Efficiency of Antioxidant Additives Mixed in Vegetable Oils

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The vegetable oils are considered a viable alternative in the manufacture of some industrial lubricants types, as replacement of the mineral base oils. The main issue that has to be solved, in the case of the vegetable oils, is the very poor oxidation resistance that limits their application and period of service. Considering that one of the most common methods for improvement of different characteristics of lubricants is the additivation, this is very often used, also for the oxidation resistance improvement. The antioxidant additives are usually designed for mineral base oils. Considering that, the purpose of the present study is to evaluate the behavior of vegetable oils mixed with suitable antioxidant additive. In this respect, two representative vegetable oils were chosen, characterized and evaluated, in comparison with two mineral base oils. There are many types of additive compositions, but the selected antioxidant additive was one which provides very good results in the mixture with mineral base oils, so, a high performance sulfur-containing hindered phenol component in combination with suitable aminic antioxidant, was chosen. The experimental results have shown a significant different behavior of the additive mixed with the two oil categories, vegetable oils and mineral base oils, behavior that can be explained in correlation with their specific chemical structure.

Keywords: vegetable oils, oxidation resistance, antioxidant additives influence

The vegetable oils become more and more interesting as a viable alternative of mineral base oils, for the manufacture of some industrial lubricants types, but, there are still many aspects that have to be considered and solved, for an extended application and period of use of this oil types [1- 3].

There are very well known the advantageous properties of this type of oils concerning their high biodegradability, fast renewability and their very good lubricating properties. On the other hand, there are also some important disadvantages, like poor thermal stability and limited oxidation resistance [4-7].

Considering that the oxidation resistance is strongly correlated with the base oil chemical structure stability that, on its turn, determines the behavior of the lubricant, it is very important to ensure a high value of this characteristic. A good oxidation resistance of the base oils ensures a proper behavior and a long time of service for the lubricants that are formulated based on these oils [8].

In this respect, the purpose of the present work paper is to present the results of the experimental studies that were focused on the possibilities of vegetable oils oxidation resistance improvement.

The most common method for improvement of different characteristics is the additivation with suitable components, named additives.

The additives used for lubricants preparation have a diverse chemical composition: can be mono component additive or can be a mixture based on two, three or more components that are different functions. The additives have to be easy soluble in the base oils, compatible with other additives and efficient. So, small quantities of additives added in the base oil, 0.3…2 % wt, have to significantly improve those characteristics that they have been designed for.

For oxidation resistance improvement, there are many types of additive compositions, within the most known and effective are the di-alky-di-thyo-phosphate, alkyl-phenols, succinic esters, alkyl-aryl-amines, di-thyo-carbamate etc [7, 9, 10].

It is important to consider that the usual additives are designed for mineral base oils and the data about behavior of the antioxidant additives on vegetable oils are very poor.

Considering all above, the work paper presents the results of experimental studies performed by some selected vegetable oils mixed with a suitable antioxidant additive and emphasizes the particular behavior of the additive on this type of oils, in comparison with mineral base oils.

Experimental part

The experimental study started from the testing of vegetable oils characteristics. In order to have conclusive and representative data about specific characteristics of vegetable oils, there were tested many of these oils types.

Based on the testing results, that were in proper correlation with specific scientific literature documentation [3, 6, 11, 12], two vegetable oils were selected, as most representative for the study purpose: soybean oil and palm oil. The main criteria of selection were the chemical structure and viscosity class, as is explained further.

The chemical structure of the two selected oils is significant different: soy bean oil chemical structure is based on more unsaturated fatty acid chain and palm oil is based on saturated fatty acid chain, as is presented in the table no.1 [11, 12]. This particular and different chemical structure of each one of these oils implicitly influences on their specific behaviour.

Characterization of vegetable oils

The selected vegetable oils were mainly evaluated by those characteristics that are representative for their application as lubricant.

The specific characteristics of soybean oil and palm oil, tested in laboratory, are presented in the table 2.

