REFERENCES

1. Kammann, Jr., K.P., and A.I. Phillips, JAOCS 62:917 (1985).
2. Kapusta, G., JAOCS 62:923 (1985).
3. Fulmer, R.W., JAOCS 62:926 (1985).
4. Sonntag, N.O.V., JAOCS 62:928 (1985).
5. Carlson, K.D., and S.P. Chang, JAOCS 62:934 (1985).
6. Lipinsky, E.S., D. Anson, J.R. Longanbach and M. Murphy, JAOCS 62:940 (1985).

Sulfurized Vegetable Oil Products as Lubricant Additives

KARL P. KAMMANN JR.* and **ASTRID I. PHILLIPS**, Keil Chemical Division of Ferro Corp., 3000 Sheffield Avenue, Hammond, IN 46320

ABSTRACT

Sulfurized products based on hog fat and its derivatives have extensive commercial use as additives for metalworking and industrial oils, but only relatively small quantities of vegetable oils find such application in North America. Products were made by sulfurization of soybean, sunflower, cottonseed, high erucic rapeseed, canola, *Limnanthes* (meadowfoam) and prime lard oils. Unlike products from the wax ester jojoba oil, the sulfurized vegetable triglycerides alone had physical properties generally undesirable for lubricant additives. When the oils were sulfurized in the presence of methyl lardate, however, the products had potential practical application. High-sulfur (active) products were made using a 50:50 ratio of triglyceride to methyl lardate, and low-sulfur (inactive) products were made using a 70:30 ratio. Compared to the other sulfurized vegetable triglyceride products, *Limnanthes* products showed the best solubility in high viscosity-index paraffinic oil. For solutions, measurements of extreme pressure, friction and wear were compared. Whereas products from jojoba were best, of the triglyceride group the *Limnanthes*-containing products generally gave the best performance. Although this oil had much promise, it is only in its early stage of commercial development. The other vegetable oils also have potential depending on cost and applications. However, overall competition with the well-established, usually lower-cost products from hog fat or greases would appear to be difficult.

TRENDS IN SULFURIZED PRODUCTS

Commercial Products

Most of the sulfurized fatty materials made and sold in the U.S. are based on animal fats. Although often considered together and generically called "lard oils," there actually is a wide variety of raw materials available, including several relatively low cost versions which often can be utilized as effectively as lard oil itself. Examples, with typical Acid Value (AV) and Iodine Value (IV) range, include: choice white grease, AV 6, IV 55-70; rendered pork fat or No. 1 pigskin grease, AV 2, IV 55-65; No. 1 lard oil, AV 30, IV 60-75; prime lard oil, AV 3, IV 65-75, and yellow grease, AV 20, IV 55-65 and higher. Yellow grease often contains cooking oil reclaimed from restaurants, which is usually of vegetable origin. "Methyl lardate," AV 1, IV 55-75 also is used. The latter is made by methanol transesterification of triglycerides and is sold for metalworking applications both as is and in the sulfurized form.

Some typical sulfurized products from hog-derived fats or methyl esters are listed in Table I. In addition, there are a variety of products made by cosulfurization of triglyceride and methyl ester.

The formulation of lubricants with sulfurized products remains an art. However, industrial lubricants may be categorized broadly as follows. Lubricants for metalworking operations, such as cutting, threading, broaching, drawing and stamping, require active sulfur more often than inactive, and the presence of free fatty acid often is preferred or at least acceptable. These formulations usually are made with lower viscosity base oils, in recent years involving the increasing use of paraffinic oils, in which solubility of additives is sometimes a problem. Large quantities of sulfurized hydrocarbons and sulfurchlorinated hydrocarbons and fatty materials also are used, especially for cutting operations. Gear oils and machine lubes, previously formulated using sulfurized sperm oil, generally incorporate inactive sulfur, low free fatty acid and higher alkyl ester "synthetic sperm oil" additives along with higher viscosity base oils. They also contain several other components with which the sulfurized material must be compatible. Automotive crankcase oils sometimes contain friction modifying additives with inactive sulfur and low acid values.

Sulfurized fatty products should, of course, have good oxidation and thermal stability. By providing films at the metal surface under the conditions of boundary lubrication they should be able to give wear reduction at extreme pressure (EP) loads, and to possibly provide friction reduction at lesser loads. There are several papers and discussions available on the role and mechanism of fatty materials in lubrication, including sulfurized products (1-3).

Economic Importance

The U.S. International Trade Commission's figure for the

TABLE I

Typical Sulfurized Products From Hog Fats or Methyl Ester

Main component	Product acid value	% Sulfur total	Copper corr.[a]	Viscosity, cSt, 40 C	Viscosity, cSt, 100 C	Specific gravity 25 C	Pour point, °C
Triglyceride	6	10	1b	1160	92	0.99	23
Triglyceride	25	10	1b	1100	80	0.98	18
Triglyceride	26	17	4b	6440	270	1.00	29
Ester	5	9	1b	20	4	9.94	10
Ester	7	17	4a	40	9	0.98	10

[a] ASTM D-130, 10% in oil.

