi, water temperature of the cooling jacket is 190°F, the sulfur content of the fuel is 0.4 percent and is input at a rate which provides 6,900 BTU per minute. The base oil was a 496 SSU at 100°F, neutral petroleum oil. In Table IV the rating of groove deposits is based on a range of 0-100, 100 being completely filled grooves. The rating for land deposits is based on a range of 1-800, 800 being completely black. The rating for underhead deposits is based on a range of 0-10, 10 being completely clean.

TABLE IV

Additive	Grooves	Lands	Under-head
1. 6% of the product of Example 2	3.8, 0.6, 0.5, 0.5	60-10-10	5.8
2. 8% of the product of Example 3	7.1, 4.0, 0.6, 0.5	200-10-10	7.2

45 The N-substituted, S-aminomethyl dithiophosphates were also found to be noncorrosive towards copper and lead bearings, as well as being antioxidants, dispersants and extreme pressure agents. The unique polyfunctionality of high molecular weight condensation products of the present invention is in sharp contrast with the low molecular weight analogs, which, for example, cannot function as lubricating oil detergents/dispersants. It is unusual to find polyfunctionality where each function depends on a different physical or chemical property of the molecule. Multifunctionality is especially unexpected where the functions are unrelated by a common property such as metallic surface activity.

60 It is evident from the above results that the compositions of this invention are excellent detergents/dispersants under the severe conditions of the Caterpillar internal combustion engine, they are also antioxidants and extreme pressure agents. Furthermore, the compositions are compatible with other additives normally found in compounded lubricating oils.

65 While the character of this invention has been described in detail with several examples, this has been

