Sulphurization of Jojoba Oil for Application as Extreme Pressure Additive

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In order to develop jojoba oil-based extreme pressure (E P) additives, a number of sulphurized jojoba oils have been prepared by varying the reaction conditions. The products differ in their amount of sulphur and in their structure. An attempt to predict their performance based on their structure reveals that it is not a simple addition of sulphur which is required; a certain level of cross linking and polymerization also are desirable to have a product which is effective as an E P additive.

For a long time sulphurized vegetable oils (1–14) along with other unsaturated fatty oils have been added to mineral oils to make lubricants that provide antiwear, low friction, increased load carrying ability and improved oxidation resistance. Sulphurized sperm oil was used in many lubricants because it had a combination of properties not matched by other additives. However, a number of substitutes have been prepared (13–18). Ellis, Flaxman and Wells (19–22) pointed out the similarities between jojoba oil and sperm oil and advantages of the products based on jojoba oil. Sulphurization of jojoba oil also has been studied (23–29) for the preparation of E P additives. An attempt has been made in the present study to correlate the structure of the products obtained by sulphurization of jojoba oil under different reaction conditions with their performance as an E P additive. A mechanism for the addition of sulphur also has been proposed.

EXPERIMENTAL PROCEDURE

In order to develop jojoba oil-based E P additives, sulphurization of jojoba oil by addition of elemental sulphur has been studied in detail. Total sulphur to be added was divided into four equal portions. Each portion was added at 125°, 130°, 160° and 180°C followed by stirring for 30 min after every addition. The sulphurized product thus obtained, SJO_1, was flushed with air and nitrogen for three hr at 185 ± 5°C, affording SJO_2 and SJO_3, respectively. SJO_4 was obtained by sulphurizing jojoba oil under nitrogen atmosphere under the above conditions, followed by flushing with nitrogen. Infra-red (IR) spectra of these products were run in CCl_4 on a Perkin Elmer 399 B spectrometer, while the nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on FX 100 Jeol model. Performance of the products as load carrying or E P additives was studied as per IP-239 and ASTM D-2266. For this purpose, blends having 1% sulphur by weight were made in solvent refined paraffinic base oil.

RESULTS AND DISCUSSION

Detailed spectral studies (IR and NMR) have been carried out on the four products. IR spectra of the products, run at the same concentration level, have been compared in the region 400-700 cm^{-1}. The 670, 500-520, 600 and 580, and 440 cm^{-1} bands were used for the C-S-C (sulphide), C-S-S-C(disulphide), -HC=CH-(*cis-*) and -HC=CH- (*trans-*) groups, respectively. Optical densities of the sulphide and disulphide absorptions of the neat as well as sulphurized products were plotted against the optical densities of *cis-* and *trans-*olefinic absorptions of the corresponding samples (Fig. 1, 2).

As observed from Figure 1, the neat oil initially showed no sulphides. The sulphide content in the four sulphurized samples decreased in the order $SJO_4 > SJO_1 > SJO_2 > SJO_3$, while the *cis-* double bonds decreased in the order $JO > SJO_1 > SJO_4 > SJO_3 > SJO_2$ and the *trans-* double bond content increased in the order $JO < SJO_1 < SJO_2 < SJO_4 < SJO_3$.

Thus, with a decrease in the *cis-* double bonds there was a corresponding increase in the *trans-* double bonds, suggesting that while *cis-* olefinic double bonds were used mainly for the reaction with sulphur, there was also some isomerization taking place to *trans-*form.

The disulphides produced on sulphurization of jojoba oil decreased in the order, $SJO_4 > SJO_1 > SJO_2 > SJO_3$ (Fig. 2) while the trend of *cis-* and *trans-* double bond content was similar to that in the case of sulphides. This is in agreement with the quantitative estimation of disulphides (Table 1). Stripping of the freshly sulphurized oil with air and nitrogen decreased the disulphide content and the *cis-* olefinic content in SJO_3 and SJO_2, but the latter contained more disulphides; this confirms the experimental values presented in Table 1 as well as the spectral data in Figure 3.