---

*To whom correspondence should be addressed.

manufacture of sulfur compounds for U.S. Sales in 1982 was 101,179,000 lb (4). This does not include phosphorodithioates or sulfurized or sulfurchlorinated phenols, but does include sulfurchlorinated hydrocarbons and fatty materials. The figure also includes hydrocarbon sulfides such as di-tert-nonyl polysulfide, diisobutylene polysulfide and various other hydrocarbon sulfides and polysulfides. These hydrocarbon sulfides are used mainly because of their very high sulfur content (e.g. 40%) and high oil solubility, mainly in applications where the polarity and lubricity of the fatty molecule are not needed.

Of the some 100 million pounds in 1982, no category was reported separately, but in 1980, "sulfurized lard oil" was reported separately, at 13,081,000 lb (4). This, however, did not include many possible other variations starting with animal fat and/or methyl ester. A rough estimate as to the total animal fat which eventually ended up in sulfurization in 1982 is 40 to 50 million pounds. Although much smaller than the quantity of animal fats, there was at one time a fair quantity of rapeseed oil used in sulfurization in the U.S. Its use has faded due to high cost and lack of continuity of supply of the high erucic oil. In Europe, on the other hand, the reverse situation is true. Considerable rapeseed oil is used there in sulfurization, with smaller amounts of animal-derived fats used. As to soybean oil in the U.S., a very rough estimate is that about 2 to 4 million lb/yr are used, of which about half is soybean oil itself (partially refined or degummed), and about half is soybean oil products, including some methyl ester and "vegetable ester bottoms."

Sulfurized Vegetable Oils

Sulfurization (or cosulfurization) of the following materials to give "improved performance" products has been reviewed: lard oil + methyl ester (5), rapeseed or soybean oil + methyl esters (6), lard oil + higher (wax) esters (7), lard oil + olefins (8,9), or triglyceride + ester + olefin (10), natural wax esters, e.g. jojoba (11,12), orange roughy (13), and synthesized wax esters, including those from vegetable fatty acids (14-17).

Natural unsaturated wax esters, such as jojoba oil, gave formulated sulfurized products that appear to meet many or most lubricant additive needs effectively, as shown by Wisniak (11) and others (12). The only problem appears to be availability and cost.

Research more specific to the use of vegetable oil as starting materials has been done by Bell and co-workers (15,16) using partially hydrogenated soybean and linseed oils. Esters were made either by transesterification, or directly from free acids. Alcohols were typically either polyols such as trimethylolbutane, or n-C_{12-18}. Sulfurized esters, which contained 9 to 11% sulfur, had excellent solubility in various base oils and good EP properties by 4-ball testing.

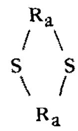
In work by Hagemann and co-workers (17), liquid wax esters were made from the unsaturated acids and alcohols obtained by hydrogenation of crambe oil and *Limnanthes* oil, followed by sulfurization with 10-11% sulfur, and the products were compared with the sulfurized natural wax esters jojoba oil and sperm oil. For example, with ASTM D-226 standard 4-ball test using 5% concentration in a paraffinic base oil, scar diameter increased in the order: jojoba < crambe < *Limnanthes* < sperm oil. Further comparisons of these wax esters have been described by Princen and Rothfus (18), including tests on thermal stability, foaming and lead corrosion of solutions in base oil. Some tests in crankcase oil and in transmission fluid also were reported.

For practical application, however, the above products from vegetable oil triglycerides have the disadvantage that cost-adding conversion steps are necessary, instead of the triglyceride itself being used directly. Wakim (6), after demonstrating that sulfurization of triglycerides alone gave resinous products mostly insoluble in base oils, made excellent oil soluble products by sulfurizing in the presence of methyl esters, usually of the same triglyceride. For example, 10% sulfur reacted with a 50:50 mix of rapeseed oil and rapeseed methyl esters, compared to a similar product from lard oil, had a lower pour point and better Timken load-carrying performance. The latter was determined using 5% solution in a high Viscosity Index, SAE 90 base oil. A similar product also was made from soybean oil, but little was reported on its applications performance.

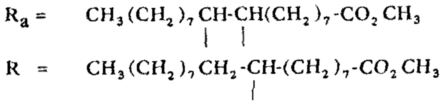
Dorinson (3), in studying the chemical nature of sulfurized fatty lubricant additives, has reviewed the previous literature on structure of sulfurized products and analyzed inactive sulfur products from sulfurization of methyl undecanoate and methyl esters made from sulfurized No. 2 lard oil. He concluded the predominant structure in sulfurized lard oil (12% S) was a molecule with two disulfide bridges linking three fatty groups, shown as structure A after methyl esterification of the oleic acid groups of the lard oil (R substituted at either 9 or 10 position).

