

Sperm Oil Replacements from Selectively Hydrogenated Soybean and Linseed Esters: Special Lubricants

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ABSTRACT

Soybean and linseed oils were selectively hydrogenated with copper-on-silica gel catalyst. The linolenate content of the oils was reduced to diene and monoene with no appreciable increase in saturates. Hydrogenated soybean oils contained 68-76% monoene, 11-18% diene, 0% conjugated diene and triene, 1-6% conjugatable diene, 0-0.3% conjugatable triene, and 23-40% isolated *trans* double bonds. Hydrogenated linseed oils contained 44-54% monoene, 35-45% diene, 0% conjugated diene and triene, 0-7% conjugatable diene, 0-0.2% conjugatable triene, and 44-59% isolated *trans* double bonds. Esters of fatty acids, derived from these selectively hydrogenated oils, were prepared with trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol, ethylene glycol, C₁₈ saturated cyclic alcohols, primary C₁₂-C₁₈ saturated (nC₁₂, nC₁₄, nC₁₆, nC₁₈) alcohol, and primary C₁₆-C₁₈ saturated (nC₁₆, nC₁₈) alcohol blends. Measurements of viscosities and of smoke, flash, and fire points indicate that these esters are possible replacements for sperm oil. Certain of them, after sulfurization, also have potential as extreme pressure lubricant additives.

INTRODUCTION

Under the Endangered Species Act, the United States has placed a ban on the sperm whale and its products. This action has forced a change to sperm oil replacements. The size of this market is estimated to be 50 million pounds annually. Extreme pressure (EP) additives prevent destructive metal-to-metal contact in lubrication at either high pressures or temperatures, or both. Quality replacements are needed in EP lubricants. Many commercial substitutes now available are not multipurpose replacements. For this reason and because of shortages and increased prices of petrochemicals, many are considering sperm oil replacements from agricultural sources.

Previously (1), we described polyol esters of commercial soybean acids, partially hydrogenated, as possible lubricants for the continuous casting of steel. Kinematic viscosity data and smoke, flash, and fire points of certain of these polyol esters indicated that they would be possible substitutes for sperm oil in lubricants.

Others (2-7) have established that certain copper-containing catalysts possess high selectivity for linolenate over linoleate and a greater selectivity for linoleate over oleate in hydrogenating polyunsaturated oils. Low pressure hydrogenations of soybean oil with copper-on-silica gel catalyst were reported earlier by Koritala (8,9). This paper reports new information on high pressure, selective hydrogenation of soybean and linseed oils with copper-on-silica gel catalyst. These hydrogenated oils containing increased amounts of monoene and nonconjugatable diene have unusual thermal and oxidative stability and also sufficient reactivity to permit sulfurization. Esters of fatty acids derived from these selectively hydrogenated oils were pre-

pared with trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol, ethylene glycol, C₁₈ saturated cyclic alcohols, primary C₁₂-C₁₈ saturated (nC₁₂, nC₁₄, nC₁₆, nC₁₈) alcohol, and primary C₁₆-C₁₈ saturated (nC₁₆, nC₁₈) alcohol blends.

Measurements of viscosities and of smoke, flash and fire points indicate that these esters from selectively hydrogenated soybean fatty acids (SHSBA) and selectively hydrogenated linseed fatty acids (SHLSA) are possible substitutes for sperm oil. Certain of them after sulfurization also have potential as EP lubricant additives. In addition, some of the polyol esters developed earlier (1) from commercial soybean acids, partially hydrogenated, were also sulfurized, tested, and evaluated as EP and antiwear additives.

EXPERIMENTAL PROCEDURES

Materials

Refined and bleached soybean and linseed oils came from commercial sources. One lot of linseed oil was re-refined and bleached in the laboratory as outlined by Koritala (8,10). A 15% copper-on-silica gel catalyst was prepared with copper nitrate trihydrate and heat activated in the laboratory (9).

SHSBA and SHLSA were obtained from saponification of the parent selectively hydrogenated oils.

Saturated C₁₈ cyclic alcohol monomers derived from linseed oil were prepared as previously reported (11).

