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Study on Sulfurized Vegetable Oil Type Extreme Pressure Additives

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Extreme Pressure (EP) additives are commonly used in lubricants to reduce wear and prevent seizures at high temperatures 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 has a lesser negative effect on the environment compared to those that are not derived from vegetable sources. Several technologies for the preparation of additives have been developed, of which the dark sulfurization process has been studied. Several physical and lubricating properties of the obtained additives have been investigated, based on which, it is possible to produce additives with favourable viscosity values and low copper corrosion grade.
Keywords: extreme pressure, additive, vegetable oil, sulfurized vegetable oil

1. Introduction

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 (Theo et al., 2007). 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 (Syed et al., 2009).

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 (Pradeep et al., 2013).

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 (Vámos et al., 1983). 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, abrasion and sticking under high-speed and impact loads (Leslie et al., 2017). 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 (Theo et al., 2011).

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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 (Don et al., 2007).

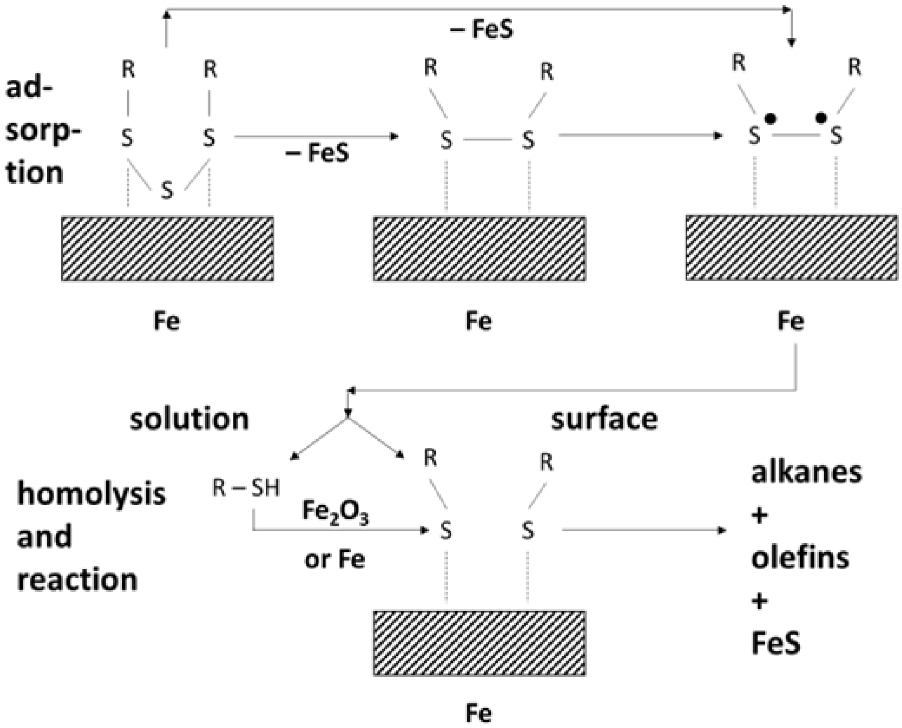

Figure 1: The mechanism of action of EP additives on iron metal surfaces

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 (Leslie et al., 2017).
The current phase of the research is aimed to examine the range of sulfur donors 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, the main objective was to select sulfur donors that can be used with favourable results for the production of EP additives based on sulfurized vegetable oils. The minimum achievable weld load value was set to 2 000 N and the maximum occurred scar diameter was set to 0.50 mm.

2. Materials

Tables 1-2 contain the data of the raw materials (vegetable oil and sulfur donors) used for the EP additives synthesis.

Table 1: Characteristics of the vegetable oil used for the synthesis

Properties	Rapeseed oil
Trade name	Refined rapeseed oil
Producer or distributor	Bunge Ltd.
Area of application	food industry, biofuels
Purity, %	99.8%

Table 2: Characteristics of the sulfur donors used for the synthesis

Properties	Sulfur	Tert-alkyl-thiol	Thioamide
Consistency	solid	liquid	solid
Colour, appearance	yellow	light brown, clear	yellow, clear
Density at 15°C, kg/m^3	2 080	860	1 420
Flashpoint, °C	over 300	100	~250

Based on the area of application and purity, the examined raw materials were found to be suitable for further investigations.

