Lubricants and Lubricant Additives: III. Performance Characteristics of Some Thioacetate, Phosphorodithioate, and Hexachlorocyclopentadiene Derivatives of Stearic Acid Amides and Esters

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ABSTRACT AND SUMMARY

A number of N-mono-, N,N-disubstituted amides, and esters of substituted fatty acids have been prepared and evaluated as base lubricants and lubricant additives for paraffin (S-105) or diester (DOS) base oils. The effect of acetylthio, phosphorodithio, thio, chloro, and bromotrichloromethyl substituents, as well as hexachlorocyclopentadiene adducts upon performance as antiwear and extreme-pressure lubricants was investigated. Sulfurized 1,4-bis(pentachlorostearoyloxy)-2-butene was most effective in extreme-pressure (EP) tests, both neat and as an additive for S-105 and DOS base oils. Several of the phosphorodithio derivatives have good antiwear properties when formulated in one or both of the base oils, and were also fair EP additives. Of the addition compounds evaluated in this study, the phosphorodithio derivatives offer the most promise for development as antiwear additives for both paraffin and diester base oils. The sulfurized products offer the most promise as EP additives.

INTRODUCTION

Since the ban on importation of sperm whale oil into the United States in 1970, considerable effort has been made to fulfill the lubrication needs formerly met by this material or its derivatives. Efforts were made to prepare wax esters chemically similar to those that constitute sperm oil (1). N-mono- and N,N-disubstituted amides and modified fatty amides have been made and evaluated as lubricants and lubricant additives as possible replacements for sulfurized sperm oil (2). Substituted fatty acid esters of mono- and polyhydric alcohols have also been prepared, and the effect of chloro, phosphato, phosphorodithio, thio, epithio, mercapto, and sulfuryl substituents upon performance as antiwear and extreme pressure (EP) lubricants was investigated (3). Various sulfurized fat- or fatty acid-derived materials have been investigated as replacements for sulfurized sperm oil (4-9). In continuation of this laboratory's lubricant investigation, and in search of potentially useful derivatives of vegetable oils, a number of modified esters and amides were made and evaluated as lubricants and lubricant additives for paraffin or diester base oils. These novel materials were prepared by addition reactions to double bonds or epoxy groups of long chain fatty acid derivatives to give compounds containing either sulfur, phosphorus, or halogen, or a combination of these elements. Bench tests showed some of these products to have good antiwear or EP lubricating characteristics, and in some cases to function in both capacities.

EXPERIMENTAL PROCEDURES

None of the compounds prepared and evaluated was of high purity. They received minimum purification, usually acid or alkaline washes followed, where advisable, by percolation through activated alumina to eliminate any residual acidity. Thus, the actual elemental analyses often differed from the calculated values. However, the cleaning-up procedure generally eliminated the starting materials, and infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy were used to ascertain that the desired reaction had actually taken place. Recovery of products from the reactions were 90%-100% of the theoretical yield; however, elemental analyses showed that in some cases the actual yields of addition products were lower.

A commercial oleic acid, Emery Industries Elaine 233 LL (Cincinnati, OH), was used as the source of fatty acid for all of the 9,10-substituted stearic acid derivatives. Linoleic acid was a 90%-95% inhouse preparation which had been obtained from safflower oil fatty acids by urea clathration (10). Undecenoic acid was an Eastman product (Rochester, NY).

Ester intermediates were made by direct reaction between the acid chloride and the alcohols, or between fatty acids and alcohols, using 3.0 g of para-toluenesulfonic acid per 100 g of fatty acid as catalyst.

Amides and imidazolidine intermediates were prepared as previously reported (3,11).

Acetylthio derivatives were made by the free radical addition of thiolacetic acid to the respective unsaturated esters and amides, as previously described (12).

2-(2-Ethoxyethoxy)ethyl 8-(1,4,5,6,7,7-hexachloro-3-octylbicyclo[2·2·1]-5-hepten-2-yl)octanoate (#20)

Samples of 150 g of 2-(2-ethoxyethoxy)ethyl oleate and 205.3 g of hexachlorocyclopentadiene were placed in a flask equipped with a condenser, nitrogen inlet tube, and thermometer. The temperature was raised to 136 C, maintained there for 30 hr, and worked up as previously described (13). NMR spectra confirmed the product and showed the absence of olefinic protons in the 5·3 ppm region.

2,2′-Thiobis[Ethyl 9(10)-bromo-10(9)-trichloromethylstearate] (#18)

Samples of 15 g of 2,2′-thiobis (ethyl oleate) and 9.1 g of bromotrichloromethane were mixed well in a flask and irradiated for 23 hr. The excess bromotrichloromethane was then removed by distillation at reduced pressure, leaving a quantitative yield of product. NMR spectra showed the absence of olefinic protons which would show up in the 5·3 ppm region.

