CHAPTER II

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

2.1 Introduction of Sulfurization

Sulfurization processes may be classified from different points of view. The reaction may be carried out with sulfur molecule, sulfurmonochloride, and other reagents containing sulfur and chlorine. It can also be carried in the presence of solvents and accelerators. Another possible classification is according to the material being sulfurized : fatty acids, olefins, mono-, di-triesters,etc., where the common element is the presence of at least one carbon-carbon double bond. The process may also be classified according to the final product. At low sulfur content the material is usually liquid, while at high sulfur content is a rubbery solid called factice.

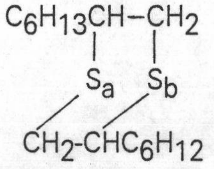
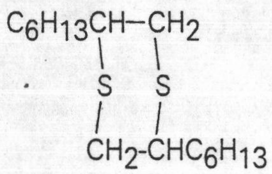
Conventionally sulfurized liquid triglycerides, such as the naturally occuring fatty oils of animal, vegetable, or mineral origin, are well-known as additives for use in the preparation of mineral oil-based metal working lubricants. A widely use and well-known class of sulfurized fatty material is sulfurized sperm oil, for in addition to good solubility,it provides good lubricity, anti-wear properties, and thermal and oxidative resistance when used as an additive in high aniline pointmineral oils.[3]

2.2 Basic chemistry of the direct sulfurization of olefinic substances.

Lubricant additives made by the direct reaction of elemental sulfur with ethylenic unsaturated organic substancesare the most familiar and useful in lubricantion technology. The best known and widely used sulfurized additives are those made by the sulfurization of fatty substances.

The overall chemistry of the reaction of the elemental sulfur with olefinic substrate is complex, being strongly influenced by the specific characteristics of the olefin and by the conditions of reaction, particularly temperature. The complexity of the reaction can be judged by the substances lists which is shown in Table 2.1 which were actually isolated from the reaction of sulfur with octene-1 for 14 hours at 140°C (198°F). [13]

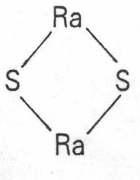
Table 2.1 Products of the reaction of octene-1 with sulfur at 140 ^{o}C

I.	$C_6H_{13}CH(CH_3)$-S_x-CH_2-$CH{=}CHC_5H_{11}$	average x = 6.7	25%
II.		average (a+b) = 6.7	30%
III.	C_8H_{17}-S-C_8H_{17} + C_8H_{17}-S-C_8H_{15}		15%
IV.	C_8H_{17}-S_a-C_8H_{16}-S_b-C_8H_{17}	average (a+b) = 4.7	15%
V.	 + C_8H_{17}-S-C_8H_{16}-S-C_8H_{17}		15%

In 1983, Dorinson[14] had reviewed the previous literature on structure of being sulfurized and analyzed inactive sulfur products from sulfurization of methyl undecanoate and methyl esters made from sulfurized No.2 lard oil. The predominant structure in sulfurized lard oil (12%) was a molecule with two disulfide bridges linking three fatty groups shown as structure A. However, there also could be a variety of other structures, such as B. (The substituent, R, could be at either 9 or 10 position)

RS_2RaS_2R

(A)



(B)

$Ra = CH_3\text{-}(CH_2)_7\text{-}CH\text{-}CH\text{-}(CH_2)_7\text{-}CO_2CH_3$

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

Wisniak and Benajahu [15] showed that in the sulfurization of jojoba oil, there was an inter molecular bridging, as can be shown graphically in Figure 2.1. It was assume that structureI represented the molecule of jojoba oil, a black dot represented a double bond, an empty dot represented a saturatd bond, and a double line represented an S-bridge. One possibility of sulfurization was represented by structure II. Case III corresponded to a dimer. Structure IV represented a dimer formed with half the original iodine value. Layer degrees of polymerization were illustrated by structure V.