Other Reagents

Trimethylolethane (TME) and trimethylolbutane (TMB) were provided by Trojan Powder Co., Division of Commercial Solvents Corp., Allentown, PA; trimethylolpropane (TMP) and pentaerythritol (PE), by Celanese Chemical Co., Division of Celanese Corp., New York, NY; and pure grade ethylene glycol (EG) by Union Carbide Corp., Chemicals and Plastics, New York, NY. A mixture of primary saturated nC₁₂, nC₁₄, nC₁₆, nC₁₈ alcohols (C₁₂-C₁₈ alcohol) and a mixture of primary saturated nC₁₆, nC₁₈ alcohols (C₁₆-C₁₈ alcohol) came from Continental Oil Co., Petrochemical Department, New York, NY. Topaz S105 paraffin oil (Topaz S105) is manufactured by Atlantic Richfield Co., Philadelphia, PA. These reagents were used without further purification.

Hydrogenations

For a typical high pressure hydrogenation, a 6 gal autoclave was charged with 6 liters of commercially refined and bleached soybean oil (acid value 0.01, anisidine value 1.48) and with 56 g of heat activated copper-on-silica gel catalyst (0.1% CuO by volume of the oil). After the vessel was purged with nitrogen and pressurized with hydrogen to 500 psi at room temperature, the charge was heated with stirring to 170 C. Exothermic reactions were controlled with a cooling coil. Hydrogen pressure was then maintained at 600 psi for 7.5 hr. Progress of the hydrogenation was followed by sampling periodically and determining the refractive indices of filtered oil samples. When the desired refractive index was reached, the autoclave was cooled to

¹Presented at the AOCS meeting in Philadelphia, September 1974.

TABLE I
Composition of Selectively Hydrogenated Soybean Oil^a

Run No.	Time at 170 C (hr)	IV ^b	GLC analysis (%)				Diene (%)		<i>trans</i> Isolated (%)	N _D 30
			Saturates		Monoene	Diene	Conjugatable ^c	Nonconjugatable ^d		
			C ₁₆	C _{18:0}	C _{18:1}	C _{18:2}	C _{18:2}	C _{18:2}		
1	5	83	10.1	4.0	75.2	10.7	4.3	5.4	39.8	1.4648
2	6	84	11.3	6.0	67.7	14.8	5.0 ^e	9.8	34.6	1.4645
3	6	89	10.1	4.1	67.6	18.0 ^f	6.2	11.8	35.5	1.4649
4	7.25	84	10.3	3.3	76.0	10.5	1.1	9.4	23.2	1.4649

^aOne gram copper-on-silica gel catalyst per 100 ml oil. Hydrogen pressure 600 psi.

^bIodine values calculated from gas liquid chromatography (GLC).

^cDetermined by UV after alkali isomerization.

^dDetermined by difference between total diene value (by GLC) and conjugatable diene.

^eContained 0.03% conjugated triene.

^fContained 0.2% conjugated diene and trace amount of conjugated triene.

80 C. After the batch was filtered with filter aid, the product and intermediate samples were analyzed. This standard procedure was followed in all hydrogenations. During selective hydrogenations of linseed oil, intermediate samples were not taken. The hydrogenations were conducted until the hydrogen uptake was nil over a period of 0.25 hr.

Preparation of Esters

Esters were prepared by the following general procedure: The alcohol desired and 1-2% excess of either SHSBA or SHLSA were refluxed in the presence of 0.5% of a catalyst consisting of three parts by weight of calcium acetate and one part of barium acetate with xylene (50% by volume, base on acids). In esterifications conducted with polyhydric alcohols, a 1-2% excess of hydrogenated fatty acids was used; in esterifications with monohydric alcohols, the excess of alcohols was also 1-2%. Theoretical amounts of water of esterification were removed by a Dean-Stark trap. After the reaction mixture was washed with water, dried, and stripped of solvent, excess fatty acids or alcohols were removed by high vacuum distillation. IR analysis of esters showed no hydroxyl present. Esters had acid values less than 2.3.

Analytical Methods

Selectively hydrogenated soybean oil (SHSBO) and linseed oil (SHLSO) and the precursory soybean and linseed oils were interesterified with methanolic BF₃ reagent, and gas-liquid chromatographic (GLC) analyses were made on a Hewlett-Packard Model 5750 gas chromatograph equipped with a hydrogen flame detector and a 6 ft 1/4 in. OD stainless-steel column packed with 10% EGSS-X on Gas Chrom. P, 100-120 mesh (organosilicon polyester packing, Applied Science Laboratories, Inc., State College, PA). The column was held at 170 C with a helium flow of 35 ml/min. IR spectra were recorded with a Beckman IR 8 spectrophotometer both for thin films of 100% materials and for carbon disulfide solutions of compounds. UV spectra were obtained on a Beckman DB spectrophotometer. Iodine value (IV) was calculated from GLC analysis or determined by official AOCS method Cd 1-25 (12).