TABLE 1

Comparison of Physico Chemical Properties of Sulphurized Jojoba Oil

Properties	SJO_2	SJO_3	SJO_4
Sulphur wt %	9.1492	8.5203	8.1000
Molecular weight	1075	1355	725
Refractive index (70°C)	1.4770	1.4774	1.4750
Specific gravity, d_4^{15}	0.9407	0.9404	0.9316
Kinematic viscosity			
cSt at 40°C	618.33	663.38	299.70
100°C	72.17	74.32	41.40
Viscosity index	196	192	194
Acid value (mg KOH/g)	2.98	2.80	2.11
Sapnification value	186	146	177
Elemental analysis			
Carbon	73.84	76.20	76.70
Hydrogen	10.76	10.71	10.68
Sulphur	9.15	8.52	8.10
Oxygen	6.25	4.57	4.52
Mercaptans	0.1939	0.1904	0.1382
Disulphides	2.4977	1.9832	2.7474

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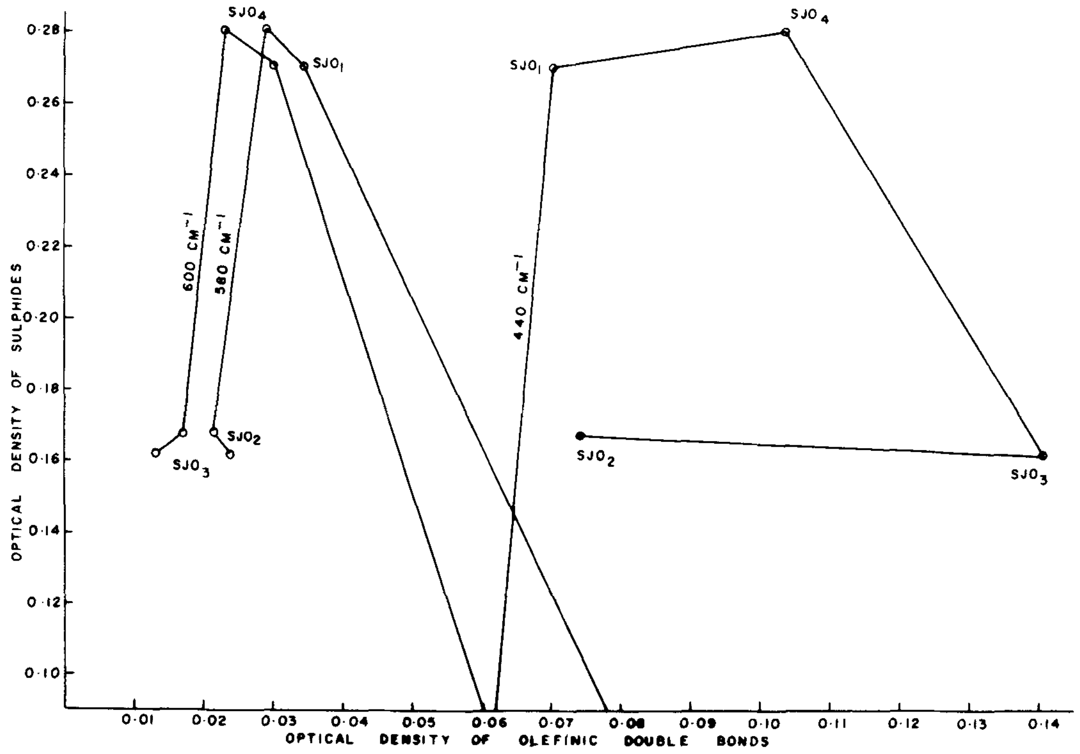


FIG. 1. Variation of double bonds (*cis*- and *trans*-) and sulphide content in jojoba and sulphurized jojoba oils.

