

[54] LUBRICANT COMPOSITIONS
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252/389, 400

[56] **References Cited**
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[57] **ABSTRACT**
Lubricant compositions comprising:
a. lubricating oil base
b. reaction product of alkenyl succinimide and
dialkylthiophosphate acid ester 0.05–10 percent
c. tetraalkyltrithiopyrophosphate 0.001–2 percent and
optionally
d. alkenyl succinimide 0.05–10 percent.

2 Claims, No Drawings

LUBRICANT COMPOSITIONS

BACKGROUND OF THE INVENTION

A great number of organic compounds have been described in the literature as extreme pressure (EP) additives. These materials are important in that they raise the load-carrying capabilities of the lubricant to reduce metal surface wear. Although there has been extensive research in this area, the theories explaining the mechanism of EP additives are mainly conjecture. Two of the most popular theories are:

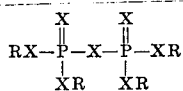
1. the additives react with the lubricated metal surface at high temperatures to form easily sheared films;

2. the additives hydrolyze to give a species which could be chemisorbed on a metal surface to provide the protective anti-wear film. These compounds can be generally classified as either ash-forming or ashless, the latter having wider applicability since this class of compounds can be used in ashless luboil formulations as well as in most other lubricant compositions.

One of the most suitable classes of EP additives known to the art are metal dithiophosphate salts such as zinc dialkyldithiophosphates. While these salts are effective, they cannot be used in ashless lubricating compositions because they are ash forming; however, it has been discovered that using the ashless succinimide-type detergent additives in place of the previously used metal-containing materials aggravates the problem of controlling bearing corrosion and wear. The development of a new class of EP additives which could be used in a wide range of lubricant compositions is extremely desirable.

THE INVENTION

This invention relates to lubricant oil compositions having improved extreme-pressure protection and bearing corrosion performance containing the reaction product of an ashless succinimide and a thiophosphate acid ester combined in a suitable base stock with a pyrophosphate derivative having the following general formula

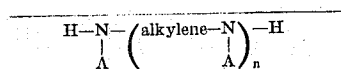


wherein each X is selected from the group consisting of oxygen and sulfur, and each R is a hydrocarbonyl radical selected from the group consisting of C₁₋₃₀ alkyl, C₆₋₁₀ aryl and C₇₋₃₀ alkaryl.

The ashless succinimide is preferably a polyalkenyl succinimide of a polyamine, as for example, polyisobutenyl succinimide of tetraethylenepentamine. However, a wide variety of succinic compounds of oil-soluble nitrogen compositions can be used provided they are hydrocarbon substituted, surface-active basic amines. The principle sources of the hydrocarbon-substituent radical include high-molecular weight petroleum fractions and olefin polymers, particularly polymers of monoolefins having from two to about 10 carbon atoms. Especially useful are polymers of 1-monoolefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, that is, olefins in which the

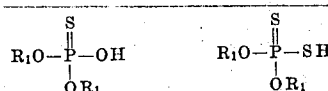
olefinic linkage is not at the terminal position, are also useful. Suitable medial olefins are 2-butene, 3-pentene, 4-octene and the like. Also useful are interpolymers as for example, those prepared by polymerizing isobutene with styrene, isobutene and butadienes, propene with isoprene, ethylene with piperylene, 3,3-dimethyl-1-pentene with 1-hexene and the like. Especially preferred are polymers of C₄₋₁₀ tertiary olefins. The average molecular weight ($\bar{M}_n$) of the succinimides is conveniently from about 200 to about 6,000, and preferably from about 400 to about 3,000.

The amines useful in this invention include alkylene polyamines and hydroxyalkyl-substituted alkylene polyamines. A preferred source of the amine group consists of alkylene polyamines conforming for the most part to the following formula:



where n is an integer, preferably less than 10, A is a hydrocarbon, hydrogen or amino radical and the alkylene radical is preferably less than C₈. Specific amines contemplated are exemplified by ethylene diamine, triethylene tetramine, propylene diamine, tetraethylene pentamine, di(trimethylene) triamine, 1,3-bis(2-aminoethylene) imidazoline and 2-methyl-1-(2-aminobutyl) piperazine.