Alkali isomerizations were carried out for 1 hr and the total amounts of conjugatable diene and triene were measured by AOCS Official Method Cd 7-58 (12). Nonconjugatable diene and triene were determined by the difference between total diene and triene by GLC analyses and conjugatable diene and triene by UV analysis. Percentage of isolated *trans* double bonds was determined by IR analyses.

Viscosities of fatty esters were taken in Cannon-Fenske-Ostwald viscometers. The viscosity indices were obtained from viscosities at 100 and 210 F by ASTM method D2270

(13). The kinematic viscosity was converted to Saybolt Universal viscosity (SUS) according to ASTM method D2161 (13).

Smoke, flash and fire points were recorded by the Cleveland open flash cup, ASTM D92-33 (13), and AOCS Official Method Cc 9a-48 (12).

Evaluation of Sulfurized Sperm Oil Candidates

Sperm oil candidates were sulfurized and evaluated under a research contract with Southwest Research Institute (SWRI), San Antonio, TX.

In conducting a typical sulfurization, fatty esters were placed in a 2,000 ml three-necked flask equipped with an electric heating mantle, a mercury-sealed motor-driven stirrer, and an adapter connected to a vacuum pump. The sample to be sulfurized was charged with the desired amount of elemental sulfur. Then, with constant agitation, pressure was reduced to 208 mm and the reaction mixture was heated slowly to 250 F. After ca. 0.5 hr (this period takes advantage of the resulting exotherm from the initial reaction), the sample was slowly heated to 360 ± 5 F. After 4 hr of constant stirring, the sample was cooled to 200 F and blown free of H₂S and other sulfur-containing species by drawing air through it. The sample was blown until entrained air tested negative on lead acetate paper.

Although SWRI had overall responsibility for sulfurizing and evaluating our sperm oil candidates, part of the work was performed at the Eastern Regional Research Center, such as the four-ball EP test ASTM Method 2596-69 (13), four-ball wear test ASTM Method 2266-67 (13), neutral number ASTM Method D-974 (13), and freezing and pour points ASTM Method D97-57 (13).

The following tests were made by SWRI: Sulfur analysis, base oil solubility test, copper strip corrosion test ASTM Method D 135-65 (13), API (American Petroleum Institute) gravity at 60 F ASTM Method D 287-64 (13), lead corrosion test FTM 5321 (14), foam test ASTM Method D 892 (13), emulsion test ASTM Method D 1401-64 (13), *n*-pentane and benzene insolubles ASTM Method D 893-52 T (13), viscosity and viscosity index ASTM Method 2270 (13), and thermal stability FTM 2504-1 (14).

RESULTS AND DISCUSSION

Fatty acid composition of unhydrogenated soybean oil, as determined by GLC, was palmitic 10.7%, stearic 3.4%, oleic 25.2%, linoleic 53.2%, and linolenic 7.5%. Calculated IV was 133. Compositions of soybean oil selectively hydrogenated with copper-on-silica gel catalyst at 170 C and 600 psi pressures are given in Table I. The linolenate content was reduced to diene and monoene with no appreciable increase in saturates. With the exception of run 3, SHSBO contained

TABLE II
Composition of Selectively Hydrogenated Linseed Oil^a

Run No.	Time at 170 C (hr)	IV ^b	GLC analysis (%)				Conjugatable ^c		Nonconjugatable ^d diene (%)	<i>trans</i> Isolated (%)
			Saturates C ₁₆	Saturates C ₁₈	Monoene C ₁₈ :1	Diene C ₁₈ :2	Diene (%)	Triene (%)		
1 ^e	0.5	112	5.9	4.5	50.1	39.5	0.0	0.0	39.5	54.0
2	4.0	116	5.8	4.9	43.9	45.4	5.8	0.1	39.6	56.7
3	3.0	106	5.3	6.9	51.9	35.9	2.8	0.03	33.1	58.6
4 ^e	5.0	108	5.8	4.9	54.1	35.2	3.2	0.06	32.0	56.8
5 ^e	5.8	113	6.0	5.8	45.3	42.9	7.3	0.19	35.6	47.8
6 ^f	4.5	115	5.9	5.0	45.3	43.8	5.6	0.1	38.2	51.0

^aOne gram copper-on-silica gel catalyst per 100 ml oil. Hydrogen pressure 600 psi.

^bIodine values calculated from gas liquid chromatography (GLC).

^cDetermined by UV after alkali isomerization.

