Lubricants and Lubricant Additives: I. Performance Characteristics of N-Mono and N,N-Disubstituted Fatty Amides and Modified Fatty Amides[1]

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ABSTRACT

A number of N-mono and N,N-disubstituted amides of substituted and unsubstituted C_{18} fatty acids have been prepared and evaluated as base lubricants and lubricant additives. The neat epithioamides possess extreme pressure lubricant characteristics and are noncorrosive at normal temperatures. The epithioamides also frequently function as extreme pressure additives and antiwear agents for paraffinic or diester base oils, sometimes in both capacities for both base oils. The intensiveness of these properties correlated directly with the degree of thiirane substitution in the compound. Performance in both these capacities at the same levels of epithioation was dependent upon the N- or N,N-substituent groups present.

INTRODUCTION

Natural oils and fats of vegetable or animal origin have a historical record as lubricants dating back to ancient times. As mechanization progressed and lubricant demands increased, the time proven animal and vegetable fat-based lubricants became relegated more and more, for reasons of cost, availability, and the advent of petroleum, to additive or bolstering roles for petroleum-based lubricants. In addition, the increasing severity of the performance requirements for lubricants and the recognized need for boundary, as well as hydrodynamic, lubrication launched an extensive search for improved lubricants and additives that would meet such service requirements. New compounds derived from natural sources, principally long chain fatty acids, are finding their niche in this important and demanding area (1).

We are reporting some recent findings concerning the use and performance of some N-mono and N,N-disubstituted amides of long chain fatty acids and substituted fatty acids as base lubricants and as antiwear and extreme pressure additives for paraffin-, diester-, and, in some instances, silicone-based lubricants. More specifically, this report concerns itself with the lubricant characteristics of some N- and N,N-substituted oleamides and oleoylimines and the additive capabilities of some of their chlorinated, epithio, dialkyl phosphono, and dialkyl phosphato derivatives. Also reported are some of the problems encountered in the preparation of epithio (thiirane) and phosphorylated derivatives and their resolution.

EXPERIMENTAL PROCEDURES

None of the compounds prepared and evaluated were isolated in a high state of purity. They were prepared, except for the 9,10,12,13-disubstituted stearamides and 9(10)-carboxystearic acid derivatives, from fatty acids, amines, and other reagents as obtained from commercial sources. The disubstituted stearamides noted above were

derived from a 90-95% inhouse preparation of linoleic acid, itself obtained by the urea clathration of safflower fatty acids (2). The 9(10)-carboxystearic acid was prepared inhouse, as reported by Roe, et al. (3).

All N-mono and N,N-disubstituted amide intermediates were prepared by conventional methods involving either condensation of the requisite amine and fatty acid or amine and fatty acid chloride.

Preparations

Because most of the starting fatty acids contained only 80-90% desired acid and because organic conversions are usually less than 100%, the preparations will contain at best 80-90% desired compound, more likely less. Since the crude preparations also were not purified, we can, therefore, expect to find variance between the elemental analyses and theory.

Butyl-9(10)-[N,N-dibutylcarboxamido]stearate: A half esterification of 9(10)-carboxystearic acid by n-butanol was made following the procedure of Roe, et al., (3) for esterification of the terminal carboxyl of the acid. This intermediate then was converted to the half acid chloride-ester by adding thionyl chloride dropwise in 10% excess of equivalence with stirring and subsequent removal of excess thionyl chloride by vacuum distillation. The crude half acid chloride-ester then was added dropwise with stirring to an equivalent wt of dibutylamine in 10 volumes of benzene containing an equivalent wt of pyridine. After the heat of reaction subsided, the pyridine hydrochloride was filtered off, and the mother liquor successively washed with two portions of aqueous hydrochloric acid and then with water until free of mineral acid. The benzene solution then was dried with anhydrous Na_2SO_4, filtered, and percolated through a column of activated Al_2O_3 to remove any residual acidity and also lower the color level. Elemental analysis on the product (sample 18) was as follows: C, 74.10 (theory 75.15); H, 12.23 (theory 12.32); and N, 2.43 (theory 2.83).