$RS_2R_aS_2R$

A



B



$$R_a = CH_3(CH_2)_7CH\text{-}CH(CH_2)_7\text{-}CO_2CH_3$$
$$R = CH_3(CH_2)_7CH_2\text{-}CH\text{-}(CH_2)_7\text{-}CO_2CH_3$$

However, there also could be a variety of other structures, such as B, similar in concept to those proposed for sulfurized jojoba oil by Wisniak (11). For active sulfur products, containing high amounts of sulfur, the mono and disulfide linkages would become disulfide and polysulfide. Dorinson also pointed out that with triglycerides both intra- and intermolecular crosslinking by sulfur is possible, and that the oligomerization or polymerization is further compounded by the presence of polyunsaturated fatty acid moieties. A factor that limits the extent of polymerization, however, is the amount of free unsaturated fatty acid in the triglyceride. The monofunctionality of this fatty acid acts as a stopper for the further formation of sulfur bridges, and this also would be true when using methyl ester with the triglyceride.

A rule of thumb for obtaining inactive sulfur in the ASTM D-130 copper corrosion test is that the ratio of S to double bonds should be 1:1 (or less) giving product with empirical formula as for dialkyl disulfide, RS_2R. Another rule of thumb is that the maximum sulfur that one can expect to react, making stable polysulfide active sulfur product, is about 2.5 atoms of sulfur per double bond, as for RS_5R.

INTRODUCTION TO PRESENT WORK

Although the various vegetable oils already have been sulfurized in one form or another, as described above, a direct comparison was needed of oils using conditions practical for potential commercialization and of the products prepared by methods which would emphasize their performance advantages and disadvantages as lubricant additives. The triglycerides chosen represented a wide range of chemical compositions believed to be favorable for sulfurization but also presently or potentially capable of being produced economically. *Limnanthes*, or meadowfoam, was chosen because of its unique higher molecular weight unsaturated fatty acid structure. Jojoba oil, although relatively high-priced, was selected as a benchmark standard in view of the previous interest and performance advantages it has shown. Prime lard oil was also used for comparison. Compositions of non-commercial and some commercial but high-priced oils not included in this work often resembled those of oils which were chosen. For example, crambe oil was not used, but its sulfurized products should be similar to those from rapeseed oil, selected because of commercial considerations.

EXPERIMENTAL PROCEDURES

All of the materials used for sulfurization were commercial products except for the *Limnanthes* oil and jojoba oil, both of which were unrefined. Table II gives some of the physical and chemical properties of the raw materials, including GC analysis of their fatty acid content. Acid values of all were below 3, except for that of prime lard oil, which was 3.0. The *Limnanthes* (or meadowfoam) oil, reportedly from the species *Limnanthes alba*, was obtained from Bohemia, Inc., Eugene, Oregon. Jojoba oil, obtained from Weyerhaeuser, Inc., Tacoma, Washington, had an IV of 82.5 and a pour point of 10 C. Prime lard oil was purchased in bulk from Geo. Pfau's Sons Co., Inc., Jeffersonville, Indiana. Soybean oil, crude degummed, was purchased in bulk from Cargill, Inc., Minneapolis, Minnesota. Methyl lardate (ML) was "Base ML" produced by Keil Chemical by methyl ester transesterification of a proprietary hog fat mix. It contains 98-99% methyl ester and had an acid value of 0.4; other properties are in Table II.

The other vegetable oils were obtained as samples from distributors: cottonseed oil, partially refined (Sea-Land Chemical Co., Cleveland, Ohio) and refined canola, rapeseed and sunflower oils (Agro Ingredients, Inc., Des Plaines, Illinois). The rapeseed oil, reportedly from a low glucosinolate variety desirable for the use of its meal for animal feed, had lower erucic acid content than often found in oils from other varieties.

Base Oils for Additive Testing

Oil A: "Amolite 22," viscosity 110 SUS at 100 F, viscosity index (VI) 95, from Amoco Oil Co.

Oil B: "150 LP Solvent Neutral" (low pour), viscosity 155 SUS at 100 F, VI 101, from Exxon.

Oil C: "SR-160," viscosity 160 SUS at 100 F, VI 95, from Sun Marketing and Refining Co.

Oil D: "Cal 100," viscosity 106 SUS at 100 F, VI 25, from Calumet Refining Co., Chicago, Illinois.

The first three are typical commercial solvent-extracted paraffinic oils used as base oils in the metalworking industry. The fourth is a widely used naphthenic oil which generally has good solvency even for sulfurized products which have poor solubility in paraffinic oils.

