

Sulfurized Esters Derived from Tallow, Lard, and Other Fats as Lubricant Additives

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Fatty esters were prepared from tallow, lard, fish oil and oleic acids, and commercially available saturated n-alcohols (C₈, C₁₀, C₁₂). The esters were generally liquid at room temperature and had iodine values ranging from 25 to 92. They were sulfurized under conditions designed to impart to them desirable high-temperature lubricant properties. The sulfurized esters, containing 6 to 7 percent sulfur, were evaluated, and generally, they corroded copper minimally, exhibited good solubilities in paraffin oil, and displayed better antiwear and extreme-pressure properties than the unsulfurized species. The lubricant properties of these esters were shown to be similar to those of sperm oil sulfurized to the same level of sulfur under identical reaction conditions. These esters, therefore, may serve as model compounds for possible sperm whale oil replacements.

INTRODUCTION

The authors' interest in the increased utilization of animal fats, and/or their derivatives in lubricant formulations, has led to an investigation of sulfurization of fat-derived unsaturated esters and the lubricant properties of the products thus obtained. Moreover, interest in sulfurized fat-derived esters has increased because of the unavailability of sperm whale oil (3) and the search for suitable replacements. The authors' specific interest in mono-functional long chain esters derived from glycerides, rather than in the glycerides themselves, or in other fatty moieties, stems from two basic considerations: 1. Sperm whale oil itself is composed principally of wax esters (70–75 percent), and 2. sulfurized wax esters reportedly possess better lubricant properties than their triglyceride counterparts, e.g., solubility and stability characteristics (2). Sulfurization itself is not a new process (1), and has traditionally been applied to lard oil (2) and sperm whale oil (2) to convert them to antiwear and extreme-pressure additives for use in gear, metalworking, and other lubri-

cant compositions. Sulfurization is generally considered an art, the conditions varying from company to company, and, therefore, not much about the effect of reaction parameters on lubricant properties has been published. There are various aspects to the sulfurization process, all rather important, including:

1. Materials amenable to sulfurization (monoene vs. polyene)
2. Sulfurization conditions
3. Chemical nature of the sulfurized species (e.g., dithiol vs. thiol ethers) (1) and
4. Importance of the carboxylic acid or ester function to lubrication (2, 6).

Although efforts have been made in the above areas, in the present report the authors are concerned only with the preparation of esters suitable for sulfurization, the sulfurization itself, and the lubricant properties of the sulfurized materials obtained.

In choosing starting materials, cost and availability were considered. Ideally, it should be possible to take an animal fat, e.g., lard or tallow, and an unsaturated alcohol, effect an alcoholysis, and obtain an ester with appropriate unsaturation for sulfurization to a given level. Unlike saturated alcohols, however, unsaturated alcohols are unavailable commercially or are prohibitively costly. Although in subsequent studies the authors prepared esters by alcoholysis of triglycerides with long chain saturated alcohols, for the present study a mixture of acid and alcohol were merely reacted in the presence of BF₃-etherate to obtain the desired ester.

The sulfurization procedure adopted was based on commercial processes. The products obtained thereby were screened in the laboratory with regard to copper strip activity, percent sulfur, solubilities, and antiwear and extreme-pressure characteristics. These are only bench-type tests, of course, and the ultimate test for sulfurized additives is acceptance by users following in-use testing and evaluation.

In the present report it has been demonstrated that sulfurized, fat-derived esters can meet performance requirements for use as antiwear lubricant additives and, moreover, serve as preliminary models for sperm oil replacements.

EXPERIMENTAL TECHNIQUE

Materials

The lard, tallow, Menhaden fish oil and 47° sperm oil were obtained from local suppliers and had chemical compositions and physical properties typical of these naturally occurring products. The oleic acid used was a technical grade commercial product consisting of 91 percent mono-unsaturated, 3 percent polyunsaturated and 6 percent saturated acids.

The saturated primary alcohols (nC_8 , nC_{10} , nC_{12}) were of reagent grade purity.

Antiwear properties were performed using a light mineral oil (Base oil A) with a kinematic viscosity of 23.6 cs, at 100 F, VI 54. The EP and solubility properties were studied using a high viscosity index paraffin base oil (bright stock) with a kinematic viscosity of 571.0 cs at 100 F, VI 96.