The thiophosphoric acids or acid compounds can be mono- or dithio-having the following respective general formulas:



wherein each R₁ is chosen from the group consisting of alkyl, aryl, alkaryl and aralkyl radicals. The alkyl radicals include straight-chain, branched-chain, aliphatic and cycloaliphatic radicals. Examples of suitable radicals include methyl, ethyl, n-propyl, isopropyl, isobutyl, secondary amyl, n-hexyl, 2-ethylhexyl, n-octyl, nonyl, n-decyl, n-dodecyl, n-octadecyl, oleyl, cetyl, ceryl and the like, as well as cyclohexyl, ethylcyclohexyl, tolyl, xylyl, naphthyl, benzyl, phenyl and the like.

Especially preferred are the alkyl dithiophosphoric acids, which can be conveniently prepared by reacting phosphorus pentasulfide and the appropriate alcohol, for example, primary alkyl (C₁₋₈), secondary alkyl (C₈ to about C₃₀) and branched alcohols such as 2-ethylhexyl, 3-ethyl-1-hexyl or 4-methyl-1-pentyl and the like. However, other conventional methods of preparing alkyl thiophosphate acids known to the art may be employed.

The pyrophosphate derivative is termed a mixed pyrophosphate. This refers to the fact that the compounds contain both oxygen and sulfur and may vary in the sulfur-oxygen content with retention of the same ester group. These compounds can be prepared according to any method known in the art. See, for example, U.S. Pat. Nos. 3,297,797 and 2,063,629. Preferred are the oxydithio- and trithiopyrophosphates.

In general, the trithiopyrophosphates are prepared by one of two methods, depending on whether they are de-

rived from alkyl or from aryl thionothiophosphoric acid.

Alkyl trithiopyrophosphates can be synthesized by reacting alkyl thionophosphoric acids with, for example, N,N'-dicyclohexylcarbodiimide.

The starting acid can be prepared by reacting a C₁₋₃₀ alkyl alcohol or mercaptan with phosphorus pentasulfide. Examples of suitable alcohols and mercaptans are butyl alcohol, butyl mercaptan, and amyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl alcohol or mercaptan, lauryl, stearyl, oleyl alcohol or mercaptan and the like. The nature of the alcohols or mercaptans used in synthesizing the thionophosphoric acids determines the nature of the alkyl groups of the trithiopyrophosphate subsequently formed.

Aryl and alkaryl trithiopyrophosphates can be conveniently prepared by reacting an aryl or alkaryl alcohol or mercaptan with phosphorus pentasulfide and then pyrolyzing the resultant thionothiophosphoric acid to the desired derivative.

A wide variety of aryl and alkaryl alcohols and mercaptans can be used in preparing suitable thionothiophosphoric acids. Examples of these are substituted and unsubstituted phenols, thiophenols, naphthols, thionaphthols and the like. C₆₋₁₀ and C₇₋₃₀ alkaryl alcohols or mercaptans having only one aromatic nucleus are especially suitable. Particularly advantageous alkaryl compounds are those having only one alkyl group attached directly to the aromatic nucleus, said alkyl group having from one to about 24 and preferably from about four to about 18 carbon atoms.

The reaction product of the succinimide and the thiophosphoric acid can be conveniently prepared, for example, by reacting the thiophosphoric acid and the basic amine at a temperature of about 80°-120°C. The thiophosphoric acid is then slowly added to the amine, stirred well, and heated to about 100°C or more and stirred for approximately 2 hours. If higher heat is applied, the reaction time can be reduced to less than 2 hours. The resulting mixture is used in this form without further purification.

The novel combination of a thiophosphate acid-succinimide reaction product and a thiopyrophosphate compound can be incorporated into a wide variety of lubricants, including synthetic oils, but are particularly advantageous when used in mineral lubricating oils. Mineral oils suitable for this invention can be obtained from paraffinic, naphthenic or mixed base blends and/or mixtures thereof. For example, neutral oils having viscosities of from 100 to about 750 SSU at 100°F may be employed. Neutral high viscosity index oils having viscosity indices (VI) of about 100 are preferred. Also suitable are oils having a viscosity index of at least 70 or suitable blends of lower viscosity index oils and viscosity improvers.

The reaction product and the pyrophosphates according to the invention can be added either separately or in combination to the lubricating oil in the amount of from 0.01 to about 10%w. A preferred composition contains from 0.05 to about 5%w.