Analytical and Test Methods

Test methods for characterizing starting materials and products are as follows: Acid Value, AOCS Da 14-42; Iodine Value, AOCS Cd 1-25; Pour Point, ASTM D-97; Kinematic Viscosity, ASTM D-445; Copper Corrosion, ASTM D-130 (run using 10% product in oil D); Four Ball Wear Test, ASTM D-4172(b) (run using 5% product in Oil A, conditions: 1 hr, 75 C, 40 kg, 1200 rpm). Oil A without additive gave a wear scar diameter of 0.94 mm.

Falex EP (extreme pressure) load and friction tests. A modification of ASTM D-3233 procedure was used, in a "step-up" test using 5% in oil. After a 5-min warmup at 250-lb load, the load was allowed to walk up to failure, but on the way up was held constant for 1 min at each increment of 250 lb. Torque (pound-inches) was noted for each increment, but is reported here for low sulfur products at 1250 lb load and for high sulfur products at 1500 lb. This was enough below the failure load of any product so that comparisons of torque (from which coefficient of friction could be determined if desired) are meaningful. Oil A without additive failed at 750 lb load. Selected tests showed that the type of oil used, whether A or D, had no effect on results.

Sulfur analysis. Sulfur content of products was determined using a Fisher Sulfur Analyzer, Model 470. A sample is burned in a vanadium oxide matrix in a stream of oxygen at about 1350 C. The effluent sulfur oxide gases equilibrate as they pass through a heated manifold into a proprietary solvent. The analyzer performs what is basically a "reverse" Karl Fischer titration. "Referee" type sulfur standards were used for calibration.

Solubility tests. Solubilities of sulfurized products in base oils were evaluated by stirring to dissolve at 40-45 C, then storing 24 hrs at room temperature (RT), 16 hrs at 4 C, then again at RT. The following ratings were given:

TABLE II

Physical and Chemical Properties of Triglyceride-based Raw Material

	Methyl lardate	Prime lard oil	Soybean oil	Canola oil	Rapeseed oil	Cottonseed oil	*Limnanthes* oil	Sunflower oil
Iodine value	71	72	132	118	115	117	100	140
Viscosity								
cSt, 40 C	4.5	22	31	43	46	36	50	43
Pour point, °C	8	5	−8	−16	−12	−1	0	−12
Fatty acids %								
14:0	2	2	–	–	–	1	–	–
16:0	23	25	11	5	4	23	2	7
16:1	3	5	–	–	–	–	–	–
18:0	9	8	4	2	1	2	–	4
18:1	50	45	25	59	25	15	6	21
18:2	11	13	52	24	16	58	4	67
18:3	–	–	7	7	9	–	–	–
20:1	1	1	1	2	10	–	59	–
22:1	–	–	–	1	35	–	10	–
22:2	–	–	–	–	–	–	19	–

s (soluble), stayed clear at RT, some products became hazy at 4 C, but returned to clear at RT; s/M (soluble/marginal), stayed clear during first period at RT, became hazy at 4 C and did not return to clear at RT (but no separation); M (Marginal), clear during first period at RT but developed haze and slight separation at 4 C; M − (marginal minus), clear initially but became hazy overnight at RT and developed slight separation at 4 C; X (not soluble), not soluble, separated at RT.

Fatty acids in triglycerides. Fatty acid methyl ester (FAME) analysis was used to determine the fatty acid distribution in the original oils. Methyl esters were made from triglycerides by commonly used procedures: saponification, extraction to remove unsaponifiables, acidification of aqueous phase, extraction and drying of extracts. The residue was esterified in BF_3/methanol/xylene.

A Hewlett-Packard 5730 gas chromatograph was used in conjunction with a Hewlett-Packard 3390A reporting integrator. GC conditions: 8′ × 1/8″ O.D. stainless steel column packed with 15% DEGS on 80-100 mesh chromosorb WH-P (Alltech Associates, Deerfield, Illinois) held at 175 C with a helium flow of ca 60 ml/min at 250 C, with injector at 200 C, with a 2.0 μl injection volume. Identification of peaks was accomplished by comparing retention times with standard FAME mixtures and single components. The product "methyl lardate" was run directly on GC, as is.

Sulfurization Procedures

In a typical sulfurization, for 12% and 17% sulfur products, material to be sulfurized, 264 g or 249 g, was charged to a 500-ml round bottom 3-neck flask and heated to 145-150 C under light nitrogen blanket. Sulfur, 36 g or 51 g, was added gradually for 10 min with constant stirring. At the end of this time, an exotherm started which raised the temperature (within 20-30 min) to typically 182 C for inactive sulfur products and typically 193 C for active sulfur products. The temperature was held at 182 ± 3 C for 2 hr and then reduced within about 20 min to about 150 C. Air was then blown into the reaction mixture at 150-140 C for 2 hr to remove any volatile sulfur-containing compounds. Some H_2S was evolved, most noticeably during the exotherm period. At the end of the air blowing period, lead acetate paper gave a negative test on the outgoing air. Yields were 98-99% by wt of starting material, except for product from methyl lardate, which was obtained in 96% yield.