Determination of Properties

Cloud points and pour points of unsulfurized esters were determined by ASTM Method D97-57. Iodine numbers were measured by the Wijs procedure, ASTM Method D1959. Antiwear properties were determined with the four-ball wear tester as described by ASTM Method D2266-72 under the following conditions: temperature, 120 C (248 F); load, 50 kg at 600 rpm for one hour. Extreme-pressure properties were measured with the four-ball EP tester (1730 rpm) in which loads were successively increased first in 20- and then in 10-kg increments until an immediate seizure occurred, representing the weld point. Kinematic viscosities of the sulfurized esters were measured as described by ASTM Method D-445 at 210 F.

Copper Strip Activity

Copper strip activity was estimated by immersing a freshly polished copper strip (0.5 in wide) in the neat sulfurization reaction mixture at 170 C (338 F) for one minute and comparing the results to those described in ASTM Method D130-65. Corrosion activity was also determined on a 5 percent solution of the sulfurized esters in bright stock at 212 F for three hours.

Preparation of Fatty Esters

Fatty acids, with the exception of the already-available oleic acid, were prepared by saponifying the appropriate fat or oil with sodium hydroxide in refluxing 95 percent ethanol, then treating the basic solution with hydrochloric acid to liberate the free acids which were recovered and mixed with an equimolar amount of alcohol (1-octanol, 1-decanol, 1-dodecanol) containing 20 percent by weight of BF_3 -etherate. The mixture was then heated to 100 C

(212 F) for 15 minutes. Water was added and the ester extracted with hexane. The hexane solution was dried over anhydrous sodium sulfate, and passed through a short Florisil column to remove unreacted free acids. Ester recovery was 95 percent; purity (98 percent) was determined by infrared spectroscopy and by TLC.

Sulfurization Procedure

The fatty esters (18.0 g, approx. 0.04 mole) were placed in a 100-ml round-bottom 3-necked flask equipped with an air condenser and a magnetic stirrer. The flask was placed in an oil bath and the temperature maintained at 172 ± 2 C (338 F). Sulfur (2.0 g, 0.0625 mole) was then added slowly over a 30-minute period. The copper strip test (170 C for one minute) was run on the reaction mixture at one hour intervals until a grade 3 or lower level was reached.

DISCUSSION OF RESULTS

Properties of Unsulfurized Esters (Table 1)

Pour points of the esters prepared ranged from 5 F to 93 F. With the exception of the *n*-dodecyl tallowate, the esters were liquids at room temperature. Alcohols chosen for the esterification of the fatty acids represent upper and lower limits of chain length with regard to both acceptable liquid and volatility characteristics of the resulting esters. Alcohols above C_{12} would have yielded solid esters (at ambient temperature), whereas those below C_8 would have resulted in the formation of esters too volatile for the sulfurization procedure.

As expected, cloud points, pour points, and iodine numbers were shown to be a function of average molecular weight (or carbon number) of the esters. Cloud points and pour points increased and iodine numbers decreased

TABLE 1—LUBRICANT PROPERTIES OF ESTERS PRIOR TO SULFURIZATION

ESTER		ESTER PROPERTIES			5% ESTER IN BASE OIL A
FATTY ACID SOURCE	ALCOHOL*	CLOUD POINT °F	POUR POINT °F	IODINE No.	WEAR SCAR mm
Base Oil A.....	...	5	-15	1.4	0.80
Tallow.....	C_6	75.2	60.8	29.9	0.80
	C_{10}	77	71.6	26.5	0.70
	C_{12}	93	93	24.5	0.51
Lard.....	C_8	66.2	50	41.7	0.84
	C_{10}	68	59	36.7	0.80
	C_{12}	77	73.4	34.1	0.58
Oleic.....	C_8	37.4	5.0	60.8	0.69
	C_{10}	55	24	56.4	0.66
	C_{12}	64.4	41	52.4	0.68
Fish.....	C_8	48.2	35.6	91.9	0.80
	C_{10}	69.8	59	84.3	0.77
	C_{12}	83	78.8	70.9	0.75
Sperm oil....	...	59.6	49.0	82.9	0.78

* Commercial saturated alcohols.

with increasing carbon number. Wear scar diameters produced by the esters (5 percent in petroleum oil) were also a function of carbon number, except in the case of the oleate esters in which the wear scar diameter obtained with the *n*-decyl oleate was smaller than that obtained with the *n*-dodecyl oleate. Generally, one would expect the antiwear properties to improve as the carbon number of the ester increased, and this is reflected by the wear scar data presented.