3. Properties of EP additives

Detailed physical and physical-chemical investigation of the examined raw materials was used the following methods:

- Appearance [Visual]
- Density 20°C, [MSZ EN ISO 12185:1998], g/cm^3
- Kinematic viscosity at 40°C [MSZ EN ISO 3104:1996], mm^2/s
- Kinematic viscosity at 100°C-on [MSZ EN ISO 3104:1996], mm^2/s
- Dynamic viscosity at 40°C (calculated) [MSZ EN ISO 3104:1996], mPa·s
- Acid value [MSZ EN ISO 660:2000], mg KOH/g
- Saponification number [MSZ ISO 6293:1994], mg KOH/g
- Iodine value [MSZ EN ISO 3961:2000], g I_2/100g
- Water content (KF – Coulometry) [MSZ EN ISO 12937:2001], wt%
- Sediment content [IEC 60422], wt%

For the evaluation of the functional effect of synthesized additives, the so-called four-ball method was applied, which is widely applied in the lubricant industry. These testing procedures were used to evaluate the extreme-pressure and anti-wear properties of all types of lubricants (oils and greases), with the four-ball machine (Shubhamita et al., 2019):

- Four-ball test – weld load [DIN 51350-4:2015], N

  The operational principle of the Four-ball test machine revolves around the utilization of a rolling motion. It entails the rotation of a single stainless steel ball against three additional stainless steel balls, all coated with lubricant film. The three stationary balls are securely held in position via a cradle. Incremental increases in load are applied until the lubricant film is depleted, leading to direct metal-to-metal contact. Subsequently, the load is further increased until welding occurs. The determination of the measured weld load serves as a basis for formulating lubricants with varying degrees of extreme pressure properties.

- Four-ball test – scar diameter [DIN 51350-5:2015], mm

  Furthermore, the Four-ball test machine is employed to assess the wear scar characteristics and coefficient of friction exhibited by a lubricant. The purpose of the test is to evaluate the efficiency of lubricants in preventing wear. During the test, a steel ball performs a rotation motion against three fixed steel balls that have been lubricated, all under predefined conditions encompassing load, speed, temperature, and duration. The effectiveness of the lubricant in hindering wear is indicated by the size of the wear scar present on the three stationary balls. After the test run has been completed, the three wear scars are measured, and the resulting average value is reported.

4. Results

The described investigations were started by determining the physical and chemical properties of raw materials. After that, lubrication technical properties were determined.
The additive samples were made with the reaction of the raw materials characterized above, and elemental sulphur (Frank et al., 1979) (Nidia et al., 2012). The sulfurization reaction took place in the liquid phase at about 140-170°C and about 1-2 bar (Emile et al., 1974). To increase the reaction yield, mixing for 2-6 hours is necessary at the reaction temperature (Donald et al., 1979).
Table 3 contains the results of the measurement of synthesized EP additives.

Table 3: Characteristics of the synthesized additives

Method	Additive-1	Additive-2	Additive-3	Additive-4	Additive-5
Appearance [Visual]	brown, viscous liquid	brown, viscous liquid	yellow, slightly viscous liquid	orange-yellow, slightly viscous liquid	brown, slightly viscous liquid
Kinematic viscosity at 40 °C [MSZ EN ISO 3104:1996], mm^2/s	1 591.5	2 763.0	46.53	55.67	52.01
Kinematic viscosity at 100 °C [MSZ EN ISO 3104:1996], mm^2/s	121.7	322.2	6.42	8.57	8.72
Sulfur content [ASTM D 5185-18], wt%	11.140	9.232	2.040	5.310	18.441
Active sulfur content [ASTM D 1662-07], wt%	0.44	0.00	1.12	2.11	6.99
Four-ball test - weld load [DIN 51350-4:2015], N	2 300	2 300	1 600	2 000	2 400
Four-ball test - scar diameter [DIN 51350-5:2015], mm	0.54	0.52	0.88	0.49	0.56

Additives labelled additive-3, additive-4 and additive-5 had a clear appearance, so they correspond to the aspects stated in the objective. The kinematic viscosity value of additive-3, additive-4 and additive-5 at 40°C and 100°C is significantly lower than that of additive-1 and additive-2.
To measure the functional effect of the synthesized additives, lubricating oil samples were made with the use of Group I type base oil with 3 wt% additive content. The results of the four-ball weld load measurements are indicated in Figure 2.