To determine the maximum sulfur that could be retained in the product, 225 g material was sulfurized using 75 g sulfur in some cases. Temperatures rose to about 205 C due to exotherm. After the final step of air blowing, the product was allowed to stand for 3 days at room temperature, then filtered with suction through Whatman #4 paper to remove unreacted sulfur. For sulfurization of jojoba oil with 25% sulfur, formation of rubbery product (factice) was avoided by adding the sulfur intermittently at 125, 150, 175, and 185 C.

Cosulfurization of Vegetable Oils and Methyl Lardate

As seen in Tables III and IV, sulfurization of most vegetable triglycerides alone gave products of a rubbery nature, or nearly so. This was true in some cases even at a 12% sulfur content; production of useful high-sulfur, active sulfur products desirable for metalworking would thus obviously not be practical. Therefore, sulfurization was carried out in the presence of large amounts of methyl lardate, which is a relatively low cost, readily available product. Although the minimum amount of methyl lardate (ML) desirable for avoiding factice formation varies according to the particular triglyceride used, a constant 70-30 weight ratio of triglyc-

TABLE III

Low-Sulfur Sulfurized Oils[a]

	%S charged (found)	Viscosity, cSt, 100 C	Soly.[b] % in oil A	Falex, 5% in oil D Fail load, lb	Falex, 5% in oil D Torque, lb-in. at 1250 lb
(Methyl lardate)	10 (10.3)	4	10s	1250	22
Prime lard oil	10	92	10s	1500	20
Soy[c]	12	867	5X[c]	1250+	26
Canola	12	factice	–	–	–
Rapeseed	12	factice	–	–	–
Cottonseed[c]	12	191	5X[c]	1250+	23
Limnanthes	12	factice	–	–	–
Sunflower	11	factice	–	–	–
Jojoba	11	135	10s	2250	18

[a] All products gave rating 2a or less in ASTM D-130 Cu Corrosion Test, 10% in oil D.

[b] s = soluble, X = insoluble.

[c] Products also were made using 10% S, but did not have improved solubility.

TABLE IV

High Sulfur Sulfurized Oils[a]

	%S charged (found)	Viscosity, cSt, 100 C	Soly. 10% in oils A, B	Falex, 5% in oil D Fail, lb	Falex, 5% in oil D Torque, lb-in. at 1500 lb
(Methyl lardate)	17	9	s	2250+	25
Prime lard oil	17	298	s	2750	25
Jojoba	17 (16.6)	438	s	4500	21
Jojoba	25 (22.3)	292	s	3250	29

[a] All the vegetable triglycerides gave factices when sulfurized with 17% sulfur.

TABLE V

Sulfurized (12% S) Oils, 70:30 with Methyl Lardate

	Prime lard oil	Soy	Canola	Rapeseed	Cottonseed		Sunflower		*Limnanthes*		Jojoba (alone)
					Prod. A	Prod. B[a]	Prod. A	Prod. B[a]	Prod. A	Prod. B[a]	
%S found	9.9 (10 chg.)	12.1	12.0	12.0	12.3		12.3	12.2	11.9	11.8	10.6 (11 chg.)
Cu corrosion[b]	1b/2a	2b	1b	1b/2a	1b/2a	1b/2a	1b	1b	1b	1a	1b
Viscosity, cSt											
40 C	378	670	798	2820	478	459	1196	904	(no flow)	2305	1500
100 C	41	65	79	240	48	46	110	80	–	167	135
Soly.[c] % in:											
Oil A	10s	10M	10S/M	10M	10s/M[e]	10s/M	5X[e]	5X	10s	10s	10s
Oil B	10s	5X	5M–	5M–	5M–[e]	5M	5X[e]	5X	5M	5M	10s
Oil C	10s	5X	5X	5X	5X[e]	5X	5X[e]	5X	5X	5X	5s
Falex test[d]											
Fail load, lb	1500	1500	1500	1500	1500+	1500+	2000+	1750	1750	2000+	2250
Torque (lb-in.) at 1250 lb	24½	22	22	23	19	19½	23	23	20½	21	18
4-Ball[d]											
Scar dia., mm	0.56	0.56	0.57	0.55	0.55	0.61	–	–	0.52	0.62	0.56

[a] Products A were from the usual 70:30 mix but Products B were from mixes 63% oil: 27% ML: 10% Oleic Acid (Emery 210).

[b] ASTM D-130 Tests were run at 10% in oil D.