^dDetermined by difference between total diene value (by GLC) and conjugatable diene.

^eRe-refined and bleached.

^fTwo grams copper-on-silica gel catalyst per 100 ml oil.

TABLE III
Esters of Selectively Hydrogenated Soybean Oil

Alcohol ^a	IV ^b	Saybolt Universal Viscosity (F)		Viscosity index	Points (F)			N _D 30
		100	210		Smoke	Flash	Fire	
TME	78	255	58.8	147	360	644	779	1.4650
TMP	76	261	59	144	320	572	788	1.4662
TMB	75	344	64.7	200	360	615	788	1.4662
PE	83	380	76.7	146	428	689	761	1.4763
EG	95	145	48.1	163	374	635	788	---
C ₁₂ -C ₁₈	69	84.2	40.7	165	338	518	420	---
Sperm oil ^c	82	109	45	223	275-325	490	655-675	---

^aTME = trimethylolethane; TMP = trimethylolpropane; TMB = trimethylolbutane; PE = pentaerythritol; EG = ethylene glycol; C₁₈ cyclic, C₁₈ saturated cyclic alcohols; C₁₂-C₁₈ or C₁₆-C₁₈, respective mixture of primary saturated straight chain alcohols.

^bIodine values calculated from gas liquid chromatography.

^cWinterized at 45 F.

TABLE IV
Esters of Selectively Hydrogenated Linseed Oil

Alcohol ^a	IV ^b	Saybolt Universal Viscosity (F)		Viscosity index	Points (F)			N _D 30
		100	210		Smoke	Flash	Fire	
TME	109.6	399	66.2	129	356	590	815	1.4698
TMP	100.0	309	64.7	201	428	644	813	1.4698
TMB	103.5	354	69.0	143	383	590	833	1.4705
PE	106.9	389	73	140	401	635	797	1.4719
EG	112.8	133	47.0	204	338	527	824	1.4672
C ₁₈ Cyclic	54.1	155	49.3	147	392	572	788	1.4626 ^c
C ₁₂ -C ₁₈	65.6	89	42.4	235	392	518	781	1.4554
C ₁₆ -C ₁₈	60.8	73 ^d	42.9	---	356	473	788	---
Sperm oil ^e	82	109	45	223	275-325	490	655-675	---

^aTME = trimethylolethane; TMP = trimethylolpropane; TMB = trimethylolbutane; PE = pentaerythritol; EG = ethylene glycol; C₁₈ cyclic, C₁₈ saturated cyclic alcohols; C₁₂-C₁₈ or C₁₆-C₁₈, respective mixture of primary saturated straight chain alcohols.

^bIodine values calculated from gas liquid chromatography.

^cN_D40.

^dDetermined at 122 F.

^eWinterized at 45 F.

no conjugated diene or triene. Run 3 had 0.2% conjugated diene and a trace amount of conjugated triene. In runs 1-3, alkali isomerization and UV analyses showed that ca. 30-40% of diene present after hydrogenation could be converted to conjugated diene. Run 4 contained almost 90% nonconjugatable diene. The SHSBO had 68-76% monoene, 11-18% diene, 1-6% conjugatable diene, 0.0-0.03 conjugatable triene, and 23-40% isolated *trans* double bonds.

Fatty acid composition of unhydrogenated linseed oil, as determined by GLC, was palmitic 6.7%, stearic 3.7%, oleic 23%, linoleic 15.6%, and linolenic 51%; calculated IV 180. Compositions of linseed oil hydrogenated with copper-on-silica gel catalyst at 170 C and 600 psi pressure are given in Table II. Runs 1, 4, and 5 were conducted with re-refined and bleached linseed oil. These runs were more exothermic and produced more monoene than hydrogenations of lin-

TABLE V
Physical Properties of Sulfurized Esters^a

Property	A	B	C	D ^b	E ^b	SSO
Sulfur (%)	10.8	8.6	11.2	11.5	10.5	11.0
Pour point (F)	51	80	39	60	78	64
Freezing point (F)	46	75	34	55	73	59
Flash point (F)	402	462	448	420	424	462
Fire point (F)	515	502	480	473	514	536
Saponification number	213.9	135.2	192.9	197.2	153.7	166.8
Neutral number	4.8	7.6	5.8	5.57	5.7	3.05
Viscosity at 210 F, SUS ^c	405	353	418	1850	383	331

^aSulfurized esters: A = sulfurized nC₁₂-nC₁₈ saturated alcohol esters of selectively hydrogenated linseed fatty acids (SHLSA), containing 10.8% sulfur; B = sulfurized nC₁₂-nC₁₈ saturated alcohol esters of SHLSA, containing 8.6% sulfur; C = sulfurized ethylene glycol esters of SHLSA; D = sulfurized trimethylolthane esters of soybean fatty acids, partially hydrogenated (PHSBA); E = sulfurized trimethylolbutane esters of PHSBA; SSO = sulfurized sperm oil.