2,2′-Thiobis[ethyl 8-(1,4,5,6,7,7-hexachloro-3-octylbicyclo[2·2·1]-5-heptene-2-yl)octanoate] (#19)

Hexachlorocyclopentadiene adduct of oleic acid (I): Oleic acid (150 g) and hexachlorocyclopentadiene (295 g) were allowed to react under nitrogen in a flask equipped with a condenser for 28 hr at 135 C, and worked up as

TABLE I

Wear and Extreme Pressure Lubricating Characteristics of Some Esters and Amides of Substituted Fatty Acids

Sample Number	Compound	Wear test Scar Diameter mm: Neat	Wear test Scar Diameter mm: 5% Additive in Topaz	Wear test Scar Diameter mm: 5% Additive in DOS	Extreme Pressure Tests, Neat: Load (kg)	Extreme Pressure Tests, Neat: Scar (mm)	Extreme Pressure Tests, Neat: Weld pt (kg)	Extreme Pressure Tests, 5% in Base Oil: Weld pt (kg) Topaz	Extreme Pressure Tests, 5% in Base Oil: Weld pt (kg) DOS	Extreme Pressure Tests, 5% in Base Oil: Scar Dia.[b] (mm) Topaz	Extreme Pressure Tests, 5% in Base Oil: Scar Dia.[b] (mm) DOS
1	N,N-Bis(3-acetylthiopropyl)-9(10)-acetylthiostearamide	--	0.578	0.895	--	--	400	200	200	3.41	3.18
2	2,2'-Thiobis[ethyl 9(10)-acetylthiostearate]	--	0.667	0.825	--	--	500	200	200	2.75	2.86
3	2,2'-Oxybis[ethyl 9(10)-acetylthiostearate]	--	0.750	0.492	--	--	400	200	200	3.75	3.66
4	N-9(10)-Acetylthiostearoylmorpholine	--	0.860	0.980	--	--	315	200	200	3.76	3.46
5	N-9(10),12(13)-(Diacetylthio)stearoylmorpholine	--	0.765	0.887	--	--	315	200	200	2.80	3.40
6	2,3-(Diacetylthio)propyl 11-acetylthioundecanoate	--	0.653	0.905	--	--	315	200	200	2.18	3.60
7	1,3-Bis[9(10)-acetylthiostearoyl]imidazolidine	--	0.780	0.887	--	--	315	200	200	3.30	3.45
8	N-(3-acetylthiopropyl)-9(10)-acetylthiostearamide	--	0.710	0.810	300	1.80	400	160	180	3.00	0.830
9	3-(0,0-Diethylphosphorodithio)propyl 11-0,0-diethylphosphorodithioundecanoate	--	0.425	0.740	--	--	400	250	200	3.90	3.00
10	Sulfurized morpholide of linoleic acid	--	0.620	0.608	600	2.21	a	200	250	2.25	2.55
11	Sulfurized 1,4-bis(pentachlorostearoyloxy)-2-butene	--	0.595	1.06	600	1.68	a	315	315	2.50	2.55
12	0,0-Dibutylphosphorodithioic acid tetrathioester reaction product with N-tris-(epoxystearoyloxymethyl)methylepoxystearamide	--	0.612	0.495	600	3.55	a	250	250	3.60	3.18
13	Bis[2-(Pentachlorostearoyloxy)ethyl] disulfide	--	0.870	0.960	400	1.33	500	320	280	3.18	3.05
14	2-Ethyhexyl (0,0-diisopropylphosphorodithio) hydroxy tallate	--	0.675	0.690	500	2.13	600	180	200	2.70	3.15
15	0,0-Dibutylphosphorodithioic acid tetrathioester addition product with N-tris(oleoyloxymethyl)oleamide	--	0.515	0.535	300	1.81	400	220	200	3.20	3.20
16	1,4-Bis[1,2(3)-dicarbobutoxy-3(2)-(9(10)-dibutylphosphorodithiocarbostearoxy)propyl]piperazine	--	0.480	0.475	250	2.25	300	160	180	2.16	3.80
17	2,2'-Oxybis[ethyl 9(10)-bromo-10(9)-trichloromethylstearate]	--	1.17	1.15	400	1.53	500	240	180	3.05	3.45
18	2,2'-Thiobis[ethyl 9(10)-bromo-10(9)-trichloromethylstearate]	--	1.10	1.03	600	1.45	a	200	200	3.23	2.45
19	2,2'-Thiobis[ethyl 8-(1,4-5,6,7,7-hexachloro-3-octylbicyclo-[2·2·1]-5-hepten-2yl)octanoate]	--	0.533	0.525	600	1.43	a	180	200	2.08	2.59
20	(2-Ethoxyethoxy)ethyl [8-(1,4,5,6,7,7-hexachloro-3-octylbicyclo[2·2·1]-5-hepten-2yl)octanoate]	--	0.885	0.915	600	1.41	a	180	180	2.70	3.15
	Control Topaz 105 sec oil	0.794	--	--	--	--	120	--	--	--	--
	Control Di 2-ethylhexyl sebacate	0.872			--	--	110	--	--	--	--
	Control Gulfpride, Single G, multiviscosity	0.447	--	--	--	--	190	--	--	--	--
	Control SAE #90 Comm. hypoid fluid	0.370	--	--	--	2.60	280	--	--	--	--