Other additives can also be incorporated into the lubricating compositions of the present invention to add special properties to the compositions or to perform various functions. For example, any of the additives recognized in the art to perform a particular function, that is viscosity index improvers, antioxidants, antifoam

agents, corrosion inhibitors, antirust agents and the like, can also be used.

The invention will be further illustrated by the following examples:

EXAMPLE I

This example describes one manner in which a succinimidethiophosphate acid reaction product may be synthesized.

Di-2-ethylhexyldithiophosphoric acid was prepared by reacting one mole of phosphorus pentasulfide with 4 moles of 2-ethylhexanol as follows:

Phosphorus pentasulfide was added in small portions at such a rate as to maintain fairly rapid evolution of hydrogen sulfide. The reaction was maintained at about 70°C until all the phosphorus pentasulfide was added. The temperature was raised to 90°C for about an hour until the reaction was complete (either the P₂S₅ all dissolved or H₂S evolution virtually ceased). The acid was then filtered from any excess P₂S₅ and reacted further as quickly as possible to avoid deterioration. No further purification steps were taken.

The di-2-ethylhexyldithiophosphoric acid thus prepared was reacted with one equivalent of polyisobutylene succinimide of tetraethylene pentamine as follows:

One mole (one equivalent weight) of di-2-ethylhexyldithiophosphoric acid was slowly added to an amount of the succinimide containing an equivalent amount of basic nitrogen and the mixture was stirred well while the temperature was maintained at 80°C. After the addition, the mixture was heated to 100°C and stirred for 2 hours. The resulting mixture was ready for use in this form, without further purification.

EXAMPLE II

This example describes a manner in which the tetra-2-ethylhexyltrithiopyrophosphate derivative may be synthesized.

Di-2-ethylhexylthionophosphoric acid (0.1 mole) was dissolved in anhydrous diethyl ether. N,N'-dicyclohexylcarbodiimide (0.05 mole) was dissolved in anhydrous diethyl ether and added dropwise over 4 hours to the acid solution. The reaction was maintained at room temperature. After a short time, a white precipitate formed. The mixture was stirred for one hour at room temperature and to two hours at reflux temperature following the addition. The by-product, N,N'-dicyclohexylthiourea, M.P. 180°-181°C, was then filtered. The product was recovered in 95-100 percent of the theoretically possible amount, based on the acid. The solvent was removed from the remaining filtrate in vacuo.

EXAMPLE III

In order to determine the load-carrying or extreme pressure capabilities of the additives of the invention, three compositions containing di-2-ethylhexyldithiophosphate-succinimide reaction product prepared according to Example I and identified as Compositions 1, 2 and 3 were formulated as in Table 1. Composition 1 was not according to the invention. Test results are shown in Table 2.

TABLE 1

Component	Composition % w		
	1	2	3
Base Oil			
HVI 100N (viscosity approximately 100 SSU at 100°F)	99.0	97.7	96.2
Reaction product of di-2-ethylhexyldithiophosphoric acid-polyalkenylsuccinimide of tetraethylene-pentamine (0.01% W P)	1.0	1.0	1.0
Tetra-2-ethylhexyltrithiopyrophosphate ^a		1.3	1.3
Polyisobutenylsuccinimide of tetraethylenepentamine ($\bar{M}_n$ approximately 2700)			1.5

^a Prepared as in Example II.
 $\bar{M}_n$ = average molecular weight

TABLE 2

Composition	Four-Ball Wear Test ^a Scar Diameter, mm	% Seizure
1	0.436	25
2	0.377	0
3	0.280	0
Variables		
Speed	600 rpm	
Temperature	200°F	
Time	2 hours	
Balls	1/2" diameter steel	

^a40 kg load

The Four-Ball Wear test is widely accepted as a repeatable screening test for EP lubricants. Scar diameters less than about 0.42 mm with no seizure indicate that a lubricant has EP properties such that satisfactory performance in automotive cam and lifter follower sets is probable. The wide differences in scar diameter and the lack of seizure are clearly indicative of the improved extreme pressure properties of the inventive compositions.

EXAMPLE IV

To further illustrate the extreme pressure properties of the compositions of the invention, 1.3%w of tetra-2-ethylhexyltrithiopyrophosphate and 1%w of the di-2-ethylhexyldithiophosphoric acid-succinimide reaction product were evaluated in the formulated lubricant composition (Composition 4) shown in Table 3.

