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Investigation of Raw Materials for Sulfurized Vegetable Oil Based Lubricant Additives

Gábor Zoltán NAGY,[1] Nikoletta LÁZÁR,[2] Roland NAGY[3]

[1] *University of Pannonia, Faculty of Engineering, Department of MOL Hydrocarbon and Coal Processing, Veszprém, Hungary, gznagy@phd.uni-pannon.hu*

[2] *University of Pannonia, Faculty of Engineering, Department of MOL Hydrocarbon and Coal Processing, Veszprém, Hungary, nikoletta.lazar96@gmail.com*

[3] *University of Pannonia, Faculty of Engineering, Department of MOL Hydrocarbon and Coal Processing, Veszprém, Hungary, nroland@almos.uni-pannon.hu*

Abstract

Extreme Pressure (EP) additives are commonly used in lubricants to reduce wear and prevent seizures at high temperature and pressure. In terms of their mechanism, these build up a film on the surface with chemisorption. This film efficiently prevents metal-metal adhesion. Industrial statistics show that extreme pressure additives are mostly used in metalworking fluids, lubricating greases and engine oils.

Sulfurized vegetable oils can be used as EP additives of lubricants. This type of EP additive is ashless, derived from renewable sources and have a lesser negative effect on the environment compared to those that are not derived from vegetable sources. To determine the appropriate vegetable oils to be used as the raw material of EP additives, the structure of triglycerides, cost-effectiveness and availability aspects must be considered. Results of experiments show that rapeseed oil and soybean oil best meet this criteria system.

Keywords*: antiwear, vegetable oil, sulfurized oil, additive.*

1. Introduction

1.1. The EP-additives

Modern lubricants use different additives to improve their different properties or to give them a new, favourable property, thus meeting the quality requirements for the lubricant [1]. There are many types of additives, in addition to EP additives, there are detergent-dispersant additives, corrosion inhibitors, oxidation inhibitors, and others. The purpose of anti-wear and EP additives is to reduce wear and prevent seizures even at very high temperatures and pressures.

It is not entirely possible to distinguish between anti-wear and EP additives. The use of an additive in one case has an anti-wear effect, while the use of this additive in another case acts as an EP additive. There are also cases where both effects are exerted by a given additive. The mechanisms of action of the two additive types (**Figure 1**) are the same and can be grouped according to their activity temperature. Anti-wear additives work at low temperatures, while EP additives work at higher temperatures [2].

EP additives are highly reactive, can impair the oxidation stability of the oil, cause corrosion in non-ferrous metals, and reduce the fatigue resistance of bearings and other equipment [3].

EP additives are designed to prevent metal-to-metal adhesion or welding if the natural protective oxide layer between the contact surfaces is removed and other active compounds in the oil are not reactive enough to prevent the protective film from disappearing. This is most often in the case of high-speed, high-load, and/or high-temperature operations [4, 5].

In terms of mechanism of action, these additives work by reacting with the surface of the metal to form a metal compound similar to anti-wear additives, but here the reaction rate is higher, the film formed is thicker and more resistant and the shear strength of the resulting film is lower than metal. EP additives can prevent scratches, abra-