[a] Beyond capacity of 4-ball tester

[b] Scar diameter at highest non-weld load

previously described (13).

2,2'-Thio-bis[ethyl 8-(1,4,5,6,7,7-hexachloro-3-octylbicyclo[2·2·1]-5-hepten-2-yl)octanoate: I (137 g), 2,2'-thiodiethanol (13.8 g), 50 ml of benzene, and 0.5 g of 2-napthalenesulfonic acid were placed in a flask equipped with reflux condenser and Dean-Stark trap. The temperature was raised to reflux and was maintained there until water had ceased to be azeotroped. The product was passed through a column of activated alumina to remove any remaining hexachlorocyclopentadiene adduct (I) as previously described (14). NMR spectra confirmed the product and showed the absence of carboxyl and hydroxyl groups.

Tetrathioester Reaction Product of 0,0-Dibutyl Phosphorodithioic Acid and N-[tris(9,10-epoxystearoyloxymethyl)methyl]-9,10-epoxystearamide (#12)

N-[tris(oleoyloxymethyl)methyl]oleamide (II): A sample of 24.2 g of tris(hydroxymethyl)aminomethane was refluxed with 230 g of oleic acid in the presence of benzene until water of condensation was no longer evolved. The crude mixture was washed with 10% aqueous HCl, water, dried over anhydrous Na_2SO_4, passed through an activated alumina column, and stripped.

Epoxidation of II: Eighty grams of the product of the above reaction was epoxidized by the dropwise addition (with stirring) of a chloroform solution of m-chloro-perbenzoic acid containing 47 g of the peracid. Excess peracids were reduced with 10% solution of sodium thiosulfite, after which the total acid was washed out with a 10% solution of $NaHCO_3$. The product was washed with water, dried over anhydrous Na_2SO_4, filtered, and stripped.

Preparation of the tetrathioester: A sample of 64.8 g of 0,0-dibutyl phosphorodithioic acid was added dropwise, with stirring and under a nitrogen blanket, to 82.8 g of the epoxidized product. The very viscous mixture was diluted with 50 ml of benzene and 50 ml of absolute ethyl alcohol and warmed, with stirring, to 60 C for 2 hr. The mixture was dissolved in diethyl ether and washed with a 10% solution of Na_2CO_3, followed by water washing, dried over anhydrous Na_2SO_4, filtered, and stripped.

Bis[2-(pentachlorostearoyloxy)ethyl] Disulfide (#13)

Samples of 22.5 g of pentachlorostearic acid, 3.9 g of mercaptoethanol, 1 g of p-toluenesulfonic acid, and 50 ml of benzene were refluxed for 16 hr, the water of reaction being concurrently removed by a Dean-Stark trap. The reaction product was transferred to a 250 ml Erlenmeyer flask, 50 ml of water and a spin bar were inserted, and iodine was added to the stirred mixture until the iodine color remained. A small amount of sodium bicarbonate was added carefully to neutralize the HI. The reaction mixture was separated, washed several times with water, dried, and stripped, leaving a quantitative yield of product.

Sulfurized Products (#10 and 11)

The sulfurizations were carried out by adding an equivalent amount of sulfur (calculated at one sulfur atom per double band) to the oil at room temperature and heating with stirring at 175-180 C for 2-3 hr. This part of the procedure was carried out in either of two ways apparently with equal success: (a) while flushing with nitrogen, or (b) while pulling a slight vacuum on the system with the house vacuum to remove any hydrogen sulfide which evolves. The mixture was then allowed to cool and stripped at 75-100 C on full house vacuum for 1 hr to complete the removal of hydrogen sulfide.