^bPreparation of esters reported previously (1).

^cSUS = Saybolt Universal Viscosity.

seed oil not re-refined and bleached in the laboratory. Run 1, quite exothermic, was completed in 0.5 hr. SHLSO from this run contains no conjugatable diene and triene. Even with increases in reaction time and ratio of catalyst to oil, these results could not be repeated, but the other runs gave products with 84-92% nonconjugatable diene. Run 6 was conducted with 2 g copper-on-silica gel catalyst per 100 ml oil. In run 6 the initial rate of hydrogenation increased greatly; however, the amount of nonconjugatable diene did not increase appreciably. The SHLSO contained 44-54% monoene, 35-45% diene, 0.0% conjugated diene and triene, 0.0-7.3% conjugatable diene, 0-0.2 conjugatable triene, and 44-59% isolated *trans* double bond.

Both soybean and linseed oil can be reduced with the catalyst as described to yield products containing increased amounts of monoene and nonconjugatable diene. These oils approach the molecular structure necessary to achieve thermal stability and yet retain sufficient reactivity to permit sulfurization.

Replacing glycerol with alcohols having 1-4 primary hydroxyl groups gave esters with random distributions of hydrogenated acid moieties and, therefore, different physical properties. Physical properties of esters of SHSBA and SHLSA (not winterized) were studied and compared with sperm oil winterized at 45 F.

A comparison of the viscosity index of SHSBA esters with that of sperm oil (Table III) reveals that only the TMB esters of SHSBA should be considered as a possible sperm oil replacement. These esters had smoke and flash points higher than those of sperm oil.

Physical properties of SHLSA esters are compared with those of sperm oil (Table IV). The TMP, EG, and C₁₂-C₁₈ alcohol esters were selected for sulfurization and test as possible sperm oil replacements because of high viscosity indices (uniform viscosity over a broad temperature range) and because of high flash points. These selected SHLSA esters have smoke, flash, and fire points higher than those of sperm oil.

In the lubrication of certain gear elements in automotive vehicles and various industrial machines, high pressure can cause a film of lubricant to rupture, with subsequent damage to the machinery. For this reason, EP lubricants are fortified with additives to augment lubricity at either high pressures or temperatures, or both. EP lubricants should have good lubricity, good cooling properties, high film strength, good load-bearing ability, and miscibility with the usual types of base oils. Sulfurized sperm oil (SSO) satisfies these requirements and has been used extensively in EP additives. For this reason, selected esters of SHSBA and SHLSA were sulfurized for evaluation as EP lubricants.

The TMB ester of SHSBA and the TMP, EG, and C₁₂-C₁₈ alcohol esters of SHLSA were sulfurized. Since

the TMB ester of SHSBA and the TMP ester of SHLSA polymerized during sulfurization, they were not evaluated as liquid EP lubricants; however, they are not excluded from possible use in other EP applications if their physical and chemical properties are suitable.

The pour, freezing, flash, and fire points of the sulfurized EG and C₁₂-C₁₈ alcohol esters of SHLSA are lower than those of SSO (Table V); however, these values are comparable to those of several commercial sulfurized sperm oil replacements. The C₁₂-C₁₈ alcohol esters of SHLSA were sulfurized to determine the effect of 10.8% sulfur (A) and 8.6% sulfur (B) on their EP properties.

Previously reported TME, TMB, and PE esters of partially hydrogenated soybean fatty acids derived from commercially hydrogenated soybean oils (1) were also sulfurized for evaluation as EP and antiwear additives. Compounds D and E in Table V correspond to TME esters (IV 78.3, VI [viscosity index] 191) and TMB esters (IV 79.2, VI 246) of the partially hydrogenated, soybean fatty acids (1) that contain 65.2% monoene, 14.9% diene, 0.2% conjugated diene, 0.2% conjugatable triene, and 28.5% isolated *trans* double bond. The PE esters (IV 80.0, VI 204 and IV 70.2, VI 252) that polymerized during sulfurization were not evaluated.