Iodine values of the esters varied from 25 to 92. Except for the menhadenate series, however, the esters exhibited iodine values that were lower than those of sperm oil. The high iodine values of the menhadenate esters were attributable to the polyunsaturation of the fish oil acids which was also not characteristic of sperm oil. Nonetheless, these esters, easily prepared from readily available starting materials, allowed the study of the effect of sulfurization on a series of compounds having a wide range of iodine values. The iodine values of the esters could have been raised, moreover, by a low temperature filtration procedure which would have removed saturates. This is a possibility for future work.

Sulfurization

Sulfurization of the fatty esters listed in Table 1 was directed towards maximizing antiwear and anticorrosion properties of the sulfurized products. To achieve acceptable anticorrosion properties, the reaction mixture was monitored by measuring its activity toward copper, and reaction was continued until a copper strip activity grade of 3 was attained. Thus, sulfurization times varied from two to eight hours depending on the degree of unsaturation in the starting materials, the highly unsaturated esters derived from fish oil acids giving an acceptable copper strip test after two to three hours of sulfurization, and the less unsaturated esters derived from tallow and lard acids after six to eight hours. Although in the sulfurization procedure 10 percent (by weight) of sulfur was added during the course of the reaction, only 6 to 7 percent sulfur was incorporated into the esters.

Analysis of the sulfurized products by infrared spectroscopy indicated that after sulfurization the ester function remained intact, and unsaturation was no longer present. Prior to sulfurization, each series of esters moved as a single spot on TLC plates. However, sulfurization produced a number of different species with different chromatographic mobilities, as indicated by TLC.

Properties of Sulfurized Esters

The sulfurized esters (Table 2) were liquid at room temperature with the exception of sulfurized *n*-dodecyl tallowate and sulfurized *n*-dodecyl menhadenate. At 210 F, the kinematic viscosities all showed an increase with increasing chain length. As a group, the menhadenate esters had relatively high viscosities, due most likely to the presence of polyunsaturation which, during the sulfurization, underwent more extensive cross-linking via sulfur bridges.

TABLE 2—LUBRICANT PROPERTIES OF SULFURIZED ESTERS

SULFURIZED ESTER	% SULFUR	REACTION		KINEMATIC VISCOSITY†	5% ESTER IN BASE OIL A WEAR SCAR
		TIME HRS.			
C ₈ -Tallowate.....	6.17	6		6.12	0.70
C ₁₀	6.54	8		6.25	0.57
C ₁₂ *.....	6.01	6		6.41	0.72
C ₈ -Lardate.....	7.48	8		6.48	0.47
C ₁₀	6.67	6		7.12	0.70
C ₁₂	6.86	6		8.20	0.74
C ₈ -Oleate.....	6.10	3		6.41	0.79
C ₁₀	7.15	4		6.80	0.77
C ₁₂	6.74	4		8.25	0.73
C ₈ -Menhadenate...	7.47	2		11.6	0.67
C ₁₀	6.44	2		12.1	0.48
C ₁₂ *.....	5.89	3		13.2	0.43
Sperm oil.....	7.33	3		36.1	0.68

* Solid at room temperature.

† In centistokes, 210 F.

Wear scar diameters obtained with the sulfurized esters did not show any definite trend relative to average carbon number of starting material. Tallowate, lardate, and menhadenate esters, composed of compounds covering a wide range of molecular weights, did show good antiwear properties under some conditions, but the oleate esters, composed mainly of a single component, showed little improvement in the wear scar with varying sulfur content and reaction times. An increase in the sulfur content and sulfurization reaction time of the tallow- and lard-derived esters did improve their antiwear activity. The polyunsaturated menhadenate esters, however, showed an improvement in the wear scar with decreasing sulfur content. The data indicates that the sulfurization reaction conditions must be optimized for each group of fatty esters to obtain good antiwear properties.

The viscosities of the sulfurized esters varied from about 6 to 13 centistokes (210 F) and increased in each series as carbon number increased. However, all the viscosities were well below that of sperm oil sulfurized under the same conditions. No trends in lubricant performance could be attributed to these variations in viscosities.