N,N-Dibutyl-9(10)-carbobutoxystearamide: Seventy-two g 9(10)-carboxystearic acid was refluxed for 146 hr with 50 g n-butanol, 40 ml toluene, and 1.0 g toluenesulfonic acid. The entire quantity of the resulting diester then was converted to the half-ester (free terminal carboxyl) by adding, with vigorous stirring, 11 g 50% solution of NaOH to an alcoholic solution of the diester (1.25 ml ethanol/g diester) at 70 C. After reaction for a few min at this temperature, the mixture was cooled and acidulated with aqueous hydrochloric acid. The half-ester was extracted with ether, then dried, and the ether stripped off. It had a neutralization equivalent of 422.0 (theory 384). This half-ester then was reacted with 14.8 g thionyl chloride at 70 C for 2 hr following which any unreacted thionyl chloride was distilled off under reduced pressure. The resulting half ester-acid chloride was added dropwise with stirring to 146 g dibutylamine and 8.9 g pyridine in 50 ml benzene. The pyridine hydrochloride was filtered off, the filtrate washed, dried, and the product recovered in the usual manner. The product (sample 19) had the following elemental analysis: C, 75.01 (theory 75.15); H, 12.27 (theory 12.32); and N, 2.56 (theory 2.83).

TABLE IA

Lubricant Characteristics of Some N-Substituted Amides

#	Sample amide	Copper corrosion test ASTM D 130[a] 60 C (100 C)	Evaporation loss at 200 C (%)	Average wear scar diameter, mm — Without additive	Average wear scar diameter, mm — 5% additive[b]	Extreme pressure — Incipient seizure, kg	Extreme pressure — Weld point, kg (sec)	Extreme pressure — Average scar diameter, mm	Extreme pressure with additive — 5% of sample no.	Extreme pressure with additive — Weld point, kg	Extreme pressure with additive — Scar diameter, mm
1	N,N-dimethyloleamide	ST	9.87	0.797	0.987		120		25	140	
2	N,N-dipropyloleamide	ST	13.4	0.908	0.885		120		30	170	
3	N,N-dibutyloleamide	ST	3.68	0.710			140		25	150	
4	N-methyl-N-butyloleamide	ST	10.05	0.607			100				
5	N-methyl-N-amyloleamide	ST				50					
6	N,N-dihexyloleamide	ST	6.26	0.893	0.898		120	---	25	180	
7	N-methyl-N-octyloleamide	ST	6.28								
8	N-methyl-N-phenyloleamide	ST									
9	N,N-dibutylerucamide	ST	6.64	0.758	0.798		120		25	200	
10	N,N-bis(2-methoxyethyl)oleamide	ST	8.80	0.626	0.725		120		25	160	
11	N,N-bis(2-ethoxyethyl)oleamide	ST	8.47	0.597	0.735		120		25	170	
12	N-(2-methoxyethyl)oleamide	ST	9.69	0.420			100		30	170	2.77
13	N-(1-methyl-2-methoxyethyl)oleamide	ST	11.43	0.705			100				
14	N-3(2-ethoxyethoxy)propyloleamide	ST	3.32	0.526			120				
15	N-3[2-(2-ethoxyethoxy)ethoxy]propyloleamide	ST	3.82	0.503			120				
16	Oleoylmorpholine	ST	6.85	0.623	0.658	40	120		25	150	
17	Oleoyl 4-propylpiperidine	ST	1.45	0.847			140				
18	Butyl 9(10)-[N,N-dibutylcarboxamido)stearate	ST									
19	N,N-dibutyl 9(10)carbobutoxystearamide	ST		0.610			120	2.45			
20	Dimorpholide of dimer acid[c]	ST									
21	N,N-dibutylamide of hydrogenated cottonseed fatty acids	ST									
22	Morpholide of hydrogenated cottonseed fatty acids	ST	3.53	0.798	0.958	60	120		25	170	
23	N,N-dibutyl-9,10-dichlorostearamide	ST	3.12	0.642			140				
24	N-3-(2-ethoxyethoxy)propyl pentachlorostearamide	ST	5.56								
25	N,N-dibutyl-9,10-epithiostearamide	ST	8.02	1.67			300				
26	N,N-dibutyl-9,10,12,13-diepithiostearamide	ST (MT)	5.71	0.842			440(46)	3.25			
27	N-3-[2-(2-ethoxyethoxy)ethoxy]propyl-9,10-epithiostearamide	ST		0.707			380(50)				
28	N-3-[2-(2-ethoxyethoxy)ethoxy]propyl-9,10,12,13-diepithiostearamide	ST (MT)									
29	N-9,10-epithiostearoylmorpholine	ST	6.94	0.702			600[d]	2.48			
30	N-9,10,12,13-diepithiostearoylmorpholine	ST (C)		1.06			380(25)	2.68			
31	N-methyl-N-phenyl-9,10-epithiostearamide	ST		0.702			600(34)	2.38			
32	N-methyl-N-[2-(9,10-epithiostearoyloxy)ethyl]-9,10-epithiostearamide	ST					440(30)	2.95			
33	N-[2-(9,10-epithiostearoyloxy)ethyl]-9,10-epithiostearamide	ST		0.523			490(3)	3.15			
34	N-3-[2-(2-ethoxyethoxy)ethoxy]propyl-9(10)-mercaptostearamide	ST		0.668			530(10)	3.47			
35	N,N-dibutyl-9(10)-(dibutylphosphono)stearamide	C		0.690			500	4.50			
36	N,N-dibutyl-[-9(10)-hydroxy-(9)10-dibutylphosphato]stearamide			0.530			150	4.50			
37	N-[9(10)-mercapto-(9)10-dibutylphosphatostearoyl]morpholine	C		0.498			360				
38	1,3-di(9,10-epithiostearoyl)hexahydro-			0.615			280[e]	3.36			