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Fatty acids content, % wt	Soy bean oil	Palm oil
Myristic, saturated C14	-	1.0
Palmitic, saturated C16	16,0	43,5
Stearic, saturated C18	-	4,3
Oleic, monounsaturated C18	23,0	36,6
Linoleic, doubleunsaturated C18	53,0	9,1
Linolenic, poyunsaurated C18	8,0	-
Other acids	-	5,5

Table 1
CHEMICAL COMPOSITION OF SOY BEAN OIL AND PALM OIL

Characteristics	Soy bean oil	Palm oil	Test Method
Viscosity: at 40 °C, cSt	34,83	40,50	ASTM D445
Viscosity: at 100 °C, cSt	8,04	8,48	ASTM D445
Viscosity Index	215	193	ASTM D2270
Pour point, °C	- 9	+ 30	ASTM D97
Flash point, °C	296	264	ASTM D 92
Iodine number, mg/100 g	120,5	54	ASTM D 5768
Rotary bomb	5	20	ASTM D2272

Table 2
CHARACTERISTICS OF SOY BEAN OIL AND PALM OIL

Evaluating the experimental results, the following aspects could be highlighted:

- soybean oil has a viscosity value within ISO VG 32 class and palm oil is characterized by a viscosity value within ISO VG 46 class;
- the specific values of viscosity index and flash point show quite similar values of these characteristics for both oils;
- a notable difference could be observed related to the pour point, iodine number and the oxidant resistance of these two selected oils, that could be explained by the specific chemical structure configuration; could be noticed that the palm oil has a better oxidation resistance but a poor behaviour at low temperature and that is due to its chemical structure that is based on saturated fatty acids radicals; in this way the saturated chains influence on these two characteristics [1, 4, 6].

Characterization of mineral base oils

In parallel with the evaluation of selected vegetable oils, for a more conclusive fundamentation of the study purpose, two types of mineral base oils were chosen. The main selection criterion was the oils viscosity class that is the basic characteristic of any lubricants. In this respect, there were selected two mineral base oils: one characterized by viscosity within ISO-VG 32 class and the other one characterized by a viscosity within ISO-VG 46 class, in accordance with the specific viscosity values of vegetable oils.

In the table 3 are presented the specific results obtained in laboratory, for the same tested characteristics as in the case of vegetable oils.

As could be observed, the characteristics of selected mineral base oils have similar values, excepting the viscosity that was express chosen from different ISO-VG class.

Biodegradablity

The literature data referring to the biodegradability of the vegetable and mineral oils show important differences; in conformity with CEC L-33-A-94 testing method, vegetable oils are characterized by biodegradability values in the range of 80 – 90 % and the mineral base oils are characterized by biodegradability values in the range of 20 – 30 % [7, 13, 14].

Comparison between vegetable and mineral oils

Comparing the two categories of base oils, vegetable and mineral, the following important differences and specific aspects could be highlighted:

-the vegetable oils are characterized by high values of viscosity index and flash point and these confer important advantages for their use as lubricants. The testing results of vegetable oils biodegradability are remarkable; the values of 80 – 90 % confer a high biodegradability that is an important advantage considering the environmental impact. On the other hand, the oxidation resistance is very

Characteristics	ISO – VG 32	ISO – VG 46	Test Method
Viscosity: at 40 °C, cSt	31,64	43,56	ASTM D445
Viscosity: at 100 °C, cSt	5,21	6,36	ASTM D445
Viscosity Index	91	92	ASTM D2270
Pour point, °C	-21	- 18	ASTM D97
Flash point, °C	208	210	ASTM D 92
Iodine number,	4	6	ASTM D 5768
Rotary bomb	65	60	ASTM D2272

Table 3
CHARACTERISTICS OF SELECTED MINERAL BASE OILS

Characteristics	Antioxidant additive	Test Method
Melting Range, °C	83-85	-
Specific Gravity 20/20°C	1.15	ASTM D1298
Flash Point, °C	150	ASTM D93
Sulfur, % wt	8.9	-

Table 4
CHARACTERISTICS OF SELECTED ADDITIVE

Mixture composition	SBO 1	SBO 2	SBO 3	SBO 4
Antioxidant additive, % wt	0.3	0.6	1.0	1.5
Soy bean oil, % wt	99.7	99.4	99.0	98.5

Table 5
MIXTURES OF SOY BEAN OIL AND ADDITIVE

Mixture composition	PmO 1	PmO 2	PmO 3	PmO 4
Antioxidant additive, % wt	0.3	0.6	1.0	1.5
Palm oil, % wt	99.7	99.4	99.0	98.5

Table 6
MIXTURES OF PALM OIL AND ADDITIVE

poor and that is a really inconvenient considering the stability of characteristics and implicitly the period of service that is significant limited. Another disadvantage is the unsatisfactory behavior at low temperature;

-the mineral oils are characterized by convenient viscosity index and flash point values but lower than those of vegetable oils. The oxidation resistance is considerably higher comparing with vegetable oils and that represent an important advantage that allows their use for an extended period of service. Pour point values are also convenient, offering a significant better behavior at negative temperature. The biodegradability is very deficitary and that explain the real concern related to environmental impact matters.