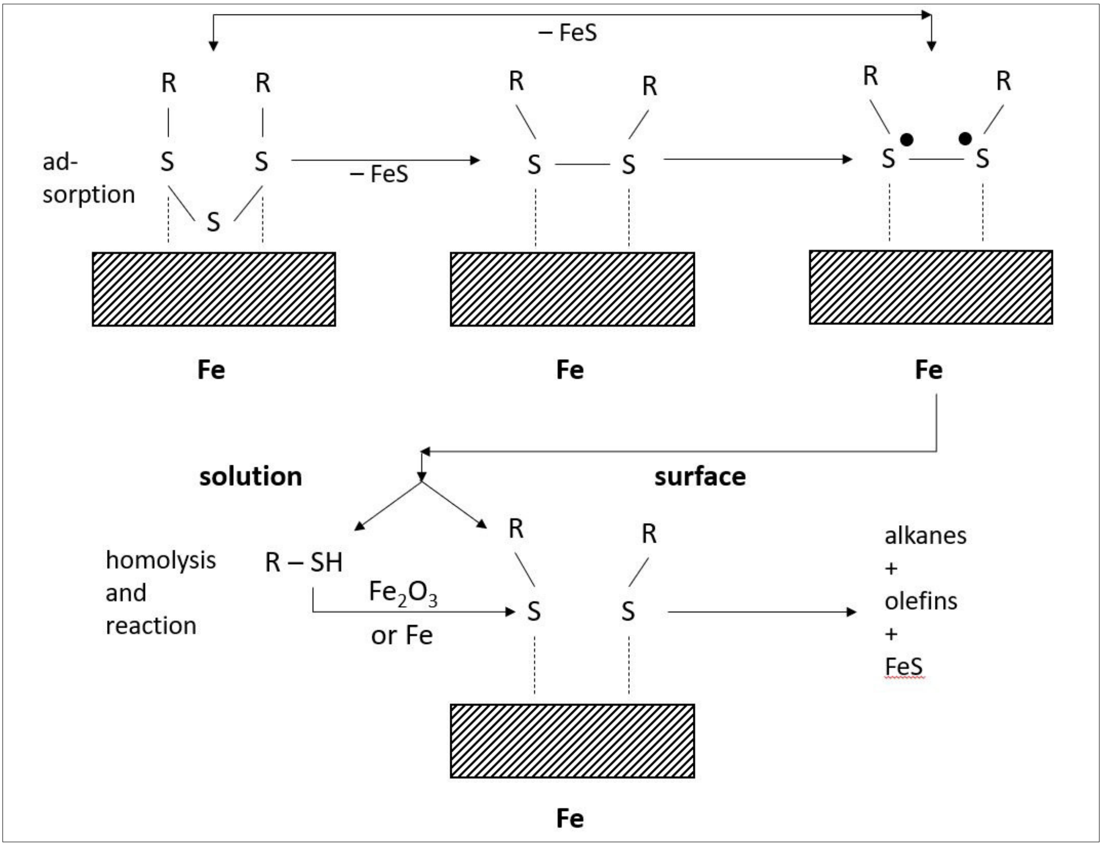

Figure 1. *The mechanism of action of EP additives on iron metal surfaces.*

sion and sticking under high speed and impact loads. During use, EP additives deplete and the surface of the metals wears evenly, resulting in a smoother surface, thus increasing the chances of hydrodynamic lubrication, resulting in less local stress and lower friction [4, 6].

Both anti-wear and EP additives are available in a wide range, but their selection must consider, among other things, economic considerations, the oil solubility, and the oxidative stability-reducing effect of the additive [4, 7].

The preparation of sulfurized EP additives requires, above all, a sulfurizable compound and a sulfurizing compound. The selectivity of the reaction can be improved by using a catalyst. Compounds containing one or more double bonds are used as sulfurizable compounds. These include vegetable oils, fatty acids and fatty acid esters, as well as olefins, acrylates and methacrylates. Orthorhombic elemental sulfur and hydrogen sulfide are widely used as sulfurizing compounds. In addition, other sulfur donors containing bounded sulfur, such as mercaptans, can be used [1, 2, 4].

In the current phase of the research, we aimed to examine the range of vegetable oils that can be used for the production of sulfurized vegetable oil additives based on literature data and to compare them based on properties that have key importance for the synthesis of EP additives. Furthermore, our goal was to select vegetable oils that can be used with favourable results for the production of EP additives based on sulfurized vegetable oils.

1.2. Vegetable oil

The value and field of application of vegetable oils depend on their fatty acid composition, so since each vegetable oil has different physical and chemical properties, so does its field of application. For example, oils containing side chains with 12 carbon atoms (e.g. lauric acid) are important raw materials for the production of detergents and surfactants, while oils containing side chains with 18-22 carbon atoms (e.g. oleic acid) are used in lubricants or as polymer additives [4, 8].

In terms of regions, the Asian market dominates both production and consumption. Rapeseed oil is the most widely used vegetable oil as a bio-lubricant on the European market, sunflower oil and soybean oil have greater importance in the US. In addition, the role of castor oil, corn oil and safflower oil are small [8].

Wax esters are oxo-esters of long-chain fatty acids and long-chain fatty alcohols. Wax esters of natural origin are mixtures of esters but also contain hydrocarbons. Wax esters have excellent performance properties due to their high oxidation stability and good resistance to hydrolysis. For this reason, stable additive compounds can be synthesized even under the conditions of the use of EP additives. The oxidation stability of each vegetable oil is illustrated in Table 1 [4, 8].

The linear structure gives the lubricant an anti-corrosion, anti-foaming, anti-wear and anti-friction effect. Due to these properties, they are excellent raw materials for high temperature and high pressure lubricants such as hydraulic fluids and EP additives. Wax esters are neutral lipids that are solid at room temperature and have limited availability in nature (cachalot oil, jojoba oil) [8].