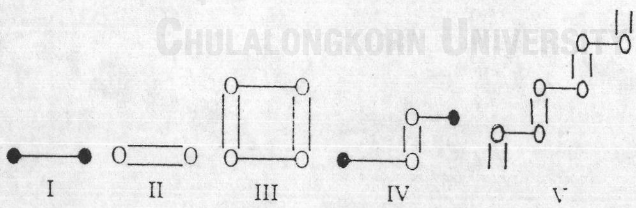


Figure 2.1 An intermolecular bridging of sulfurized jojoba oil.

A large degree of intermolecular polymerization has already been pointed out that there is a significant increase in the molecular weight (MW) and viscosity when the oilis almost saturated with S, as shown in Figure 2.2 and Figure 2.3 .

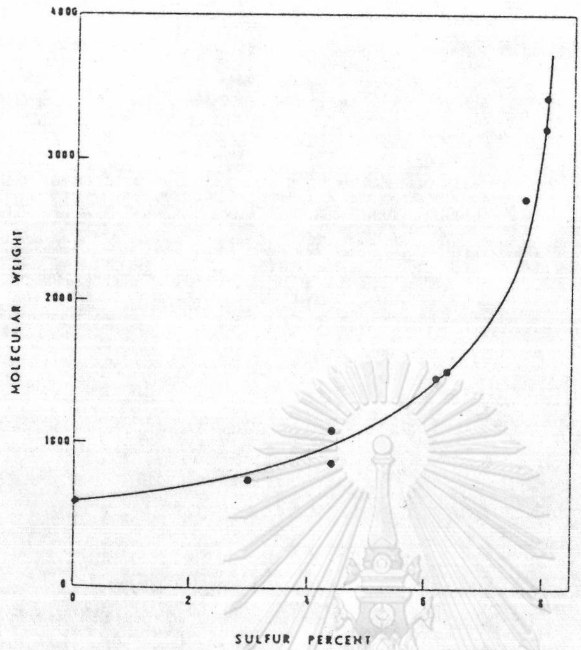


Figure 2.2 Molecular weight as a function of S content.

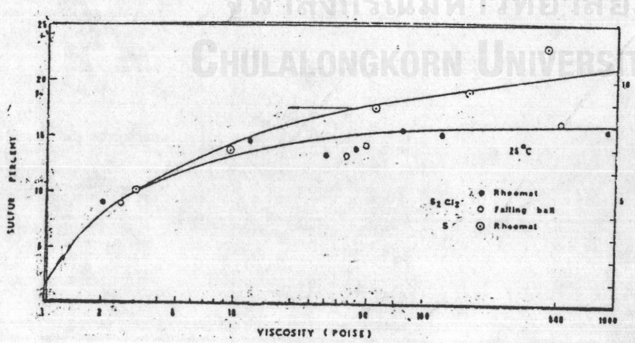


Figure 2.3 Viscosity as a function of S content.

2.3 The reaction mechanism

The reaction between S and olefins has been explained by polar and radical mechanisms (Bloomfield [16], 1974; Bateman et al. [18], 1958 ; Ross [17], 1958) with the possibility that the different stages of the reaction are associated with different mechanisms.

Ross [17] and Bateman et al.[18] proposed the reaction mechanism with polar scission of polysulfide on the basis of reaction kinetics and the identified products of the sulfurization reaction as follow ;

Initiating step :

$$TS_{(a+b)}T \longrightarrow TS_a^+ + TS_b^-$$

whereT may be analkyl group, C_nH_{2n+1} or an alkenyl group, C_nH_{2n-1}

Propagating step :

$$TS_a^+ + RCH{=}CH_2 \longrightarrow TS_aCH\ (R)\cdot CH_2^+$$

$$TS_aCH\ (R)\cdot CH_2^+ + RCH{=}CH_2 \longrightarrow TS_aCH\ (R)\cdot CH_3 + RCH{=}CH^+$$
$$\longrightarrow TS_aC\ (R){=}CH_2 + RCH_2CH_2^+$$

$$RCH{=}CH^+ + S_8 \longrightarrow RCH{=}CHS_a^+$$
$$RCH_2CH_2^+ + S_8 \longrightarrow RCH_2CH_2S_a^+$$

Terminating step :

$$RCH{=}CH^{+} + TS_b^{-} \longrightarrow RCH{=}CHS_bT$$

$$RCH_2CH_2^{+} + TS_b^{-} \longrightarrow RCH_2CH_2S_bT$$

$$TS_aCH\ (R){\cdot}CH_2^{+} + TS_b^{-} \longrightarrow TS_aCH\ (R){\cdot}CH_2S_bT$$

A fundamental deficiency in this mechanism is its failure to show the origin of $TS_{(a+b)}T$.