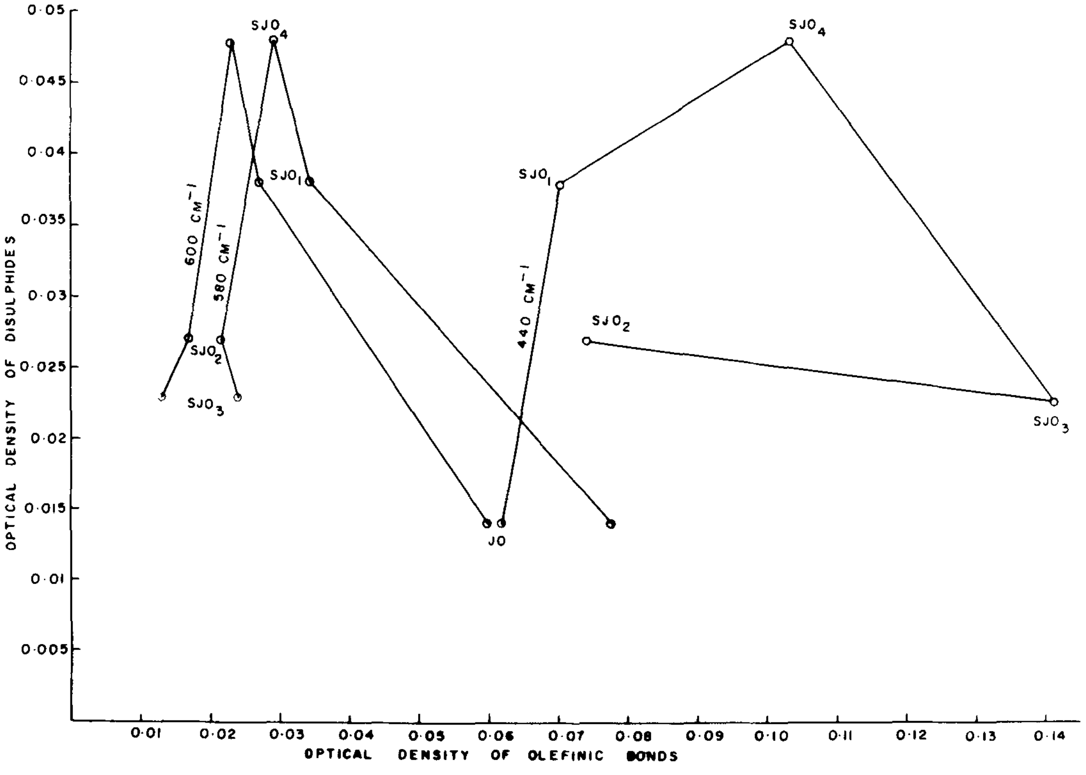


FIG. 2. Variation of double bonds (*cis*- and *trans*-) and disulphide content in jojoba and sulphurized jojoba oils.