Solubility of sulfurized fats in paraffin oil is an important criterion for their utility as lubricant additives. When evaluating potential additives, solubility over an extended period of time in high viscosity index paraffin oil (bright stock) is usually the first test applied. In the course of discussions with lubricant formulators, however, one formulator indicated a preference for testing solubilities in a light petroleum oil rather than the bright stock. At any rate, in the authors' evaluations, solubilities were determined in bright stock. Table 3 presents the solubility data thus obtained, which are generally very satisfactory. All sulfurized esters were soluble at the 5 and 10 percent level in bright stock (over a 90-day period exposed to daylight).

TABLE 3—SOLUBILITY* OF SULFURIZED ESTERS IN BRIGHT STOCK

SULFURIZED ESTER	% IN OIL†				
	25	20	15	10	5
C ₈ -Tallowate.....	S	S	S	S	S
C ₁₀	S	S	S	S	S
C ₁₂	I	I	S	S	S
C ₈ -Lardate.....	S	S	S	S	S
C ₁₀	S	S	S	S	S
C ₁₂	I	S	S	S	S
C ₈ -Oleate.....	S	S	S	S	S
C ₁₀	S	S	S	S	S
C ₁₂	S	S	S	S	S
C ₈ -Menhadenate.....	S	S	S	S	S
C ₁₀	I	S	S	S	S
C ₁₂	I	I	I	S	S
Sperm Oil.....	S	S	S	S	S

* Over a 90 day period.

† S = soluble; I = insoluble.

Insolubility was observed only for the C₁₂ alcohol esters at the 15, 20, and/or 25 percent level, and for the *n*-decyl menhadenate at the 25 percent level. However, the sulfurized esters in the oleate series were uniformly soluble at all levels tested. These, in bright stock, gave a clear red-green solution, which darkened on standing exposed to air and light but, nonetheless, remained stable for at least 90 days.

Copper corrosion tests performed on the 5 percent solutions of the sulfurized fatty esters in bright stock (212 F for three hours) gave grade 1 results. The sulfurized menhadenate esters and sperm oil gave the darkest tarnish (1b) of any of the products tested.

The behavior of the sulfurized esters as extreme pressure (EP) lubricant additives is summarized in Table 4. Weld points for all the sulfurized esters ranged between 160 and 180 kg. Sperm oil that was sulfurized to the 7 percent sulfur level under conditions described herein had a comparable weld point, 190 kg. A commercially sulfurized sperm oil (10 percent sulfur) had a weld point of 210 kg in the same base oil. From the data in Table 4, it seems that the amount or distribution of unsaturation or source of the fatty acid may not be a major factor in EP performance. The sulfur content and the chemical nature of the sulfur bonding, both of which are a function of the specific conditions used in the sulfurization, appear to be important factors contributing to EP performance.

CONCLUSION

Fatty esters, derived from different sources, with varying degrees of unsaturation and chain length, were found to be satisfactory antiwear and extreme-pressure lubricant additives after sulfurization. Because of their low level of copper corrosion activity at elevated temperatures, one

TABLE 4—SULFURIZED AND OTHER ESTERS AS EXTREME-PRESSURE LUBRICANT ADDITIVES*

Sulfurized Ester	% SULFUR	WELD
		POINT (Kg)
Sulfurized Ester		
C ₈ -Tallowate.....	6.17	170
C ₁₀	6.54	170
C ₁₂	6.01	180
C ₈ -Lardate.....	7.48	170
C ₁₀	6.67	160
C ₁₂	6.86	160
C ₈ -Oleate.....	6.10	170
C ₁₀	7.15	180
C ₁₂	6.74	180
C ₈ -Menhadenate.....	7.47	170
C ₁₀	6.44	160
C ₁₂	5.89	160
Sperm oil.....	7.33	190
Unsulfurized Esters		
C ₈ -Lardate.....	0	130
C ₁₀	0	130
C ₁₂	0	120
Bright Stock.....	0	130

* As 5% additive in (high viscosity index) bright stock.

possible use for these sulfurized derivatives would be as additives in motor oils which are exposed to temperatures in the 280–300 F range. In addition, properties of sulfurized esters described herein are comparable, and in some cases superior, to those of sperm oil sulfurized under identical conditions.

These sulfurized esters represent our initial attempts at making satisfactory lubricant additives which could serve additionally as replacements for sperm whale oil in various applications. In the future, the authors' efforts will be directed towards preparing similar esters by more direct methods, and in further optimizing the sulfurization procedure to improve the lubricity of the products obtained.

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