The sulfurized esters of hydrogenated fatty acids were evaluated in four base oils used in EP automotive and industrial applications. Performance of SSO replacements were compared (Table VI) in engine crankcase base oil (AA), engine transmission base fluid (BB), R G O-100 gear lubricant (CC), 100/100 viscosity solvent-extracted neutral oil (DD), and Topaz S105. With the exception of Topaz S105, the base oils were supplied by SWRI. SSO and two commercial SSO substitutes (Comm Sub A, Comm Sub B) are included for further comparison. It should be emphasized that many commercial sulfurized replacements are sold as "packages" containing a number of additives, such as viscosity improver, metal-deactivator, antioxidants, and EP agents. Additives are used extensively in petroleum-based lubricants as well as in synthetic lubricants (15). The sulfurized esters of hydrogenated fatty acids contained no additives nor were they winterized before sulfurization. SSO replacements were added to each base oil at 10% by wt concentration levels. The blended oils were stored for 24 hr at 35 F, 24 hr at room temperature, 24 hr at 35 F and then 1 month at room temperature. All sulfurized materials had good solubilities in all the base oils.

Both wear and EP test data were obtained with all sulfurized additives as 5% by wt concentration in Topaz S105. Wear and EP tests for A, SSO, Com Sub A, and Com Sub B were on the basis of 10% by wt concentrations in all the base oils. Although data suggest that Topaz S105 was a reasonable choice for screening candidate materials, replace-

TABLE VI
Performance Comparison of Sulfurized Additives in Base Oils

Base oil ^a	Sulfurized additive ^b	Extreme pressure Weld point (kg)	Wear Average wear scar (mm)	Copper ^c corrosion	Lead corrosion (mg/in. ²)	Kinematic viscosity ^d Cs at F		Viscosity index	API ^e gravity (degree API at 60 F)	Emulsion test (ml)		Foam test ^f (ml)							
						100	210			Oil	H ₂ O	Emul	I	II	III				
AA	None	140	0.635	1B	0.2	---	---	---	---	---	---	---	---	---	---	---	---	---	
	10% A	360	0.640	4A	11.0	---	128.7	13.3	113	27.5	2	1	77	20-0	70-0	10-0	---	---	
	10% B	---	---	2A/B	26.9	---	107.6	11.8	107	28.0	1	0	79	0-0	0-0	0-0	5-0	---	
	10% C	---	---	3B	7.1	---	125.74	13.10	107	27.8	1	0.5	78	0-0	45-0	0-0	---	---	
	10% D	---	---	4A	22.5	---	129.93	13.17	118	29.3	1	2	77	0-0	45-0	0-0	---	---	
	10% E	---	---	4A	0.0	---	108.8	11.8	105	28.2	2	0	78	0-0	50-0	0-0	---	---	
	10% SSO	300	0.583	1A/B	22.5	---	131.19	13.57	101	27.8	1	0	79	0-0	40-0	20-0	---	---	
	10% Com Sub A	280	0.480	3A	30.30	---	134.19	13.61	111	27.6	1	0	79	45-0	30-0	20-0	---	---	
	10% Com Sub B	240	0.575	1B	3.50	---	127.97	13.20	113	27.7	75	0	79	10-0	20-0	20-0	---	---	
	None	120	0.625	1B	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
BB	10% A	320	0.713	4B	0.0	---	533.6	35.1	107	24.7	8	38	34	0-0	0-0	0-0	---	---	
	10% B	---	---	2A/B	33.2	---	441.6	31.34	110	25.8	1	14	65	5-0	10-0	5-0	---	---	
	10% C	---	---	3B	75.7	---	576.25	36.66	106	25.6	1	10	69	20-0	20-0	0-0	---	---	
	10% D	---	---	4A	27.1	---	614.34	38.20	105	26.6	25	0	55	120-0	90-0	0-0	---	---	
	10% E	---	---	4A	0.1	---	434.0	31.3	108	26.0	40	39	1	0-0	0-0	0-0	---	---	
	10% SSO	280	0.628	1A	12.7	---	537.80	36.02	113	25.7	9	24	47	0-0	0-0	0-0	---	---	
	10% Com Sub A	320	0.653	3A	27.4	---	543.52	36.09	121	25.9	5	22	53	0-0	0-0	0-0	---	---	
	10% Com Sub B	240	0.591	1B	4.7	---	549.00	35.37	103	25.7	40	37	3	0-0	10-0	0-0	---	---	
	None	130	0.603	1B	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
	10% A	360	0.698	4A	0.0	---	235.4	20.5	109	25.4	21	24	36	0-0	40-0	10-0	---	---	
CC	10% B	---	---	2A/B	36.1	---	195.9	31.3	109	26.3	4	1	75	5-0	0-0	5-0	---	---	
	10% C	---	---	3B	22.0	---	242.61	20.86	108	25.9	37	40	3	210-0	130-0	20-0	---	---	
	10% D	---	---	3B	59.7	---	283.96	23.84	117	25.8	25	0	79	170-0	90-0	40-0	---	---	
	10% E	---	---	4A	0.2	---	196.9	18.0	108	25.5	23	7	50	0-0	0-0	0-0	---	---	
	10% SSO	260	0.642	1A	19.0	---	240.77	20.94	110	26.2	8	11	61	510-20	150-0	180-0	---	---	
	10% Com Sub A	280	0.675	3B	31.4	---	244.79	20.90	113	25.9	6	20	54	420-0	160-0	120-0	---	---	
	10% Com Sub B	270	0.613	3A	4.6	---	239.76	20.75	118	26.2	6	15	60	530-0	80-0	110-0	---	---	
	None	110	1.020	1B	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
	10% A	270	0.783	4C	1.1	---	26.6	5.0	131	31.0	21	24	35	50-0	20-0	55-0	---	---	
	10% B	---	---	2A/B	44.7	---	27.72	4.55	117	31.7	11	14	55	5-0	0-0	0-0	---	---	
DD	10% C	---	---	4A	27.8	---	27.38	5.07	131	30.5	12	1	67	160-0	50-0	20-0	---	---	
	10% D	---	---	4A	77.0	---	27.96	5.16	141	31.5	4	0	75	180-0	70-0	90-0	---	---	
	10% E	---	---	4C	4.6	---	23.7	4.6	115	31.6	24	21	35	65-0	40-0	40-0	---	---	
	10% SSO	300	0.697	1B	12.9	---	27.78	5.05	122	31.4	12	2	66	250-0	20-0	80-0	---	---	
	10% Com Sub A	360	0.713	1B	20.6	---	27.72	5.26	140	31.3	33	13	34	220-0	20-0	100-0	---	---	
	10% Com Sub B	270	0.620	1B	16.8	---	27.68	5.09	125	31.1	5	0	75	280-0	30-0	100-0	---	---	
	None	120	0.794	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
	5% A	300	0.735	4C	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
	10% A	360	0.780	4C	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
	5% B	200	0.530	1A	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
5% C	240	0.595	1A	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
5% D	280	0.535	1A	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
5% E	220	0.673	1B	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
5% SSO	230	0.558	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
10% SSO	300	0.623	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
5% Com Sub A	220	0.606	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
10% Com Sub A	320	0.500	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
5% Com Sub B	230	0.596	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
10% Com Sub B	280	0.670	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	