2. Results

2.1. Investigation of vegetable oils that can be used as a raw material of EP additives

Glycerol esters of long-chain fatty acids can be used as raw materials for EP additives. Examples are white meadowfoam oil, rapeseed oil, Crambe tataria oil, soybean oil, peanut oil, sunflower oil, olive oil, corn oil, coconut oil and palm oil. In addition to triesters, monoesters such as jojoba oil, an ester of long unsaturated fatty acids and long unsaturated alcohols, can be used. Mixtures of triesters and monoesters can also be used. Non-edible raw materials (castor oil, white meadowfoam oil, Crambe tataria oil) enjoy a market advantage, both for economic and environmental reasons [8].

Table 1. *Comparison of oxidative stability index of some vegetable oils*

Vegetable oil	Oxidation stability index at 110 °C
White meadowfoam oil	246.9
Refined white meadowfoam oil	67.3
Cold-pressed jojoba oil	55.9
Crude jojoba oil	34.5
Refined jojoba oil	31.4
Refined soybean oil	19.9
Refined castor oil	56.1

2.1.1. White meadowfoam oil

The white meadowfoam is a perennial plant native to the northwestern region of the United States. The oil is extracted from its seeds, which contain about 27% oil [9].

Crude white meadowfoam oil contains long-chain fatty acids (≥97% C20), making it a very stable and unique source of unsaturated long-chain fatty acids. Due to this unique chemical composition, many developments are underway to become an industrial oil crop. During its decomposition, monoene fatty acids are formed, which, for example, has an unusually high oxidation stability index compared to other vegetable oils, which is well illustrated in Table 1.

For this reason, it is recommended for areas that produce very valuable products [8].

However, the disadvantage of it is that the diene-structure causes solubility problems during sulfurization due to the formation of crosslinks. By sulfurizing the oil for two hours at 180°C with 20 % sulfur, the product is obtained almost insoluble in hydrocarbon oils [9].

2.1.2. Rapeseed oil

In terms of the composition of rapeseed oil, it consists of a high amount (about 60%) of monounsaturated oleic acid and a low amount (about 5.5%) of saturated fatty acids. The main disadvantage of rapeseed oils is their relatively high content of linoleic acid (C18: 2) and linolenic acid (C18: 3).

Rapeseed oil is excellent for use in biotechnological processes. The synthesis of oil in rapeseed can be influenced to produce specific, chemically modified triglycerides. Due to its high oleic acid content, it is a popular raw material in the food industry due to its good quality and low saturated fatty acid content [8].

2.1.3. Crambe tataria oil

Crambe tataria is a drought-tolerant, low-nutrient plant native to Ethiopia that has been grown and processed on an industrial scale in the U.S.

since 1990. The oil content of the seeds in the Crambe tataria is approx. 30% with a high erucic acid content (>50% C22:1) and a low free fatty acid content (<0.5%).

Refined Crambe tataria oil is mainly used as a source of erucic acid, but there is also a lot of research into its conversion to a wax ester (EPOBIO project), which could be used for lubrication purposes, including as a base for EP additives.

However, it contains large amounts of linoleic acid and linolenic acid, which negatively affect oxidation stability. Erucic acid has high viscosity but has a negative effect on cold flow properties due to its high melting point [8].

2.1.4. Jojoba oil

After the banning of sulfurized cachalot oil, there was a lot of research to replace it in the late 1970s. One way to replace cachalot oil is with jojoba oil, which has several benefits, such as a more pleasant smell than cachalot oil. Furthermore, crude jojoba oil does not contain glycerides, so fewer purification steps are required before use [9].

The jojoba plant is an evergreen shrub with tiny seeds. It is also used in many fields, such as the pharmaceutical industry, the cosmetics industry, and the production of biofuels. However, its disadvantage is that its annual production is 5 kilotons, which does not meet global trade needs [8].

Jojoba oil has a low or no glyceride chemical composition and most of its compounds have a carbon number between 36 and 42. This narrow carbon number range and linear structure give jojoba oil unique properties. So jojoba oil is a monoester with a high molecular weight and is made up of straight-chain fatty acids and fatty alcohols that also contain a double bond. The molecular structure is represented in Figure 2, in which *m* and *n* are between 8 and 12.

Jojoba oil is mainly a fatty acid ester of decyl alcohol. Its advantageous properties include its unusually high oxidation stability, especially at high temperatures. This has been shown to be due in part or whole to the tocopherol and other natural antioxidants it contains [10].

Soluble in organic solvents due to its physical properties, but not miscible with ethanol, methanol, acetic acid or acetone. A light golden, non-volatile liquid with low acid content. Several other physical properties are summarized in Table 2.