pyrimidine	0.500		70		3.00
Dioctylsebacate	0.872		50	320(30)	
100 or 102 sec paraffin oil	0.803			110	
Topaz oil S-105	0.794			100	
SAE 90 commercial hypoid fluid	0.370			120(15)	
				260	

aASTM = American Society for Testing and Materials, ST = slight tarnish, MT = moderate tarnish, C = corrosion, and SAE = Society of Automotive Engineers.
bSame additive employed as reported in col. 9.
cEmery Industries Empol 1022.
dNo weld, no decomposition, load limit of four ball tester.
eStopped before weld point; sample decomposed or gave off noxious fumes.

N,N-Dibutyl-9,10,12,13-diepithiostearamide (epoxidation step): N,N-Dibutyllinoleamide (132.5 g, 0.34 mole) was epoxidized by the dropwise addition, with vigorous stirring, of a solution of m-chloroperbenzoic acid in chloroform (137.0 g of peracid in 1300 ml $CHCl_3$). Temperature was maintained at 20-25 C during the addition. After an additional 30 min of stirring following the addition, the unconsumed peracid was destroyed by the addition of a 10% solution of sodium sulfite until a negative test was obtained with starch-iodide indicator paper. The by-product m-chlorobenzoic acid was neutralized and washed out with an aqueous solution of sodium bicarbonate (66.5 g $NaHCO_3$ in 600 ml H_2O). The chloroform solution was washed, dried, and stripped. The recovered epoxide, essentially N,N-dibutyl-9,10,12,13-diepoxystearamide, had an oxirane content of 6.0%. Theory is 7.56%.

Epithioation-benzoic method (4): The above diepoxide (100 g) was added slowly, dropwise, with vigorous stirring to a slurry of 111.4 g thiourea, and 178.0 g benzoic acid in 1 liter of acetone. A period of 3 hr was required for the addition. The benzoic acid was neutralized by the addition with vigorous stirring of 78 g Na_2CO_3 in sufficient water to dissolve it. Stirring was continued for an additional hr after the addition of sodium carbonate solution. The reaction mixture was extracted with benzene, the extract washed, dried, and stripped. The recovered N,N-dibutyl-9,10,12,13-diepithiostearamide (sample 26) had the following elemental analysis: C, 69.64 (theory 68.57); H, 10.93 (theory 10.76); N, 3.10 (theory 3.07); and S, 11.17 (theory 14.06).

N-(9,10,12,13-diepithiostearoyl)morpholine (epoxidation step): A sample of 115 g linoleoylmorpholine was epoxidized by the dropwise addition at 20 C with vigorous stirring of 134 g m-chloroperbenzoic acid in 1500 ml chloroform. After stirring for an additional 30 min, the excess peracid was reduced with 10% Na_2SO_3 and the total acid neutralized and extracted with 32.5 g $NaHCO_3$ as a 10% aqueous solution. After several water washes, the chloroform was stripped off and the N-(9,10,12,13-diepoxystearoyl)morpholine recovered. It had an oxirane content of 7.23% as opposed to an anticipated 8.39%.