Farmer and Shipley [19] explained the attack of biradical sulfur $\cdot S_x \cdot$ derived from the opening of the octatomic sulfur ring S_8 on the olefin as the initial step of a free-radical chain mechanism. The eventual product was the alkyl-alkenyl polysulfide.

Bateman et al. [18] mentioned that the temperature of reaction was an important consideration in extending findings, such as those to the sulfurization of olefinic materials for use as lubricant additives. Sulfurization of fatty substances for lubricant additives was carried out at temperatures in the range of 175-190^{o}C (350-375 ^{o}F). At temperatures in the neighborhood of 190 ^{o}C, loss of H_2S from sulfurized substances becomes a factor to consider, as shown in the following equation ;

$$RCH_2SCH_2R \longrightarrow RCH{=}CHR + H_2S$$

2.4 Theory of lubrication

The application of lubricants in the petroleum industry may be properly visualized, a review of the basis types lubrication is included. These are hydrodynamic, boundary, and extreme lubrications (Figure 2.4). Consider the meshing of gears in a gear box, two bearing surfaces, or the metal-to-metal contactis found in any metal working operation, such as cutting, drilling, drawing, etc. A good lubricant, but also prevents as a coolant which draws the friction heat away from the parts, not only acts imitate metal-to-metal contact.

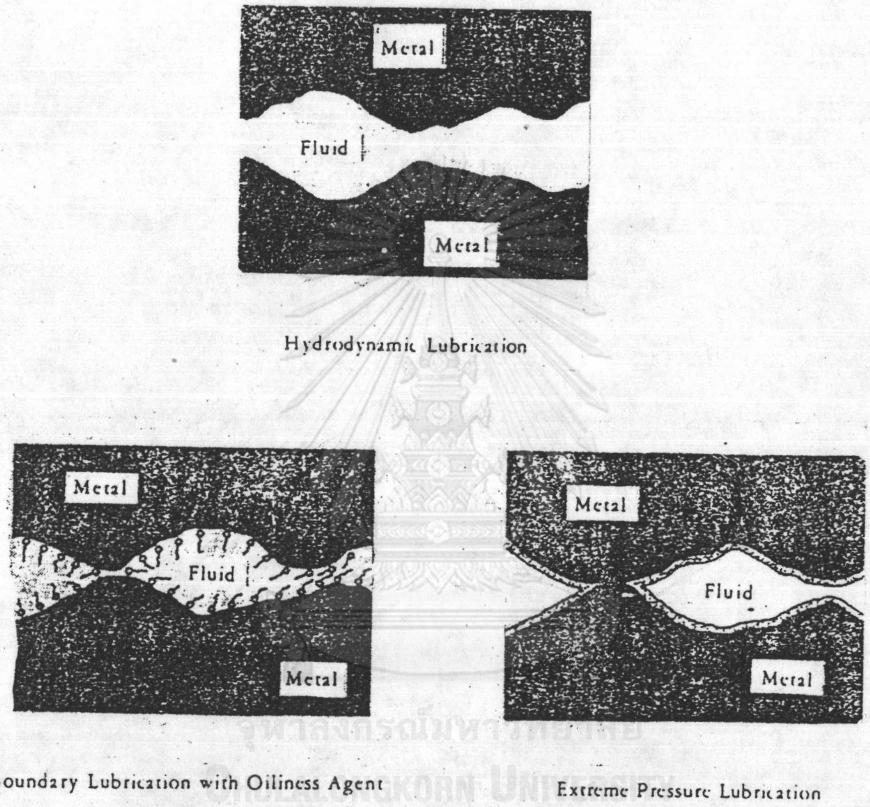


Figure 2.4 Basis types of lubrication.