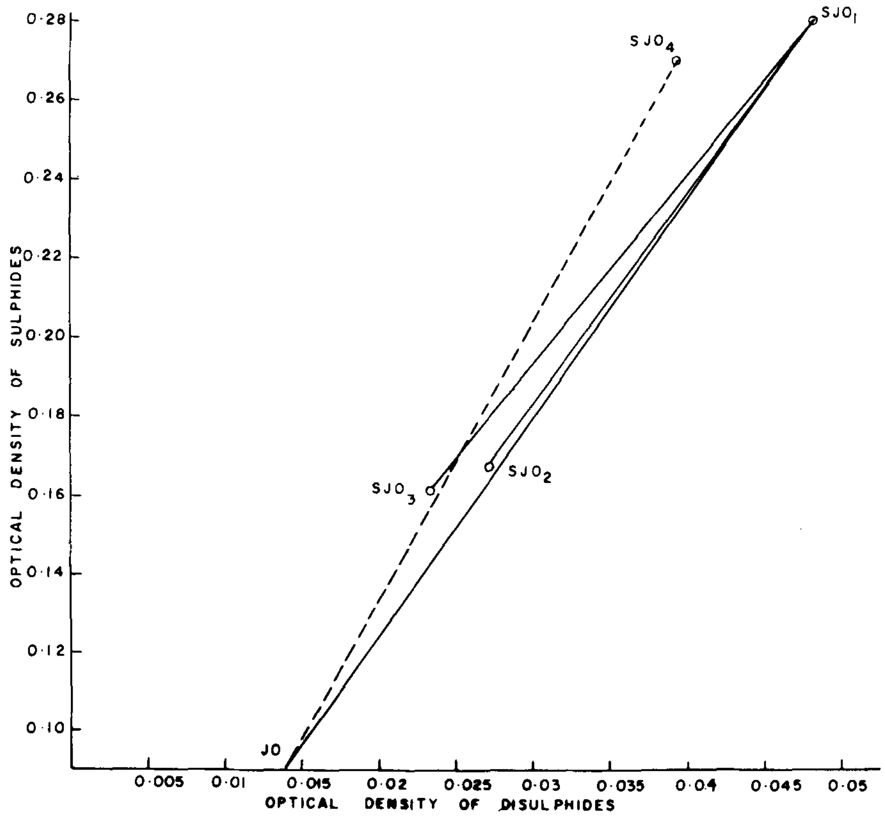


FIG. 3. Relative content of sulphides and disulphides in sulphurized jojoba oils.

Except for the two esters (C_{34} and C_{36}) which have one double bond in the whole molecule, all the other constituents contain two double bonds per molecule and constitute a major part (98.8%) of the oil. Besides the olefinic bonds, the only other functional group present in the oil is the ester.

The NMR spectrum of neat jojoba oil showed, on an average, four olefinic protons, two protons of methylene adjacent to $-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-$ (calc. 1.25 + 2.70 = 3.95 ppm) at 4.00 ppm, two protons of methylene adjacent to $-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-$ at 2.18 ppm, eight protons of four methylene at 2.18 ppm, eight protons of four methylene groups adjacent to both the double bonds in each of the alcohol and acid moieties of the esters $-CH_2-CH=CH-CH_2-$ (calc. 1.25 + 0.7 = 1.95 ppm) at 2.00 ppm, eight protons to the electronegative groups between 1.40 and 1.57 ppm, 49 protons of alkyl methylene and methine between 1.11 and 1.25 ppm and six protons of the methyl group at 0.86 ppm, suggesting that the ester molecules are straight chains without alkyl substituents (Table 2).

The SJO_4 showed an average decrease of 1.34 olefinic protons from the neat jojoba oil which were converted during sulphurization, while an average of one proton appeared at 2.25 ppm; the latter were the methylene protons adjacent to the sulphide group, $-CH_2-S-$ (calc 1.25 + 1.00 = 2.25 ppm) or the methine protons adjacent to the double bond, $CH - C = C$)calc. 1.5 + 0.75 = 2.25 ppm) the latter suggesting that the proton on methylene adjacent to the double bond was being removed. The number of protons in the 1.47-1.57 ppm region increased to 10, compared to eight protons in the original oil. This was due to the formation of thiols, the -SH proton appearing in the above region. Also, an

TABLE 2

Average Number of Protons in Jojoba and Sulphurized Jojoba Oils

Peak position (ppm)		Jojoba oil	Sulphurized jojoba oil		
			SJO_2	SJO_3	SJO_4
5.30	$CH=CH$	4	1.3	2	2.66
4.00	$\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2$	2	2	2	2
3.78		—	1	1	—
2.80		—	1	1	1.33
2.25		—	—	—	1
2.18	$-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2$	2	2	2	2
2.00	$CH=CH-CH_2$	8	2.5	2	4
$\left.\begin{matrix}1.57\\1.40\end{matrix}\right\}CH_2$		$\left.\begin{matrix}6\\2\end{matrix}\right\}8$	$\left.\begin{matrix}6\\4.5\end{matrix}\right\}10.5$	$\left.\begin{matrix}6\\4.5\end{matrix}\right\}10.5$	$\left.\begin{matrix}6\\4\end{matrix}\right\}10$
1.11-1.25	CH_2CH_2	49	30	53	49
0.86		6	12	12	6

average of 1.33 protons appeared in the region 2.80 ppm which were the methine protons adjacent to the disulphides -CH-S-S (calc. 1.5 + 1.0 + 0.3 = 2.8 ppm) (Table 2).