[c] s, M, X = *soluble, marginal, not soluble. See description of solubility tests.*

[d] Falex and 4-ball tests were run 5% in oil A (except for sunflower products, in oil D). Oil without additive failed at 750 lbs. Falex load, and in 4-ball test gave wear scar 0.94 mm. diameter.

[e] Products also were made using 10% S but did not show improved solubilities.

TABLE VI

Sulfurized (17% S) Oils, 50:50 with Methyl Lardate

	Prime lard oil	Soy	Canola	Rapeseed	Cottonseed	Sunflower	*Limnanthes*	Jojoba (100%)
S found, %	16.4	14.1	15.1	16.3	16.3	16.5	16.6	16.6
Viscosity, cSt								
40 C	211	217	278	414	225	480	1130	–
100 C	26	26	32	47	28	50	113	438
Gardner color, 2% in oil A	13	17	15	12	13	14	13	10
Solubility, % in:								
Oil A	20s	5X	5X	5M	5s/M	5X	20s	20s
Oil B	10s	5X	5M–	5M–	5M	5X	5M	10s
Oil C	5s	5X	5X	5X	5X	5X	5X	5s
Falex tests[a]								
Fail load, 1b	2500	2250	2750	2500	2000	2250	3000	4500
Torque, lb-in. at 1500 lb	25	38	33½	27	25	26½	26	21

[a] Falex tests were run at 5% in oil D.

ride to ML was decided upon for the low sulfur products. Even with this much ML, a factice or a near factice was nevertheless obtained with *Limnanthes* oil. This problem was avoided by the addition of 10% free unsaturated acid (oleic) before sulfurization. Other, similar oleic-containing mixes also were used for cottonseed and sunflower oils, so that the *Limnanthes* product was not an isolated case lacking comparison. Table V gives the results of preparation and evaluation of the 70:30 ratio products. It was considered desirable to obtain the highest possible sulfur content in a product which was still relatively inactive to copper in the ASTM D-130 test, as indicated by lb rating, with 2a being marginal. With prime lard oil, this condition could not be obtained with 12% sulfur. Therefore, its 70:30 mix was sulfurized with just 10% sulfur for comparison with the vegetable oils.

With higher sulfur products, higher methyl lardate content was needed to avoid factice formation, and a 50:50 ratio with triglyceride was used (Table VI). For some of the oils, the products were determined to contain nearly the full 17% sulfur charged. When this was found (⩾16.5% S), sulfurizations were carried out using a charge of 25% sulfur, and results of these experiments are given in Table VII.

RESULTS AND DISCUSSION

The present work was directed at showing some basic problems and advantages that the various vegetable oil products

TABLE VII

Sulfurized (25% S) Oils, 50:50 with Methyl Lardate

	Rapeseed	Sunflower	*Limnanthes*	Jojoba (100%)
S found, %	20.4	20.4	21.3	22.3
Viscosity, cSt 100 C	–	–	266	292
Solubility, % in oil A	5M	5X	20s/M	20s
Falex tests				
Fail load, lb	1750	–	2250	3250
Torque (lb-in.) at 1500 lb	27½	–	25	29

might have as lubricant additives. As may be seen from Tables III and IV, a main problem of sulfurized vegetable triglycerides compared to lard-based products is that of poor solubility in paraffinic oils. This was overcome to some extent, depending upon the particular vegetable oil, by the presence of relatively large quantities of methyl lardate during sulfurization. From Tables V and VI, showing both low sulfur and high sulfur products, it may be seen that sulfurized jojoba oil had the best solubility of the vegetable products in the paraffinic base oils, followed by *Limnanthes* and cottonseed oils. The other vegetable products were somewhat poor, especially sunflower oil. On the other hand, products from lard oil had very good solubility, even when made without methyl ester. Some metalworking applications, such as particular broaching and threading operations, require active sulfurized fat with total sulfur content of 2-3% in the lubricant, therefore requiring solutions of ca 10-20% sulfurized product in base oil. While most lubricants do not require these levels, sulfurized products with high solubility (10-20%) are nevertheless desirable because they can be used by compounders to make a concentrate.

In actual metalworking operations, a combination of lubricant effects is usually present, sometimes opposite, and hard to define. In most cutting operations, high EP load-carrying or antiweld is desired, and of course, protection of the tool surface against wear is always important. In general lubrication, low friction usually is desirable and translates into lower wear and reduced energy requirements. In the laboratory tests carried out to evaluate load carrying and friction reduction, the jojoba products were far superior to all the rest. The other vegetable oil products were generally headed by *Limnanthes*, which was best on load carrying, and by cottonseed, which was best on friction, as indicated by low Falex torque. The high sulfur cottonseed oil, however, ranked below the others on load carrying. In 4-ball wear tests, which were run with just the inactive sulfur products, the products gave significant improvement compared to oil alone, but there were only small differences observed between the various products. The high-sulfur lard oil product performed well in all of the performance tests, and both high- and low-sulfur lard oil performed even better in Falex tests when made from lard oil alone without methyl ester.