Petroleum products, both with and without additives, have been found to excel as lubricants. They not only posses the proper metal wetting characteristics but also the body necessary to maintain a substantial lubrication film. [20]

The principal function of a gear lubricant is to provide a constant film which will effectively reduce the metallic contact between the opposing surfaces, thereby reducing the amount of wear. This is achieved by incorporating so-called boundary lubricants in the oil to produce, by physical adsorption or chemical reaction, a film which will be soft and easily sheared but difficult to penetrate or remove from the surfaces. [21]

A modifier dissolved in oilis attracted to the metal surface by strong adsorption forces. Actually, the polar head is attracted by the metal which the long hydrocarbon chain is preferentially attracted by the base oil which is also composed mainly of hydrocarbons. The result is anchoring of the molecule with the polar end on the metal surface and the long chain sticking out into the oil, perpendicular or normal to the metal surface. Consequently, according to the Order Liquid theory, other friction-modifier molecules through hydrogen bonding and Debye orientation forces get their polar groups attaracted wiht a force of about 15 Kcal/mole in dimer fashion. Due to Vander Waal forces, the molecules tend to align themselves parallel to each other in multimolecular clusters. At the same time, the orienting field of the adsorbed layer induces the positioning of the clusters with their methyl groups stacking upon the methyl groups of the tails of the adsorbed monolayer. As a result, they all line up straight up, normal to the metal surface. That is repeated many times, depending on the strength of the orienting polar group.

Figure 2.5 shows the mechanics of this phenomenon. The example used in this case is stearic acid but it adequatedly represents any chemisorbed friction modifier. Figure 2.5 Chemisorption of stearic acid on iron-iron oxide substrate. The bond between polar group and metal is called adhesion and it is estimated to be about 13 Kcal/mole. The forces between the hydrocarbon tails are cohesive ares and help pack the molecules closely together. Interactions between carbon atoms of methylene chains are about 0.84 Kcal/mole. Interactions between methyl radicals through London dispersion forcesis about 0.1 Kcal/mole. That is why if a slip to occur, it should take place at the nonpolar methyl ends of the fatty acid molecules, at the methyl-methyl midplane location [22]. This type of boundary additive is used mainly in worm gear lubricants which the bronze wheel forms achemically reactive partner and where lowfriction is especially desirable.

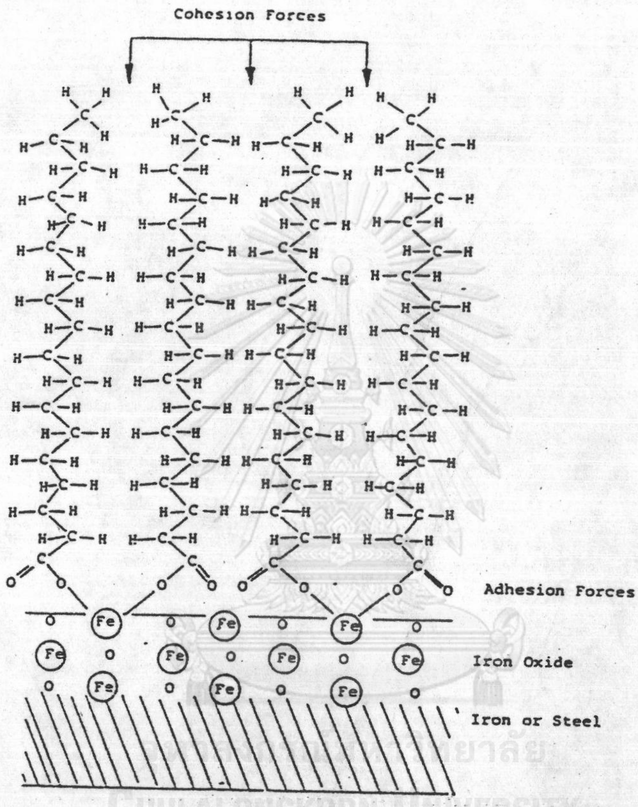


Figure 2.5 Chemisorption of stearic acid on iron-iron oxide substrate.