The molecular weight of SJO_4 was 725, suggesting that the product was a monomer which was in confirmation with the six protons of two end methyls of a long chain molecule. This further suggested that the product was a simple addition of sulphur atoms to the double bond.

Samples SJO_3 and SJO_2 showed a decrease in the average number of olefinic protons. The latter contained the least number of double bonds. This was also supported by its IR spectrum, which showed more or less complete absence of *cis*- double bonds except for *trans*-ones. Both samples showed the presence of disulphide linkage at 2.80 ppm to more or less the same extent, but less than that present in SJO_4. The protons adjacent to the monosulphides were present at 2.25 ppm but in negligible amount. In addition, in the two samples, there were extra protons appearing in the 3.78 ppm region suggesting the presence of -S-CH-S-S- linkage which was, however, absent from the SJO_4 sample. Another main distinguishing feature between the two samples was the appearance of 12 protons of the methyl groups. In the 1.40-1.57 ppm region, the two samples showed 10.5 protons as compared to the 10 protons in the SJO_4, suggesting the presence of higher amounts of thiols. This was confirmed by the quantitative estimation of thiols (Table 1).

The average molecular weight of SJO_3 was 1355, suggesting the molecule to be dimer. There were [1355 − (606 × 2)]/32 = 4.47 atoms of sulphur for every two molecules of the ester. The appeararnce of four methyl groups in its NMR spectrum suggested that each monomer of the dimer underwent branching during reaction with sulphur. It looked as if it was not a simple addition of sulphur to the double bonds or cross linking between two molecules but also involved breaking of bonds and their rearrangements, resulting in the presence of four methyl groups.

As seen above, SJO_2 is more or less similar to SJO_3 but showed a very significant decrease in the number of alkyl methylene ($-C-CH_2-C-$) protons in the 1.11-1.25 ppm region (30 against 49 of the JO). The average molecular weight of the sample was 1075, suggesting that the product was neither a monomer nor a dimer.

The decrease of an average of 10 methylene groups and presence of four methyl groups suggested that in the monomeric units of the dimeric sulphurized oil, ca. 9-10 methylenes were being lost followed by branching (rearrangement) resulting in four methyl groups in each of the monomers. The average molecular weight of the unsulphurized monomeric units would be 606 − 140 (10 CH_2) = 466. The number of sulphur atoms combining with such monomeric units worked out to be [1075 − (2 × 466)]/32 = 4.47 atoms to form the dimer.

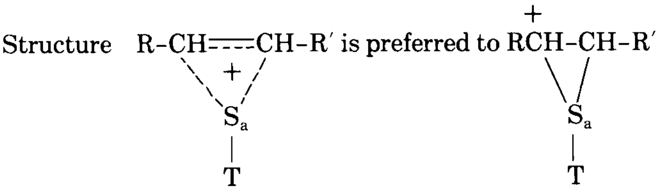
As can be seen above, the same number of sulphur atoms combined in both SJO_2 and SJO_3, while the molecular weight of the former was lower than the latter. Therefore, percent sulphur content of the former should be higher than the latter, which was observed experimentally (Table 1).

MECHANISM OF JOJOBA OIL SULPHUR INTERACTION

Sulphurization of jojoba oil is basically a sulphur-olefin reaction. Both free radical chain and polar chain mechanisms have been postulated for the sulphur-olefin reactions. On the basis of structural moieties concluded from spectral data and the physicochemical characteristics of sulphurized oils, the mechanism of sulphurization of jojoba oil proposed to best explain the structure-performance correlation is discussed below:

The SJO_4 sample was monomeric and showed the presence of (i) $-CH_2-S-$; (ii) -CH-S-S or -CH-S-S-S; (iii) -SH, and (iv) -CH-CH=CH groups. Thus, the formation of SJO_4 was the result of simple addition of sulphur to the double bond. Hence the reaction mechanism is different from the one which leads to polymeric material.