1,4-Bis[1,2(3)-dicarbobutoxy-3(2)-9(10)-0,0-dibutylphosphorodithio carbostearoxy) propyl] piperazine (#16)

A sample of 68.4 g of tributyl aconitate was heated with 536 g of oleoyl alcohol in the presence of sodium methoxide at 80 C, under full forepump vacuum, until there was no further elimination of butyl alcohol. The crude product was washed with aqueous HCl, then with water, dried, and percolated through an activated alumina column, then stripped. A sample of 77.2 g of this product was heated at 90 C with 9.7 g of anhydrous piperazine, with stirring, for 15 hr. The crude product was dissolved in a 1:1 solution of benzene and hexane mixture, washed repeatedly with water, dried, and stripped. Samples of 23.2 g of the resulting product and 9.7 g of 0,0-dibutylphosphorodithioic acid were heated to 60-70 C for 8 hr, with stirring. The crude reaction product was dissolved in diethyl ether and washed three times with 35 ml of 10% sodium bicarbonate, followed by several water washes. The washed product was dried over anhydrous Na_2SO_4, filtered, and stripped. The other compounds listed in Table I were prepared by suitable modification of the procedures

TABLE II

Key Elemental Analysis and Estimate of Purity

Sample number	% Phosphorus Found	% Phosphorus Calc.	% Sulfur Found	% Sulfur Calc.	% Chlorine Found	% Chlorine Calc.	Estimate of purity[a] %
1			14.98	16.27			92
7			8.79	8.50			>95
9	8.87	10.39					85
10			14.63	–			**[b]
11			3.58	–	32.91	–	**[b]
12	5.34	5.61					95
13					28.09	34.50	81
14	5.34	5.79					92
15	3.78	5.77					65
16	2.49	3.78					65
17					10.85	20.65	52
18					12.10	20.30	60
19			2.20	2.67			82
20					31.76	31.72	>95

[a] Those samples estimated >95% purity had complete elemental analyses within experimental error of calculated values. These include samples 2-6 and 8, which have been published, see reference 12.

[b] **Structures of sulfurized products not known.

described above, except compounds 1-6 and 8 which have been previously reported (12).

LUBRICANT EVALUATION TEST PROCEDURES

The wear scar diameters were determined using a Precision Four-Ball Wear Tester following a modified procedure of ASTM D 2266-67. The samples were run for 1 hr at 600 rpm at 120 C and under a 50 kg load, with and without an additive. After cleaning the balls with naphtha and hexane, the scar diameters were measured with a Precision Scientific Company (Chicago, IL) microscope assembly.

To extreme pressure tests were made with a Precision Scientific Four-Ball Extreme Pressure Tester, following ASTM procedure D 2596-67T. Tests were run at 1,440 rpm, without application of external heat, for 1 min or until the balls welded, whichever occurred first. The balls were then washed clean with solvent and the scar diameters measured with a Precision Scientific microscope assembly.

The weld point loads reported are reproducible to within one loading increment (± 10 kg for 10 kg loading increments; ± 20 kg for 20 kg loading increments).

RESULTS AND DISCUSSION

The performance of the esters and amides as lubricants and additives for Topaz S-105 paraffin oil (S-105) and di-2-ethylhexyl sebacate (DOS) are reported in Table I. Estimated content of the phosphorous-, sulfur-, or chlorine-containing products in each of the samples is given in Table II.

In examining the data in Table I, it can be seen that the acetylthio derivatives were only moderately effective as EP additives at the 5% level, and gave about equal results with both base oils. Two of them, i.e., sample 1 in S-105 and sample 3 in DOS, were somewhat better as antiwear additives, but the others were poor in this regard.

Better results in general were obtained with the phosphorodithio derivatives. Sample 9 gave good test results at the 5% level in S-105 for both antiwear and EP performance, and was moderately effective as an EP additive to DOS. Sample 12 gave good EP test results in both base oils, and also was moderately effective as an antiwear additive in both base oils. Sample 15 was moderately effective as an EP and antiwear additive in both base oils. Sample 16 gave good antiwear performance in both base oils, but was poor in both as an EP additive. Three of the 5 phosphorodithio compounds evaluated in this study, samples 9, 12, and 16, gave wear scars <0.5 mm at the 5% level in one or both base oils. Anther, sample 15, gave wear scars <0.6 mm at the 5% level in both base oils.

The sulfurized products, samples 10 and 11, and the pentachlorostearic acid derivative, sample 13, were good EP additives in both base oils, but only fair to poor as antiwear additives. The other halogen-containing compounds, samples 17-20, were only fair to poor in both EP and antiwear performance as additives in both base oils.

Sample 11, containing both sulfur and chlorine, gave the best performance as an EP additive of the various compounds evaluated in this study, with a weld point value of 315 kg in both base oils at the 5% level, and exhibited fair antiwear performance in S-105, with a wear scar <0.6 mm.

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