These long chain fatty acids are not suitable however for the more severe condition which are encountered in some steel-steel gear where loads and sliding speeds are high. Forthese applications, additives are required to form films with higher melting points and have greater adherence to the metal surface. These additives are generally known as "Extreme Pressure (EP)" additives. These types of additives are usually more chemically reactive oil-soluble materials containing one or more of the elements chlorine, phosphorus, sulfur, lead and zinc.

Under mild operating conditions, these additives produce a mainly hydrocarbon film which is firmly attached to the metal surface by their reactive groups. Under more severe conditions, they decompose and react with the metal surfaces to produce a film which is softer, less brittle, more adherent and more effective than the oxide layer. The films found are largely inorganic, for example iron phosphates, cholrines and sulphides. This type of film is illustrated schem atically in Figure 2.6.

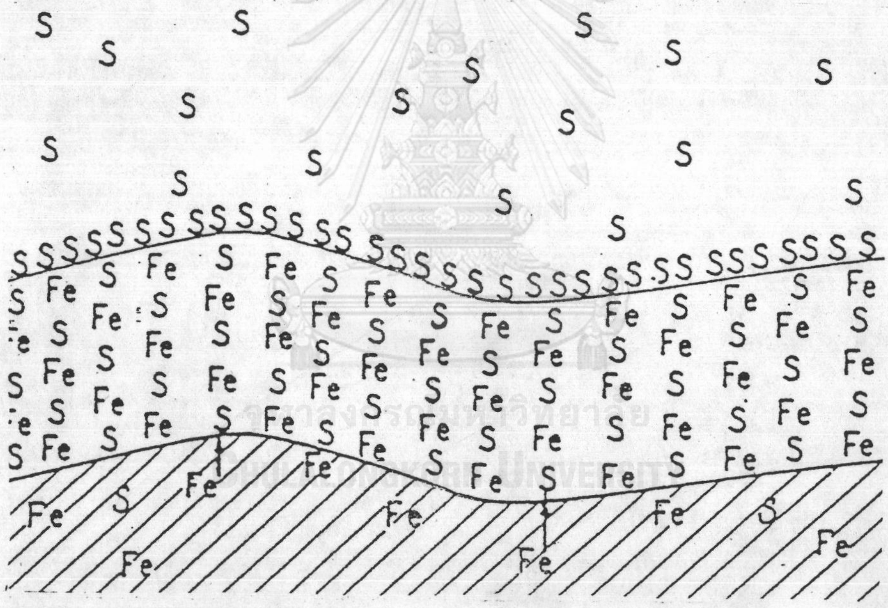


Figure 2.6 Inorganic film of iron sulphide on iron formed by sulfur in the oil.

Phosphorus containing additives are generally effective under relatively mild conditions, whereas additives containing chlorine and sulfur are required for more severe operating conditions. A combination of additives such as sulfur and phosphorus is used to giving good anti-wear protection under mild conditions and protection against scuffing when operating under more severe conditions.

To be effective, the additive should be adsorbed onto the metal surface. That is, highly polar substances are therefore advantageous. To achieve this economically, the oil should not contain components or other additives which are more polar than the EP additive since this may give insufficient EP activity or require the EP additive to be used at a higher concentration than would otherwise be necessary. [21]

2.5 Literature review

There are many reports investigating the replacement of sperm oil in different ways. Some reports have investigated the role and mechanism of fatty materials in lubrication, including sulfurized products. Some works were summarized as follows :

Hutchinson and Kammann [23] studied compositions which were suitable substitutes for natural sperm oil and which had very similar physical characteristics to the natural product.. It has been found that wax esters derived from a mixture of unsaturated C_{18} fatty acid and saturated C_{10-16} alcohols blended with triglycerides give compositions which are useful as substitutes for natural sperm oil. Wax esters prepared from tall oil fatty acids are especially useful. The preferred triglyceride is lard oil or pigskin grease. The physical characteristics of the compositions including iodine value, cloud point and pour point are comparable to the natural product and in some instances are superior to natural sperm oil as lubricant additives.