TABLE 3

Composition 4	
	%w
HVI 100N (viscosity approximately 100 SSU at 100°F)	46.5
HVI 250N (viscosity approximately 262 SSU at 100°F)	38.1
Copolymer 2-methyl-5-vinylpyridine, lauryl methacrylate (M _n approximately 800,000)	4.6
Polyisobutenyl succinimide of tetraethylene pentamine (M _n approximately 2700)	1.7
Isooctylphenoxytetraethoxy ethanol	0.2
Silicone polymer, 12,500 cs	

TABLE 3-Continued

Composition 4	
viscosity at 25°C	10 ppm
Oil soluble carbonated Ca petroleum sulfonates	6.6

Composition 4 was then subjected to the Cam and Lifter Wear and Scuff Test using a 1967 425 cu. in. displacement Oldsmobile engine, in which twice the normal (production) valve spring pressure was applied.

15	Test Conditions:	
	Test Cycle:	Engine:
	10 min run	Speed, rpm: 2500
	20 min down	Load, bhp: 0-2
20	Test Duration:	
	Engine 5hr. (30 cycles)	Coolant out, °F: 95
	Total 15hrs.	Oil Sump, °F: 120

Tested along with Composition 4 were two other oil formulations that were identical with the exception that they did not contain the additive combination according to the invention. These two oil formulations showed severe visible scuffing of cams and lifters at the conclusion of the test, while the cams and lifters lubricated with Composition 4 had no visible scuffing, only 6 × 10⁻⁴ inches of measured wear.

EXAMPLE IV

To illustrate the antioxidant properties of compositions according to the invention composition 5, as shown in Table 4, was formulated and tested as described below.

TABLE 4

Composition 5	
	% w
HVI 100N (viscosity approximately 100 SSU at 100°F)	46.5
HVI 250N (viscosity approximately 262 SSU at 100°F)	38.1
Copolymer of 2-methyl-5-vinylpyridine, lauryl methacrylate and stearyl methacrylate	4.6
Polyisobutenyl succinimide of tetraethylene pentamine (M _n approximately 2700)	1.7
Trithiopyrophosphate ^a	1.3
Reaction product of di-2-ethylhexyldithiophosphoric acid-polyalkenylsuccinimide of tetraethylene-pentamine	1.0
Iso-octylphenoxy tetraethoxyethanol	0.2
Carbonated calcium sulfonates	6.6
Silicone polymer, 12,500 cs viscosity at 25°C	10 ppm

^a according to the invention

The effectiveness of these materials as oxidation inhibitors was demonstrated by evaluating Composition No. 5 in the CLR L-38 (FTM 791a Method 3405) test. This test subjects the oil to 285°F (bulk temperature) to demonstrate the oxidation stability (as indicated by corrosive weight loss of the copperlead connecting rod bearing) of a lubricant. Composition No. 5 produced less than 50 mg weight loss in 40 hours. This performance is similar to that expected of a formulation in which 1.4%w zinc dialkyldithiophosphate was substituted for 1.3%w trithiopyrophosphate. If neither compound were included, catastrophic weight loss (greater than 1000 mg) would be expected.

Other disclosed compositions not exemplified in the above examples give equivalent, although not identical, results. The additives disclosed herein are suitable for use in multipurpose hydraulic fluids as well as in a wide variety of both ashless and ash-forming lubricating oils. 5

We claim as our invention:

1. An ashless lubricant composition comprising a major amount of a mineral lubricating oil which is a neutral hydrocarbon oil with a viscosity index of at least 70 and 10

A. from about 0.05 to 10 percent by weight of a reaction product of polyisobutenyl succinimide of

tetraethylenepentamine wherein the succinimide has an average molecular weight between 400-3,000 and di-2-ethylhexyldithiophosphoric acid, said reaction being carried out by heating an equivalent weight of each reactant at a temperature of about 80°-120°C and utilizing said product without further purification and

B. from about 0.001 to 2 percent by weight of tetra-2-ethylhexyltrithiopyrophosphate.

2. The composition of claim 1 having additionally from 0.05 to 10 percent by weight of a polyisobutenyl succinimide of tetraethylenepentamine.

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