Epithioation-sulfuric acid method (5): Sulfuric acid (30.4 g, 0.31 mole) in 100 ml water was added to 42.2 g (0.62 mole) thiourea and the mixture cooled to 5 C. N-(9,10,12,13-Diepoxystearoyl)morpholine (118 g, 0.31 mole) dissolved in 250 ml 1,4-dioxane was added dropwise with stirring over a 2 hr period to the thiourea-sulfuric acid solution. The temperature was maintained at 5 C during the addition but was afterwards raised to 40 C, and the reaction mixture stirred for 2 hr while cooling. The reaction mixture then was neutralized by the addition of 33 g (0.31 mole) sodium carbonate in 300 ml water with vigorous stirring. The neutralized mixture was warmed to 40 C, stirred for an hour, cooled, and extracted with three 125 ml portions of diethyl ether (benzene is also a suitable solvent). The ether extract was washed, dried, and stripped. (If desired, the epithio compound in benzene may be percolated through an activated aluminum column to remove any hydroxy derivative present). The elemental analysis of the N-(9,10,12,13-diepithiostearoyl)morpholine (sample 30) was as follows: C, 64.22 (theory 63.89); H, 9.58 (theory 9.99); N, 3.78 (theory 3.39); and S, 13.21 (theory 13.92).

N,N-dibutyl-9(10)-[dibutylphosphono]stearamide: N,N-Dibutyloleamide (100 g, 0.25 mole), dibutyl phosphite (148 g, 0.75 mole) and benzoyl peroxide (1.290 g, 0.0053 mole) were reacted at 115 C for 3-1/2 hr. Additional benzoyl peroxide (1.290 g) was added after the first hr and again after the second hr. (Except for the peroxide initiator, this is the process reported by Sasin, et al. [6].) The reaction mixture then was washed with 10% Na_2CO_3 several times followed by water washes, then dried, and stripped exhaustively under reduced pressure to remove any unreacted dibutyl phosphite. The product (sample 35) gave

TABLE IB

Physical Characteristics of Some Neat N-Substituted Amides

| Sample[a] | Kinematic viscosity at | | Viscosity index[b] | ASTM[b] slope | Kinematic viscosity at | | Percent change | Density gm/ml at 30 C |
	100 F	210 F			-40 F initial	-40 F after 3 hr		
1	8.55	2.58	158	0.715	solid			0.8806
2	13.74	3.31	124	0.738				
3	12.37	3.27	152	0.704	3210	3237	0.7	0.8621
4	12.48	3.32	157	0.697	solid			
5	17.39	4.23	169	0.669				0.8673
6	20.22	4.41	143	0.698	4459	4903[c]	9.9	0.8558
7	19.91	5.19	227	0.598				0.8646
9	24.46	4.74	125	0.720				0.8594
10	15.81	3.60	122	0.736	4778	---	---	0.9136
11	15.97	3.74	137	0.715				0.8943
12	37.50	6.04	117	0.720				
13	58.77	6.92	75	0.777				
14	40.05	6.44	122	0.707				
15	39.80	6.77	138	0.679				
16	24.00	4.69	125	0.720				0.9341
17	22.75	4.77	145	0.695				0.8905
18	36.54	5.78	109	0.736	3400			
19	92.37	17.48	219	0.493				
20	1138.0	44.37	81	0.677				
21	18.24	3.95	124	0.724				0.8691
22	28.88	5.16	119	0.729				0.9300
23	73.0	7.76	71	0.726				
25	64.40	7.77	92	0.744				1.0884
26	102.75	10.19	86	0.734				0.9926
27	63.92	8.84	123	0.682				0.9573
29	55.39	7.46	105	0.724				
30								1.0624
31	d							0.9241
33	347.1	34.9	153	0.544				
34	76.8	11.69	157	0.606				0.9189
35	33.0	5.81	131	0.703				
36								1.0366
37	411.18	27.48	99	0.651				1.0930

[a]Sample numbers correspond to same compounds in Table IA.

[b]American Society for Testing and Materials Viscosity Index Tables, ASTM Data Series, DS39a (7).

[c]Mushy solid present.

[d]Increasing flow time with time.

a phosphorus analysis of 5.09% (theory 5.28%) and showed strong absorption bands at 9.3, 9.75, and 10.2 μ, characteristic of phosphonates.