Vienna et al. [3] studied sulfurization with elemental sulfur of a fatty mixture consisting essentially of about 80-95 weight percent prime burning lard oil and about 5-20 weight percent alkyl oleate. It has been found that a sulfur-containing oil-soluble product is suitable to use as a substitute for sulfurized sperm oil additives for imparting extreme pressure (EP) properties to high aniline point mineral oil lubricants.

Kenny et al. [24] investigated fatty esters prepared from tallow, lard, fish oil and oleic acids, and commercially available saturated n-alcohols (C_{18}, C_{10}, C_{12}). The esters were generally liquid at room temperature and had iodine values ranging from 25-92. The sulfurized esters, containing 6-7% S, were evaluated, and generally, they corroded copper minimally, exhibited good solubilities in paraffin oil, and displayed better anti-wear and EP 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 may serve as model compounds for possible sperm whale oil replacements.

Wisniak et al. [15] investigated the sulfurization of jojoba oil with sulfur monochloride and S in order to study the kinetics and parameters of process and the characteristics of the final product. The linear relation between the number of the double bonds and the chlorine, S contents (Figure2.7 and 2.8) indicated that the basic reaction was one addition to the double bond. The MW and viscosity of the sulfurized oil show a paralled behavior with S content. (Figure 2.2 and 2.3)

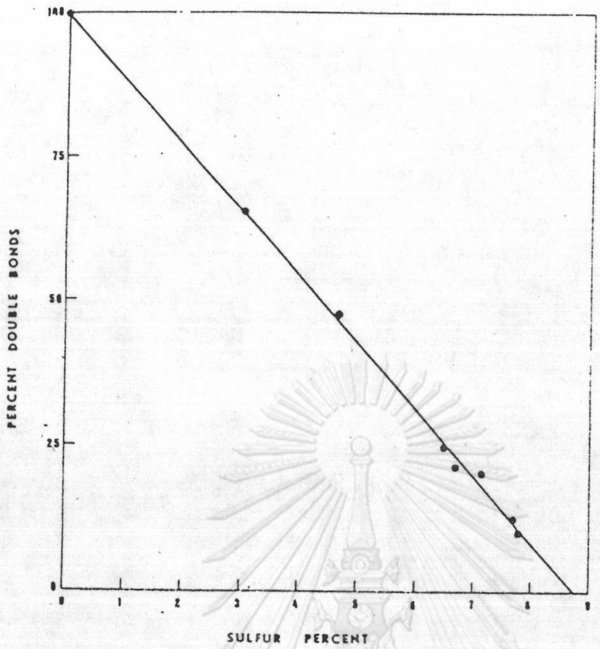


Figure 2.7 Percent double bonds as a function of S content.

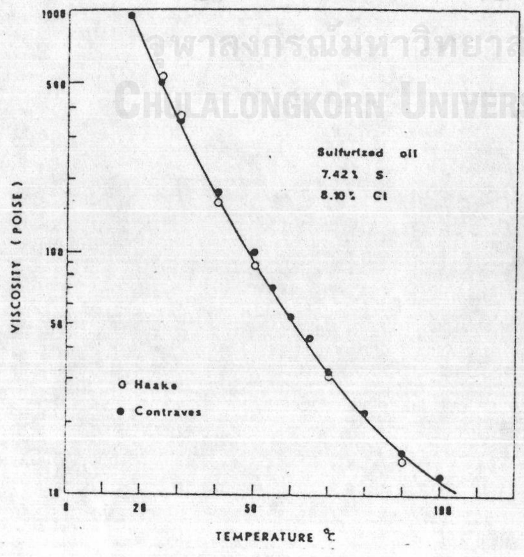
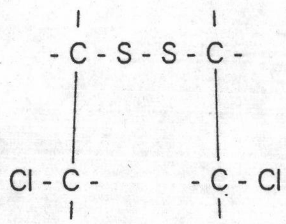


Figure 2.8 Viscosity as a function of temperature.