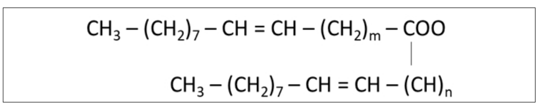

Figure 2. *Molecular structure of jojoba oil*

Table 2. *Main properties of jojoba oil*

Properties	Value	Test method
Density (g/cm^3)	0.863	ASTM D-1298
Refractivity index, nD20	1.4652	ASTM D-1218
Kinematic viscosity at 40 °C (cSt)	26	ASTM D-445
Kinematic viscosity at 100 °C (cSt)	7.5	ASTM D-445
Viscosity index	257	ASTM D-189
Acid number (mgKOH/g)	2.0	ASTM D-664
Flashpoint (°C)	310	ASTM D-92
Iodine value (gI_2 /100g)	80	ASTM D-2075
Average molecular weight (g/mol)	604	GPC

2.1.5. Soybean oil

Soybeans are native to Northeast Asia, where the climate is temperate. Soybeans are sensitive to temperature changes and require four different seasons. Worldwide soybean cultivation is estimated at 257.5 million tons, and the main soybean-growing countries are the US and Argentina.

Refined soybean oil is a good lubricant but is not preferred for many applications because it oxidizes too quickly. This problem, and thus its short shelf life, can be eliminated in several ways, such as by chemical modification (partial hydrogenation and epoxidation), the use of additives, esterification with palm oil, or possibly mixing with jojoba oil. Jojoba oil is effective in reducing the formation of hydroperoxide and other volatile components in soybean oil, making any mixture of jojoba oil and soybean oil more stable than pure soybean oil. Mixing them in an 80:20 soybean oil:jojoba oil ratio is most effective for the oxidative stability of soybean oil [8].

2.2. Selection of vegetable oils that can be used as a raw material of EP additives

There are many types of vegetable oils, each with a different structure and thus different properties. Jojoba oil, white meadowfoam oil, rapeseed oil and Crambe tataria oil are the best criteria for the use of vegetable oils as EP additives, and soybean oil can also be used. However,

Table 3. *Typical composition of investigated vegetable oils*

Vegetable oil	Average fatty acid distribution of triglycerides that build up vegetable oils, %			
	< C18	C18	C20	C22 <
White meadow-foam oil	0.6	2.1	65.7	31.6
Rapeseed oil	4.8	88.1	2.4	4.7
Crambe tataria oil	3.6	34.3	10.7	51.4
Jojoba oil	1.8	78.5	0.2	19.5
Soybean oil	11.4	83.3	0.5	4.8

Table 4. *Applicability of investigated vegetable oils*

Vegetable oil	Suitability for EP additive synthesis	Regional availability	Raw material cost
White meadowfoam oil	Suitable	Difficult supply	High
Rapeseed oil	Excellent	Easily available	Low
Crambe tataria oil	Suitable	Difficult supply	High
Jojoba oil	Excellent	Difficult supply	High
Soybean oil	Excellent	Available	Medium

an examination of a mixture of these may give satisfactory results.

Based on the previous reference, triglycerides containing C18-C22 fatty acid chains can be advantageously used as a raw material for the synthesis of lubricant additives **[4, 8]**. Of the investigated vegetable oils, rapeseed oil, jojoba oil and soybean oil, which contain the highest proportion of triglycerides in this carbon number range, meet this condition the most. The average distribution of fatty acids found in the studied vegetable oils is shown in **Table 3 [9, 10]**.

Among the studied vegetable oils, the composition of the previously used cachalot oil corresponds to the composition of jojoba oil, since it is similarly a wax ester, one of the properties of which is the high oxidation stability. However, the use of jojoba oil is neither advantageous nor economically advantageous.

Like jojoba oil, white meadowfoam oil and Crambe tataria oil are not available in sufficient quantities in Europe. However, the oil in the Crambe tataria would have to be converted to a wax ester to be used as a base for EP additive, which has additional costs.

The suitability of the investigated vegetable oils for synthesis and their evaluation from an economic point of view is briefly summarized in **Table 4.**

For these reasons, rapeseed oil and soybean oil, or a mixture of these, are expected to yield favourable results in our further research.

3. Conclusions

Based on the information available in the literature, we examined the range of vegetable oils that are most suitable for the production of sulfur-based vegetable oil-based EP additives based on the published results.

Based on a review of the literature, the fatty acid components of vegetable oils that can be used as EP additives should have a carbon number of 18 to 22, and 90% of the fatty acids should preferably contain one but no more than three double bonds.

Based on the comparison of the results and taking into account the economics and availability conditions, we will use rapeseed oil and soybean oil, or a mixture of them, for the synthesis of EP additive samples in the next experimental phase of the research.

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