N-3-[2-(2-ethoxyethoxy)ethoxy]propyl-9(10)-mercapto-stearamide: A CCl_4 solution containing 173.0 g (0.38 mole) N-3-[2-(2-ethoxyethoxy)ethoxy]propyloleamide was treated in the cold with a bromine-carbon tetrachloride solution containing 60.9 g (0.38 mole) bromine. The unreacted bromine was removed by a thiosulfate wash, and the washed brominated product (containing 23.31% bromine) was added to a solution of dimethyl sulfoxide (DMSO) and sodium sulfide (91.0 g $Na_2S \cdot 9H_2O$, 0.38 mole) at 80 C. The reaction mixture was stirred and maintained at 80 C for 3 hr, the DMSO washed out with water, and the product extracted with hexane. An elemental analysis on the product (sample 34) showed 4.24% sulfur present. The theory for complete conversion of the bromine content is 5.72%.

N,N-dibutyl-9(10)-hydroxy-10(9)-dibutylphosphatostea-ramide: Dibutyl hydrogen phosphate (44.7 g, 0.21 mole) was added with stirring to 110 g N,N-dibutyl-9,10-epoxy-stearamide containing 3.4 g (0.21 moles) oxirane oxygen at 85-90 C and the reaction allowed to continue for 1-1/2 hr (5). The reaction product was dissolved in commercial hexane and any unreacted dibutyl hydrogen phosphate washed out with a small portion of 10% aqueous $NaHCO_3$ (until CO_2 is no longer liberated). The hexane extract was then slightly acidulated with HCl, washed, dried, and stripped. This product (sample 36) had a mol wt of 700 (expected 619) and had the following elemental analysis: C, 66.56% (theory 65.91); H, 11.04 (theory 11.30); N, 2.90

(theory 2.26); and P, 3.04 (theory 4.20).

N-[9(10)-mercapto-10(9)-dibutylphosphatostearoyl]-morpholine: Dibutyl hydrogen phosphate (120 g, 0.175 mole) was added dropwise to 51.0 g (0.133 mole) of well stirred 9,10-epithiostearoylmorpholine at 85-90 C. Stirring and heating were maintained during the 3 hr period allowed for reaction. Unreacted dibutyl hydrogen phosphate was washed out of a hexane solution of the reaction mixture with aqueous 10% $NaHCO_3$, followed by several water washes. The hexane solution then was dried with anhydrous sodium sulfate. During drying and afterwards, there was a loss of solubility of the phosphorylated product in the hexane and a phasing out into two liquid layers. (Before phosphorylation the original epithio compound was freely soluble in hexane.) The recovered product (sample 37), after stripping, gave the following elemental analysis: N, 2.89 (theory 3.32); S, 3.27 (theory 2.17); and P, 1.68 (theory 2.10).

Lubricant Evaluation Test Procedures

Kinematic viscosities were determined in thermostated baths maintained at 100 and 210 ± 0.03 F using calibrated Zeitfuck viscometers. Viscosity index values were obtained from American Society for Testing and Materials Viscosity Index Tables calculated from kinematic viscosity, ASTM Data Series, DS 39a (7). Densities were determined pycnometrically at 30.0 ± 0.01 C. Evaporation losses were determined by observing the wt loss suffered by 10 ml sample maintained at 200 C for 3 hr in a 50 ml volumetric flask with a sustained air flow of 1 liter/min over the surface of the sample.

TABLE II

Performance of Some N-Substituted Amides as
Extreme Pressure and Antiwear Additives for Paraffin Base Oils