^aBase oils: AA = Southwest Research Institute's (SWRI) crankcase base oil; BB = SWRI transmission base fluid; CC = SWRI (RGO-100) gear lubricant; DD = Mayco's (100/100 viscosity) solvent-extracted neutral oil; Topaz S105 = Atlantic Richfield's Topaz S105 paraffin oil (similar to 102 paraffin oil).

^bA = sulfurized nC₁₂-nC₁₈ saturated alcohol esters of selectively hydrogenated linseed fatty acids (SHLSA), containing 10.8% sulfur; B = sulfurized nC₁₂-nC₁₈ saturated alcohol esters of SHLSA, containing 8.6% sulfur; C = sulfurized ethylene glycol esters of SHLSA; D = sulfurized trimethylolethane esters of soybean fatty acids, partially hydrogenated (PHSBA); E = sulfurized trimethylolbutane esters of PHSBA; SSO = sulfurized sperm oil; Com Sub A = commercial substitute A; Com Sub B = Commercial substitute B.

^cCopper-strip corrosion test ASTM Method D 135-65 (1.3): 1 = slight tarnish, 2 = medium tarnish, 3 = dark tarnish, 4 = corrosion.

^dCs = centistokes.

^eAPI = American Petroleum Institute.

^fFoam test ASTM Method D 892 (1.3), sequence of bubbling 5 min and settling 10 min: (I) at 75 F., (II) at 200 F., (III) at 75 F. after collapsing the foam.