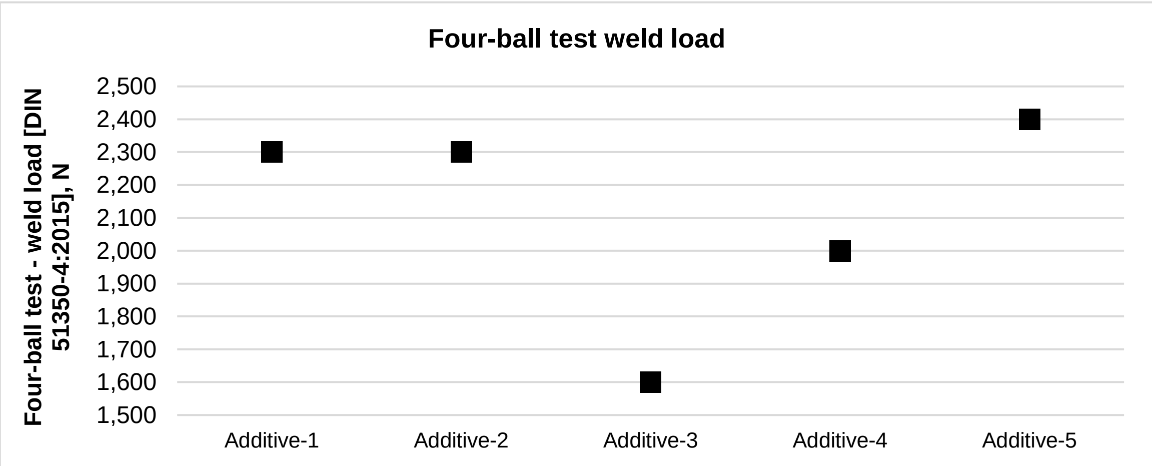

Figure 2: The four-ball test weld load results of the base oil solutions of synthesized additives

The worst weld load result (1 600 N) was obtained in the case of Additive-3. In the case of Aditive-4, the weld load result is better compared to Additive-3. The measured values of the weld load of Additive-1 and Additive-2 samples are close to each other and above the requirements. The viscosity values of Additive-1 are more favourable than in the case of Additive-2 and it provides better usability. Based on their active sulfur content results, there is also no significant difference between the two samples. The best weld load result (2 400 N) was achieved with the Additive-5 sample. All of this is a consequence of its relatively high active sulfur content (6.99 wt%). In the case of structural materials and workpieces containing copper, active sulfur content must be taken into account when formulating the lubricant.
The results of the four-ball scar diameter measurements are indicated in Figure 3.

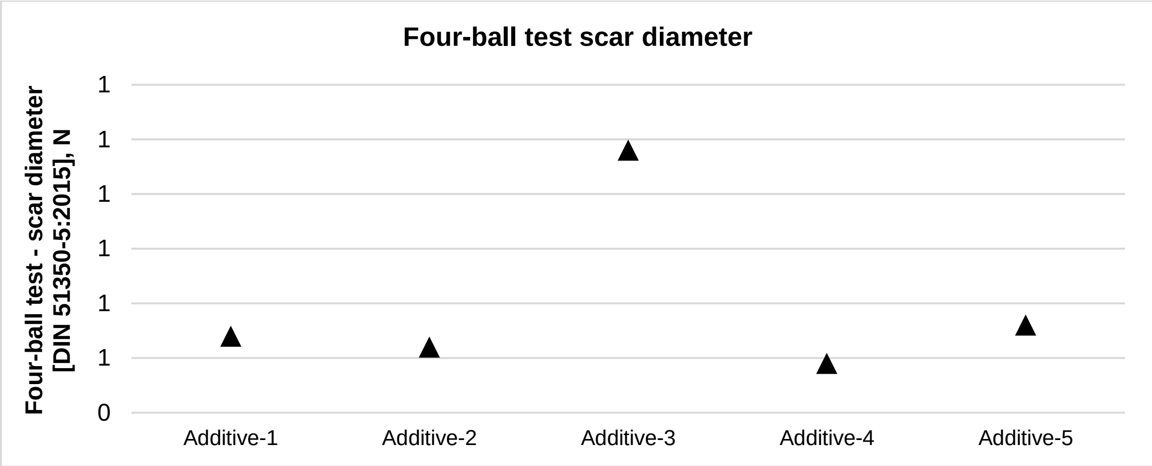

Figure 3: The four-ball test scar diameter results of the base oil solutions of synthesized additives

In addition to the worst weld load result, the worst wear scar diameter result (0.88 mm) also occurred in the case of Additive-3. In the case of Aditive-5, the result is better to a great extent compared to Additive-3. In the case of Additive-1 and Additive-2 samples, the wear scar diameter values are also close to each other as in the case of weld load results of them. The lowest wear scar diameter result (0.49 mm) was achieved with the Additive-4 sample. Its weld load result (2 000 N) is also appropriate to the objective.
In addition to the additives with a lower viscosity can be advantageously used in industry, as they dissolve more easily in oil and are easier to handle. Additives labelled additive-3, additive-4 and additive-5 had a clear appearance.