| Base oil | Additive[a] | | mm | | | Extreme pressure performance | | |
	Sample no.	Amount %	Load kg	Average wear no additive	Scar with additive	Load kg	Weld point, kg (sec)	Scar diameter, mm
100 or 102 sec paraffin oil	---	---	50	0.803	---	---	100	---
	23	5	50	---	0.917	---	---	---
	29	5	---	---	---	120	---	2.00
	29	5	---	---	---	140	---	2.80
	29	5	---	---	---	160	---	3.25
	29	5	---	---	---	---	180(10)	---
	29	10	---	---	---	170	---	3.55
	29	10	---	---	---	---	180(5)	---
	26	5	---	---	---	140	---	1.90
	26	5	---	---	---	200	---	2.35
	26	5	---	---	---	220	---	2.75
	26	5	---	---	---	---	240(5)	---
	26	10	---	---	---	---	230(21)	---
	30	5	50	---	0.620	150	---	2.47
	30	5	---	---	---	200	---	2.98
	30	5	---	---	---	210	---	3.11
	30	5	---	---	---	---	220(10)	---
	30	10	50	---	0.512	220	---	1.96
	30	10	---	---	---	250	---	1.99
	30	10	---	---	---	300	---	2.47
	30	10	---	---	---	---	310(5)	---
	27	5	50	---	0.782	---	150	---
	34	5	50	---	0.807	---	160	---
	30[b]	5	50	---	0.798	---	140	---
	35	5	50	---	0.803	---	---	---
	36	5	50	---	0.498	---	160	---
	37	5	50	---	0.552	---	---	---
	19	5	50	---	0.818	---	---	---
	24	5	50	---	0.953[c]	140	---	2.10
	24	5	---	---	---	170	---	2.91
	24	5	---	---	---	---	180(22)	---
Topaz S105	32	5	50	---	0.460	120	---	2.65
	32	5	---	---	---	160	---	3.28
	32	5	---	---	---	180	---	3.32
	32	5	---	---	---	---	190(17)	---
Paraffin oil 102 sec	33	5	50	---	0.668	120	---	1.80
	33	5	---	---	---	160	---	2.18
	33	5	---	---	---	180	---	2.43
	33	5	---	---	---	190	---	2.51
	33	5	---	---	---	---	200(52)	---
	28	5	50	---	0.702	120	---	1.37
	28	5	---	---	---	160	---	2.31
	28	5	---	---	---	180	---	1.59
	28	5	---	---	---	190	---	2.26
	28	5	---	---	---	---	200(5)	---
	31	5	50	---	0.500	120	---	2.53
	31	5	---	---	---	130	---	2.62
	31	5	---	---	---	---	140(20)	---
Topaz S105	38	5	---	---	0.450	120	---	2.81
	38	5	---	---	---	130	---	2.94
	38	5	---	---	---	---	140(15)	---
Topaz S105	---	---	50	0.806	---	---	120(15)	---

[a]Sample no. same as in Table I.
[b]Lower thiirane content.
[c]Partially soluble.

Corrosion tests were run in accordance with ASTM D130 (7). Polished copper strips were immersed for 3 hr at the specified temperature, then removed, and compared with a polished original. The corrosion observed was rated in accordance to the classification schedule given in the ASTM test (7).

The scar diameters were determined using a Precision Four-Ball Wear Tester, following a modified procedure of ASTM D 2266-67 (7). 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 using a Precision Scientific Co., Chicago, Ill., microscope assembly.

The extreme pressure tests were made using a Precision Scientific Four-Ball Extreme Pressure Tester following ASTM procedure D 2596-67T (7). The tests on the samples were run at 1440 rpm without application of external heat for 1 min or until balls welded (whichever occurred first). The balls then were washed clean with solvent, and the scar diameters were measured using a Precision Scientific microscope assembly. The point of incipient seizure seldom was determined because of the limited quality of material available. 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

In the preparation of N-mono and N,N-disubstituted mono- and diepithioamides via the epoxide-thiourea reaction, a wide variability of oxirane to thiirane conversion frequently and unpredictably was encountered, even though the procedure of Bordwell and Anderson (4) employing a threefold equivalence of thiourea and benzoic

TABLE III

Performance of Some N-Substituted Amides as Extreme Pressure
and Antiwear Additives for Di-2-ethylhexyl Sebacate