On the basis of these facts, it emerged the following picture of the attack of the double bond by S_2Cl_2. An S bridge was normally formed between two different oil molecules.



The difference between sulfurization with S and sulfurization with S_2Cl_2 is the formation of two bridges between two S atoms in the first case, and only one bridge in the second case. The difference in structures permits to advance the idea that the mechanical properties of jojoba oilsulfurized with S_2Cl_2 will be substantially different from those of jojoba oil sulfurized with S.

Bell, Gast and Thomas [25] synthesized wax esters from soybean and linseed oils with properties similar to those of sperm whale oil.The synthesis required selective hydrogenation of the oils, hydrogenolysis of fatty acids to fatty alcohols and esterification of hydrogenolysis products. Similarity of physical and chemical properties indicate that these wax esters are possible replacements for sperm oil. After sulfurization, the wax esters could not be expected to meet all lubricant specifications but they have good EPproperties and are superior sulfurized sperm oil and commercial additives.

Miwa and Rothfus [26] studied lubricant tests which were performed on sulfurized jojoba oil and on reference sulfurized sperm whale oil. Data from these comprehensive tests indicated sulfurized jojoba oil prepared heat-treatedly filtered oil to be comparable or superior to sulfurized sperm whale oil as an EP additive for motor oils, gear lubricants, and automotive transmission fluids.

Lee et al. [27] studied and provided EP additives which are used in lubricant compositions. The EP additives of this invention are prepared by sulfurizing a mixture comprising of 50-85 % by weight of an ester of a higher fatty acid and glycerol, or a mono-lower-aliphatic ester of fatty acid, or mixtures and 50-15 % by weight of a mono-alpha-unsaturated olefin having about 15-20 carbon atoms. The EP additives of this invention are especially useful in improving the high pressure characteristics of greases, gear oils, way lubricants and the like.

Buisson et al. [28] studied the liquid fraction of the deep water fish species orange roughy *(Hoplostetbus)*, blackoreo *(Allocyttussp.)* and small spined oreo *(Pseudocyttus maculatus)*. The orange oil was refined and deodorized. This study compared the properties of orange roughy, oreo species,jojoba, and sperm whale oils and suggested that orange roughy oil might replace sperm oil or substitute for jojoba oil as an EP additives in lubricants. The results showed a technical basis on which to consider an industry based on orange roughy oil. Applications for the oil could be in the cosmetic and high-grade lubricant fields, the waxes in the polish, textile, cosmetic and pharmaceutical industries and the sulfurized derivative of orange roughy oil in the lubricant industry.

Dorinson [14] studied the chemical nature of sulfurized fatty lubricant additives which were prepared from the direct reaction of elemental sulfur with substances containing the double bond in their structures and compared with results published in the literature for the sulfurization ofoctene-1. This information showed that the predominant structure of sulfurized lard oil was a molecule with two disulfide bridges linking three fatty groups and the influence of triglyceride structures in lard oil on the viscosity and solubility of the sulfurized product. It has been shown that the desirable antiwear and antiscuff behavior of sulfurized fatty additives in lubricants is relatively insensitive to the specific nature or source of the additive so long as the sulfur and the fatty moieties are persent at the proper level.

Kammann and Phillips [29] investigated products made by sulfurization of soybean, sunflower, cottonseed, 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, the products had potentially practical application. Compared to the other sulfurized vegetable triglyceride products, *Limnanthes* products showed the best solubility in high viscosity index paraffins oil. For solutions, measurements of EP, namely, friction and wear, were compared. Whereas products from jojoba were best of the triglyceride group, the *Limnanthes*-containing products generally gave the best performance. A main problem of sulfurized vegetable triglycerides compared to lard-based products is that of poor solubility in paraffinics oils. On the other hand,products from lard oil had very good solubility.