Unusually high sulfur content (20-22%) was obtained for some vegetable oil products (Table VII). With *Limnanthes* oil, this high sulfur product retained good solubility properties. Falex results, however, showed little or no advantage in tests using this very high sulfurized oil, compared to 17% sulfur product. In fact, 22% sulfurized jojoba oil looked considerably poorer in Falex tests than did the corresponding 17% product. However, where higher sulfur per se is desirable in formulations, or where there may be other lubrication advantages not indicated by Falex results, some of the vegetable oils might be preferred over animal fats as raw materials.

It is obvious from the results reported in Tables III, V and VI that superior sulfurized products were made from vegetable triglycerides in the presence of methyl lardate, compared to products from the triglycerides alone. This apparently is the result of chain-stopping by the methyl lardate, lowering the molecular weight of the sulfur-containing polymers. Chain-stopping was increased further by the addition of oleic acid when a 70:30 mix of triglyceride to ML was sulfurized. The relatively small amount of oleic used (10%) gave decreased product viscosity, but there was little effect on product performance, unless the somewhat higher 4-ball scar measurements are considered significant.

From the results of this work one can attempt to correlate the effect of fatty acid structure with physical and performance properties of the product. Triglycerides that contained a lower degree of unsaturation and little or no linolenic acid appeared to be the best. Sunflower oil with its low linolenic but overall high unsaturation tended to give factices and insoluble products, as did soybean, canola and rapeseed oils, the latter three having significant linolenic content (7-9%). However, results from the particular rapeseed oil used would perhaps not agree with results from European rapeseed oils and with other, higher erucic, lower linolenic products. The cottonseed oil, which had relatively high IV without linolenic acid and contained 26% saturated acids, gave surprisingly good products in most respects. Lard oil, which also lacked linolenic acid and had low IV compared to the vegetable oils, gave products with outstanding solubility and lubrication results.

Limnanthes oil, with its absence of linolenic acid and presence of about 90% acids with 20 and 22 carbons, gave very favorable results when sulfurized in the presence of methyl lardate, in spite of the high viscosity of the products. Its fatty acids, including the diunsaturated C_{22} acid, have double bonds in the 5 and 13 positions (18).

The viscosities of sulfurized vegetable oil products were always higher than those of the corresponding lard oil product, and this would be a factor, sometimes positive, sometimes negative, in choosing a product for base oil formulation. For example, in oil A, 5% solutions of 17% sulfurized products (Table VI) had viscosities as follows at 40 C: *Limnanthes*, 26.5 cSt; prime lard oil, 23.3 cSt; oil A alone, 21.2 cSt. In addition, there obviously is much further evaluation work which could be done which might influence the choice of a product. This includes compatibility and effect on other additives such as the chlorinated paraffins often heavily used in metalworking lubricants. However, compatibility probably would be a more sensitive factor in gear and automotive lubricant packages, with components such as dialkyl dithiophosphates, than in metalworking formulations. Other informative tests would include oxidation and thermal stability of formulated oils and evaluation of emulsion and foaming characteristics when water is present. Several specific, simulated in-use performance tests could be run such as high speed and high torque gear lubricant tests and transmission fluid tests.

Lard oil-based sulfurized products, including those sulfurized alone without ester, historically have been shown to have adequate and often outstanding overall performance as lubricant additives, depending on application. Many of the products from lower grade animal greases generally share these advantages; their main disadvantages are poor low temperature handling properties and semisolid appearance, sometimes including the presence of titered fat or stearines. In most cases these disadvantages do not outweigh price advantages. In other cases, higher load carrying and/or lower friction provided by some sulfurized vegetable oil products may translate into specialized applications. With customers becoming increasingly selective about particular performance and physical properties, the increased use of vegetable oils in sulfurization is anticipated, especially if the price differential between vegetable oil- and animal-based raw materials narrows.

ACKNOWLEDGMENTS

Ronald E. Thompson assisted in the analysis of starting materials and products. Roger P. Hunz provided helpful discussions regarding product applications and performance.