	Additive					Extreme pressure performance		
	Sample no.[a]	Amount %	Load kg	Average wear no additive	Scar with additive	Load kg	Weld point, kg (sec)	Scar diameter, mm
Di-2-ethylhexyl sebacate	---	---	50	0.872	---	---	110[b]	---
	26	5	50	---	0.837	120	---	1.51
	26	5	---	---	---	180	---	1.59
	26	5	---	---	---	---	---	2.47
	26	5	---	---	---	---	200(4)[c]	---
	26	10	---	---	---	240	---	2.95
	26	10	---	---	---	260	---	3.55
	26	10	---	---	---	---	270(10)	---
	29	5	50	---	0.915	80	---	1.57
	29	5	---	---	---	120	---	2.03
	29	5	---	---	---	140	---	2.41
	29	5	---	---	---	160	---	2.94
	29	5	---	---	---	180	---	3.00
	29	5	---	---	---	---	200(5)	---
	29	10	---	---	---	190	---	3.27
	29	10	---	---	---	---	200(4)	---
	30	5	50	---	0.810	150	---	2.32
	30	5	---	---	---	220	---	2.98
	30	5	---	---	---	240	---	3.11
	30	5	---	---	---	---	250(15)	---
	30	10	---	---	---	250	---	2.87
	30	10	---	---	---	270	---	2.28
	30	10	---	---	---	300	---	2.47
	30	10	---	---	---	340	---	2.48
	30	10	---	---	---	---	350(7)	---
	27	5	50	---	0.960	---	150	---
	34	5	50	---	0.905	---	180	---
	30[d]	5	50	---	0.867	---	150	---
	35	5	50	---	0.980	---	---	---
	36	5	50	---	0.498	---	160	---
	37	5	50	---	0.535	---	---	---
	19	5	50	---	0.945	---	---	---
	24	5	50	---	0.362	160	---	3.38
	24	5	---	---	---	180	---	3.06
	24	5	---	---	---	200	---	2.93
	24	5	---	---	---	220	---	3.05
	24	5	---	---	---	---	230(17)	---
	32	5	50	---	0.797	120	---	2.55
	32	5	---	---	---	140	---	2.95
	32	5	---	---	---	200	---	3.43
	32	5	---	---	---	210	---	3.52
	32	5	---	---	---	---	220(20)	---
	33	5	50	---	0.443	120	---	1.69
	33	5	---	---	---	140	---	1.82
	33	5	---	---	---	150	---	2.18
	33	5	---	---	---	---	160(60)	---
	28	5	50	---	0.565	120	---	1.93
	28	5	---	---	---	160	---	2.48
	28	5	---	---	---	170	---	2.78
	28	5	---	---	---	---	180(3)	---
	31	5	50	---	0.907	120	---	2.35
	31	5	---	---	---	140	---	3.17
	31	5	---	---	---	150	---	3.23
	31	5	---	---	---	---	160(10)	---
	31	5	---	---	---	---	---	---
	38	5	50	---	0.937	120	---	2.30
	38	5	---	---	---	140	---	2.48
	38	5	---	---	---	160	---	2.74
	38	5	---	---	---	170	---	2.89
	38	5	---	---	---	---	180(10)	---

[a]Sample no. same as in Table I.
[b]Incipient seizure 70 kg.
[c]Incipient seizure 190 kg.
[d]Lower thiirane content.

acid to that of the epoxide was being followed. Replacement of the benzoic acid by acetic acid decreased the variability but drastically reduced conversions. Recourse to the method of Kaufmann and Schickel (5) employing thiourea and sulfuric acid in equivalence to the epoxide present resulted in considerable improvement in maximum degree of conversion attainable but provided little relief from the problem of conversion variability encountered in successive preparations of the same compound. It eventually became evident from a review of the accumulated experimental data that the rate of addition of epoxide to the reaction mixture was the neglected but important parameter, a slow but constant rate of addition being consonant with high consistent conversions and rapid or erratic additions conducive to low and highly variable conversions. Uneven intermittent addition rates, as might result from total or spasmodic plugging of stopcock bores, are conducive to unpredictable, but usually intermediate, conversion levels irrespective of the overall duration of the addition period.

TABLE IV

Performance of Some N-Substituted Amides as
Extreme Pressure and Antiwear Additives for Silicone Oils

| | Additive | | | | | Extreme pressure performance |
	Sample no.	Amount %	Load kg	Average wear no additive	Scar with additive	Weld point, kg (sec)
Silicone oil (GE 1017)	none	none	5	2.36	---	130
	none	none	50	4.16	----	---
	29[a,b]	5	5	---	1.38	190
	29[a,b]	5	50	---	4.32	---
	26[a,b]	5	5	---	0.41	230
	26[a,b]	5	50	---	3.07	---
	30[a,b]	5	5	---	1.62	180
	30[a,b]	5	50	---	3.36	---
	36[a,b]	5	5	---	1.41	160
	36[a,b]	5	50	---	3.54	---
	37[a,b]	5	5	---	1.34	200
	37[a,b]	5	50	---	3.52	---

[a]Sample no. of additive corresponds to sample no. of Table I.
[b]Insoluble and ineffectual in General Electric SF 97 and Dow Cornings DC200 and DC510.