5. Conclusions

EP additives, also known as anti-seize additives, are additives found in lubricants whose purpose is to reduce wear and prevent seizing at high temperatures and pressures. In terms of their mechanism of action, they create a film on the surface by chemisorption, with which they can prevent contact with metal structural materials. Its share of the 4.5 million tons of additives used in the world is 7%. It is used in the largest quantities in the automotive industry and in metalworking auxiliary materials.
Based on the information available in the literature, the range of sulfur donors most suitable for producing sulfurized vegetable oil-based EP additives was examined, based on the published results.
Based on our tribological tests (Four-ball test, weld load and scar diameter), Additive-4 was found to be the best. During the tests, the fact was taken into account that Additive-4 has a clear appearance, as stated in the objective.Based on the comparison of the results and taking into account the economics and availability conditions, it is the most preferable to use rapeseed oil and tert-alkyl-thiol, for the synthesis of EP additive samples in the next experimental phase of the research.In addition, additives with a lower viscosity can be advantageously used in industry, as they dissolve more easily in oil and are easier to handle.
In industrial settings, where high-pressure and high-load conditions are prevalent, the EP/AW additives derived from sulfurized vegetable oil offer exceptional lubrication performance. They effectively reduce friction and wear. This not only enhances the efficiency and reliability of machinery but also extends its operational lifespan, resulting in significant cost savings for industrial operators.
The use of these additives aligns with the growing demand for environmentally friendly and sustainable solutions in the industrial sector. Sulfurized vegetable oil is derived from renewable sources, making it a more environmentally conscious alternative to traditional additives derived from petroleum-based compounds. This aligns with the sustainability goals of many industries, including the push towards reduced carbon emissions and minimized environmental impact.
The unique composition of sulfurized vegetable oil EP/AW additives offers compatibility with a wide range of base oils, including mineral oils, synthetic oils, and even bio-based lubricants. This versatility allows for their seamless integration into existing lubricant formulations, providing enhanced performance without the need for significant changes or adjustments to established industrial processes.

References

Don M.P., Martin W., Ekkehard D.,2016, Lubrication Fundamentals. Third Edition, 35-60. CRC Press, Boca Raton, USA.

Donald A.L., John A.B., 1979, Extreme pressure additives for lubricants, US4149982, USA.

Emile N.H., 1974, Novel sulfur-containing compositions. US3926822, USA.

Frank L.E., Phillip S.L., Robert E.A., 1979, Vegetable oil derivatives as lubricant additives. EP0353872A1, EU.

Leslie R.R., 2017, Lubricant Additives, Chemistry and Applications, Third Edition, 211-278. CRC Press, Boca Raton, USA.

Hammond E.W., 2003, Vegetable oils: Types. and properties, Second Edition, 5899-5904. Academic Press, Cambridge, USA.

Karak N., 2012, Vegetable oils and their derivatives, 54-94. Woodhead Publishing Ltd., Sawston, England.

Fernando S., Hanna M., Adhikari S., 2007, Lubricity characteristics of selected vegetable oils, animal fats and their derivatives. Applied Engineering Agriculture, 23, 5–11, DOI: 10.13031/issn.0883-8542.

Mihail I., Dragana R., Xianmei W., Zoran S.P., Thomas A.U., 2015, Functionalized vegetable oils as precursors for polymers by thiol-ene reaction. European Polymer Journal, 67 (1/2), 439-448.

Bharat B., Gupta K., 1991, Handbook of Tribology: Materials, Coatings, and Surface Treatments. McGraw-Hill Inc., New York, USA.

Nidia S. Caetano, Joana I.M. Teixeira, Teresa M. Mata: Enzymatic Catalysis of Vegetable Oil with Ethanol in the Presence of Co-solvents, Chemical Engineering Transactions, VOL. 26, 2012, DOI: 10.33.03/CET1226014

Pradeep L.M., Sudeep P.I., Michael N., Satish V.K., Michael R.L., 2013, Tribology for Scientists and Engineers, 317-318. Springer, New York, USA.

Shubhamita B., James N.V., Michael S.W., 2019, Industrial gear lubricant additive package with biodegradable sulfur component. US10208267, USA.

Syed Q.A.R., 2009, A Comprehensive Review of Lubricant Chemistry, Technology, Selection and Design 149-181. ASTM International, West Conshohocken, USA.

Theo M., Kirsten B., Thorsten B., 2011, Industrial Tribology, Tribosystems, Friction, Wear and Surface Engineering, Lubrication 320-335. Wiley, Weinheim, Germany.

Theo M., Wilfried D., 2007, Lubricants and Lubrication, Second Edition 88-119. Wiley, Weinheim, Germany.

Vámos E., 1983, Tribological Handbook, Friction, wear and lubrication of machines and machine parts, 36-116. Technical Publishing House, Budapest, Hungary.