REFERENCES

1. Papay, A.G., Lubrication Engineering 39:419 (1983).
2. Hermann, C.L., and J.J. McGlade, JAOCS 51:88 (1974).
3. Dorinson, A., Lubrication Engineering 39:519 (1983).
4. Synthetic Organic Chemicals, U.S. Production and Sales, 1982, USITC Publication 1422, U.S. Govt. Printing Office, Washington (1983). Ibid. (for 1980) USITC Publication 1183 (1981).
5. Vienna, P., and M.J. Den Herder, U.S. Pat. 3,850,825 (Nov. 26, 1976).
6. Wakim, J.M., U.S. Pat. 3,986,966 (Oct. 10, 1976).
7. Hutchison, R.B., and K.P. Kammann Jr., U.S. Pat. 3,740,333 (Jun. 19, 1973).
8. Recchuite, A.D., U.S. Pat. 4,321,153 (Mar. 23, 1982).
9. Sanson, H.E. III, and W.R. Hartman Jr., U.S. Pat. 4,188,300 (Feb. 12, 1980).
10. Lee, D.A., and J.A. Boslett, U.S. Pat. 4,149,982 (Apr. 17, 1979).
11. Wisniak, J., and H. Benajahu, Ind. Eng. Chem., Prod. Res. Dev. 14:247 (1975).
12. Miwa, T.K., J.A. Rothfus and E. Dimitroff, JAOCS 56:765 (1979).
13. Buisson, D.H., D.R. Body, G.J. Dougherty, L. Eyres and P. Vlieg, JAOCS 59:390 (1982).
14. Kenney, H.E., E.T. Donahue and I. Schmeltz, Lubrication Engineering 30:394 (1974).
15. Bell, E.W., U.S. Pat. 4,031,019 (Jun. 21, 1977).
16. Bell, E.W., L.E. Gast, F.L. Thomas and R.E. Koos, JAOCS 54:259 (1977).
17. Hagemann, J.W., J.A. Rothfus and M.A. Taylor, Lubrication Engineering 37:145 (1981).
18. Princen, L.H., and J.A. Rothfus, JAOCS 61:281 (1984).
19. Jolliff, G.D., I.J., Tinsley, W. Calhoun and J.M. Crane, Station Bulletin 648, Nov. 1981, Agr. Expt. Station, Oregon State University, Corvallis, OR.

Uses of Soybean Oil in the Application of Herbicides

GEORGE KAPUSTA, Department of Plant and Soil Science, Southern Illinois University,
Carbondale, IL 62901

ABSTRACT

Field studies were conducted in 1982 and 1983 at Southern Illinois University to evaluate soybean oil as a carrier for preemergence and postemergence herbicides and as an enhancing agent for postemergence herbicides. Preemergence and postemergence herbicides applied with rotary nozzles in a soybean oil carrier volume as low as 5 L/ha afforded weed control equal to that achieved when the herbicides were applied in 187 L/ha water with flat fan nozzles. Soybean oil as an enhancing agent for four postemergence soybean herbicides was equal to petroleum crop oil concentrate with three of the herbicides but distinctly less effective with the fourth herbicide.

INTRODUCTION

Farmers have used oils for many years directly for the control of weeds and insects and as additives to herbicides to increase their efficacy. Oils also have been used as solvents in the manufacture of pesticides (1). The development of selective herbicides and insecticides relegated oils for the direct control of pests to minor status. Petroleum oil fractions have been added to 2,4-D and 2,4,5-T for the control of woody species in rangeland (2) but have not been used with 2,4-D for weed control in cereal grains because of potential injury to the crop. Several decades ago it was found that a phytobland oil added to atrazine improved the control of many weeds in corn (3). Later, the use of emulsifiable crop origin oils (oil extracted from crops such as soybeans, cotton, flax, etc.) at 2.3 L/ha was found to be as effective as 9.3 L/ha of petroleum oil in enhancing weed control in corn with atrazine and cyanazine (4-6).

More recently, the development of selective postemergence herbicides for soybeans, cotton and other important economic crops has increased the application of these herbicides on millions of hectares each year. The nine major farm crops are grown on approximately 182 million hectares in the U.S. and on 800 million hectares in the world annually (7). A very high percentage of the cropland in the U.S. is treated with one or more pesticides, sometimes with multiple applications.

PESTICIDE APPLICATION

Pesticides must be diluted in a carrier to be applied uniformly. The carrier to date has been water almost exclusively, applied with hydraulic sprayers that have not changed in 50 years. Volumes as high as 200 L/ha are used routinely, resulting in very inefficient spray operations because of the need for frequent refilling of the spray tank.

Recently, pesticide application with rotary atomizers was commercialized. This type of spraying depends on a spinning cone that discharges the spray solution from the rim of the cone as a series of very uniform droplets. The major advantage of rotary nozzles is that they can apply pesticides very uniformly in carrier volumes as low as 2 to 3 L/ha. This makes practical the use of crop origin oils as a carrier for pesticides, because the cost would be only several dollars per hectare.

POTENTIAL MARKET FOR CROP ORIGIN OILS

The use of postemergence herbicides on crops such as soybeans and cotton is increasing dramatically in the U.S. and many other countries. It is estimated that approximately 25% of the soybean acreage in Illinois is sprayed with postemergence herbicides annually for a total of one million hectares. Almost all of these applications include the addi-