As base lubricants, most of the unmodified N-mono and N,N-disubstituted amides of oleic acid (Tables IA and IB, samples 1-17) and certain fatty acid mixtures (samples 21 and 22) exhibit viscosity index values in excess of 100 and wear-scars and weld loads generally comparable to those of unbuilt paraffinic or diester oils. Some of these amides, particularly those incorporating an ether group in the N-substituent group, exhibit lower wear-scars than do the unbuilt controls, and the N-alkoxyalkyl oleamides almost equal the wear-scar performance of a built oil, such as Gulfpride Single G, MS, multiviscosity. Several of these materials, therefore, appear to have potential as lubricants at normal environmental temperature. Few, however, would qualify as subnormal low temperature lubricants as evidenced by viscosity characteristics at -40 F. Only one, N,N-dibutyloleamide, sample 4, meets the viscosity requirements at -40 F set forth in military specifications MIL-L-6081C for grade 1010 lubricants. However this compound partially solidified at -65 F and fails to meet the specifications for grade 1015 lubricant under MIL-L-6081C.

On the basis of bench evaluation, the most promising sphere of application for these amides, when suitably modified, is as antiwear and extreme pressure (EP) additives. With few exceptions, the modified N-mono or N,N-disubstituted amides of Table I, samples 25-38, have EP performances, i.e. weld points, superior to that of the control SAE no. 90 commercial hypoid fluid. This is particularly true for the neat epithio and diepithio derivatives where weld points in excess of 400 kg are common and values of 600 and 600+ kg have been observed for two of these compounds, 9,10,12,13-diepithiostearoylmorpholine and 3-[2-(2-ethoxyethoxy)ethoxy]propyl-9,10,12,13-diepithiostearamide, respectively. These two specific compounds also function as EP and antiwear additives, the first one particularly so with a paraffin base oil and the second in di-2-ethylhexyl sebacate (DOS). The performance characteristics of these samples, 28 and 30, and the other modified amides as additives for paraffin and DOS base lubricants are reported in Tables II and III, respectively.

In selected instances the modified N-mono and N,N-disubstituted amides also function as EP antiwear additives for silicone oils (Table IV). N,N-Dibutyl-9,10,12,13-diepithiostearamide was the most effective of those evaluated at the 5% level in this respect with General Electric SF-1017 silicone oil. It was poorly soluble and ineffective in three other silicone oils, GE SF-97 and Dow Corning DC-200 and 510, as were the other modified N-substituted amides evaluated.

It has been a general observation that the insertion of

the thiirane group, -C—C-, into the acyl moiety of the
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amide invariable confers EP lubricant characteristics to the basic compound and does so without imparting any significant corrosivity after 3 hr at 60 C, as determined by the copper strip test (ASTM D 130-68) (7). The degree of enhancement in this performance category at the same level of epithioation varies with the precursor compound. Obviously, in the current series of compounds with basically similar acyl moieties, this means that the N- or N,N-substituent groups are factors of major influence in determining EP performance characteristics.

The antiwear performance of the epithio compound is dependent to an even greater degree upon the N- or N,N-substituent group. On the whole the antiwear performance of the epithio compounds neat is usually poor, most often poorer than that of the unepithioated precursor. However, many of these compounds are surprisingly effective as antiwear additives for paraffinic or diester base oils (sample 24, Table III, and 32, Table II) and in some instances for both (sample 36, Tables II and III). Again, the N- or N,N-substituent group plays a most decisive role in the performance of the epithioamide as an additive in a particular type of base oil, i.e. paraffinic, diester, or silicone. If all other factors are equal, performance correlates with the degree of epithioation, i.e. diepithiostearoylmorpholine is more effective than epithiostearoylmorpholine.

In an attempt to improve further the performance of modified amides as additives, two phosphorylated derivatives were prepared (8). The performances of these products are reported in Tables I, II, and III, samples 36 and 37. The test results show that phosphorylation is conducive to good antiwear performance in either base oil. The effect on the EP performance of the neat materials, although based upon one sample, appears to be adverse. The effect on their performance as EP additives is not known.

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