TABLE VII
Thermal Stability Test^a

Tests	Sulfurized ^b additive	Sulfurized sperm oil	Sulfurized commercial package	
	A		A	B
Viscosity increase 100 max. (%)	194.24	107.70	100.95	171.10
Acid number	11.03	10.15	8.22	11.98
<i>n</i> -Pentane insolubles 3% by wt max.	1.19	0.16	0.11	2.04
Benzene insolubles 2% by wt max.	0.96	0.11	0.09	0.85
Catalyst loss (%)	0.24	0	1	2.21

^aAll tests carried out at 10% by wt additive concentration in engine transmission base oil, Mayco (100/100 viscosity) solvent-extracted oil.

^bSulfurized saturated C₁₂-C₁₈ alcohol esters of selectively hydrogenated linseed acid.

ments performed differently in each of the base oils; therefore, the choice of a given additive will depend on its intended application.

EP tests were made on a Precision Scientific (Chicago, IL) four-ball EP tester (1,440 rpm) in which loads were successively increased first in 20 and then 10 kg increments until an immediate seizure occurred, representing the weld point. Scar diameters were determined with a Precision four-ball wear tester. Samples were run for 1 hr at 600 rpm at 120 C and under a 50 kg load with and without additive. After the balls were cleaned with naphtha and hexane, scar diameters were measured under a microscope assembly No. 73607 with measuring grid (Precision Scientific). All sulfurized products showed both EP characteristics and antiwear properties. At 5% concentration in Topaz S105 additives A, C, and D exhibited EP properties better than those of SSO, as well as Com Sub A and B; additives C and D showed better antiwear properties than the two commercial products.

Although additives A, C, D, and E appeared to be effective EP agents, they gave a copper corrosion test of 3B to 4C. EP additives should not have a copper corrosion rating higher than 2C. The higher than desired corrosion ratings and antiwear values may have been caused either by a too high sulfurization level or by sulfur-contained impurities, or both. For these reasons, EP and antiwear tests were run with additive B (containing 8.6% sulfur) as a 5% blend in Topaz S105. The additive showed an EP test weld of 200 kg and wear test scar of 0.530 mm. As expected, additive B gave a lower EP test weld value than A but the wear test scar was greatly improved. Copper corrosion tests run with B as a 10% blend in base oils AA, BB, CC, and DD showed acceptable values of 2A-2B. These results would indicate that with proper adjustment of either sulfur concentration or addition of metal-deactivators, or both, the additives would possibly improve greatly in EP, antiwear, and anti-copper corrosion properties.

In base oils AA, BB, CC, and DD, additives A and D exhibited lead corrosion tendencies much less than did SSO or Com Sub A and B. Additives B and C had higher than expected lead corrosion in base oils BB, CC, and DD.

Values of kinematic viscosity data, viscosity indices, and API gravities of all materials tested as 10% blends in the four base oils are within most industrial and military specifications for lubricants containing EP additives. Except for viscosities of B at 100 and 210 F, values for all additives were comparable. The higher viscosity values would indicate the presence of high mol wt compounds formed during sulfurization. This observation was considered additional evidence for the possibility of improving EP, antiwear, and anti-copper corrosion properties of these sperm oil replacements by proper adjustment of sulfur concentration or

sulfurization method.

In summarizing emulsion test data of additives as 10% blends in the four base oils, almost all additives form stable emulsions with the four base oils and are suitable for marine engine lubrication and cutting oils. Additive C in base oil CC, as Com Sub B in base oil BB, appears to be more suitable for steam turbine lubrication. However, A in base oil BB and A in base oil CC exhibit excellent de-emulsification properties and should find application in forced-feed circulating lubrication systems, provided that the other physical and chemical properties required of such systems are also met.

Foam test data of additives as 10% blends in the four base oils demonstrate that, except for additives C in base oil BB, all candidate additives met foam test requirements in the four base oils. In base oil BB, additives A and E, SSO, and Com Sub A showed no foaming tendency. All additive materials foamed extensively in base oil DD; however, additives A and E exhibited the least foaming tendency of all the additive materials. Sulfurized additive A met all thermal stability specification requirements except for percent viscosity increase (Table VII). However, gear lubricants, in addition to EP additives, contain appropriate antioxidants to prevent such a high viscosity increase. The low loss of copper catalyst was surprising because the thermal stability test is more rigorous than the copper corrosion test.

Since most lubricants are formulated with not one additive but with a number of them, each having certain performance characteristics (15), sperm oil replacement candidates could not be expected to meet all lubricant specifications. However, the sulfurized candidate additives have good EP properties and are superior to commercial additives in regard to lead corrosion and foaming tendencies. Copper corrosion exhibited by our candidate additives is higher than desired but can be considerably improved by including either an appropriate metal deactivator or antioxidant, or both.

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