Probably sulphur adds to the olefinic double bond to form cyclic persulphonium ion structure (Scheme 1)



because of its greater stability. The persulphonium ion then yields the episulphide. This episulphide then yields the thiol, sulphide and disulphide by proton (H^+) transfer and rearrangement of the alkyl groups. Structure III could be mono-, di- or polysulphide depending upon the number of sulphur atoms. The product SJO_3 is a dimer and shows the groupings of the type $-S-CH_2-S-S$ (IR, NMR and molecular weight) in addition to those seen in SJO_4. Sulphides are present in negligible amount. In this case, the persulphonium ion (I) interacts with another molecule of the oil so that hydride ion transfer from active α-methylene groups in the olefin takes place yielding sulphides, disulphides and polysulphides formed by cross-linking between two molecules.

Linkages in the SJO_2 sample are similar to SJO_3 except that during rearrangement a part of the alkyl chain is lost, resulting in smaller molecules.

PERFORMANCE OF SULPHURIZED JOJOBA OILS

Wear scar, weld load and mean Hertz load values for SJO_2, SJO_3 and SJO_4 are presented in Table 3. Of the

TABLE 3

Performance of Sulphurized Jojoba Oils

Additives	Wear scar[a] dia mm	WL Kg[b]	MHL Kg[b]
SJO_2	0.332	501	75
SJO_3	0.350	631	73
SJO_4	0.362	562	68

[a] As per ASTM 2266: 20-kg load, 1800 rpm 54°C and one hr.
[b] As per Institute of Petroleum, U.K., 239.


T =
(OR)
[I]
[II]
[III]
(TSa-1)
(SJO4)
ESTER MOLECULE
H⁻ TRANSFER FROM OLEFIN
i) H⁻
ii) REARRANGEMENT
S8
(SJO2 & SJO3)

SCHEME 1.

three products, SJO_4 containing more *cis*-olefinic double bonds was expected to be most unstable. Also, a high amount of disulphides and polysulphides made SJO_4 very reactive. This accounted for the relatively high weld load and higher wear rate observed due to corrosion. Because it was a low molecular weight monomer and had low viscosity, the boundary film strength was also poor, contributing to higher wear. SJO_3 had the highest molecular weight, indicating cross linking by sulphur atoms. As larger molecules with higher viscosity are attributed with greater film strength, this accounted for the lower wear value observed as compared to the monomer SJO_4. The least number of double bonds and lowest amount of polysulphides present in SJO_2 contrbuted to its thermodynamic stability which was indicated by low weld loads and lower wear observed as compared to SJO_3 and SJO_4. Although total sulphur and disulphides were greater in SJO_2 than in SJO_3 due to the conversion of thiols into disulphides during air flushing, the overall reactivity of SJO_2 could be less because of less polysulphides present than in SJO_3. The weld load values indicate the amount of active sulphur present in formulation. In actual practice, as destructive welding does not take place, very high weld loads are not considered significant. For assessing the E P property, mean Hertz load is the main criterion as it represents the load carrying capacity over the entire range of operation until welding takes place. Of the three SJOs, SJO_2 had the highest MHL value indicating that this product was superior to SJO_3 and SJO_4 with respect to the E P property. Wear sear diameter obtained with SJO_2 was also within acceptable limits.

The spectral data analysis (IR and NMR), molecular weights and viscosities of the three sulphurized oils suggested that their structural features related well with their performance.

Maximum amount of mono- and disulphides, monomeric nature of the molecule, higher olefinic content and low viscosity (Table 1) make SJO_4 the least stable under the severe conditions of load and friction and hence the least suitable of the three as an E P additive. Between the SJO_2 and SJO_3 samples (with more or less similar structure), the viscosity and molecular weight of the latter were higher, while the total number of sulphur atoms combined in the two cases was the same. The former, with higher content of useful sulphur combined, optimum molecular weight and least number of olefinic double bonds was relatively more stable but had the required level of reactivity as an E P additive as indicated by the load carrying capacity. It was also observed that some double bonds of the oil molecules undergo isomerization from *cis*- to *trans*- forms during sulphurization. This has been reported in the reaction of the oil with selenium (30). Sulphur falls in the same group of the periodic table. Thus, to develop jojoba oil-based E P additives, it is not a simple addition of sulphur which is required; a certain level of cross linking and polymerization are also desirable to have an effective product.

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