All these results obtained by experimental tests and the related comments are in proper correlation with the literature data in the field and with the other previous studies experiments [6, 11, 12, 15, 16].

Influence of additives

As it was presented above, the purpose of the present study is to evaluate the possibilities of vegetable oils oxidation resistance improvement by additivation with suitable components.

Within the many types of antioxidant additives, the most known and used types of additive compositions, are based on di-thyo-phosphate type compound, hindered phenol compound, alkyl-amine components, aryl-amine components, di-thyo-carbamate compounds etc, as it was also emphasized [17, 18].

Whereas the scientific documentation in the field and experimental data highlight the poor vegetable oils oxidation resistance, it was necessary to select a very effective antioxidant additive, for enhance the chance of this characteristic improving [7, 10, 18]. In this respect, the chosen antioxidant composition was a high performance sulfur-containing hindered phenol additive in combination with suitable aminic antioxidant that provides very good results on mineral base oils. The specific characteristics of this antioxidant additive composition are presented below.

Experimental study development

Focusing on the main goal of the study – the influence of antioxidant additives on vegetable oils behavior, the following directions of experimental testing were developed:

-evaluation of the additive dosage influence on the vegetable oils oxidation resistance;

-comparing of the testing results obtained in parallel, from vegetable oils mixed with selected additive and from mineral base oils mixed with selected additive;

-concluding on the optimum dosage of additive that allows the accomplishment of the convenient values of vegetable oils oxidation resistance, or defining of the new directions of the study development for more conclusive information achievement.

In the first stage of the experimental study, several mixtures of oils and additives were prepared; for their preparation, each type of oil, vegetable and mineral, were mixed with different dosages of selected additive.

The concentration of the additive in the oils was gradually increased, starting from the dosages recommended for mineral base oils, to the significant higher concentrations that allowed reaching a notable improvement of the vegetable oils oxidation resistance.

So, there were used the following concentrations of additive mixed in oil: 0.3; 0.6; 1.0; 1.5%, all expressed in weight percent.

In the tables number 5-8 are shown the specific compositions of the mixtures.

The significance of the samples encoding is presented further:

SBO – soybean oil;
PmO – palm oil
M 32 – mineral oil ISO-VG 32
M 46 – mineral oil ISO-VG 46

Mixture composition	M 32.1	M 32.2	M 32.3	M 32.4
Antioxidant additive, % wt	0.3	0.6	1.0	1.5
ISO-VG 32 mineral oil, % wt	99.7	99.4	99.0	98.5

Table 7
MIXTURES OF MINERAL BASE OIL ISO VG 32 AND ADDITIVE

Mixture composition	M 46.1	M 46.2	M 46.3	M 46.4
Antioxidant additive, % wt	0.3	0.6	1.0	1.5
ISO-VG 46 mineral oil, % wt	99.7	99.4	99.0	98.5

Table 8
MIXTURES OF MINERAL BASE OIL ISO VG 46 AND ADDITIVE

1,2,3,4 - indicators corresponding to the following dosages of antioxidant additive: 0.3; 0.6; 1.0; 1.5%, expressed in weight percent.

The evaluation of vegetable and mineral oils oxidation resistance was realized by using of rotary bomb oxidation test method, in conformity with ASTM 2272 standard [20]. The testing procedure is further presented.

The oil sample is placed in a vessel that contains, as catalyst, a polished copper coil. Then, the vessel is charged with oxygen to 6.3 at and placed in a bath at a constant temperature of 150°C. Oxidation stability is measures by the specific time needed for reaction between oxygen and oil sample and is expressed in terms of the time required to achieve a 1.75 at pressure drop from maximum pressure.

Applying this methodology, all the formulation presented before, consisting in vegetable oils and mineral oils mixed with selected antioxidant additive, were tested.

The specific experimental results of oxidation resistance test, obtained for vegetable oils as well as for mineral base oils, are presented in the tables number 9 – 12.

Table 9
OXIDATION RESISTANCE OF ADDITIVATED SOY BEAN OIL

Compound	Soybean oil	SBO 1	SBO 2	SBO 3	SBO 4
Rotary bomb test method, minutes, ASTM D 2272	5	20	30	35	38

Table 10
OXIDATION RESISTANCE OF ADDITIVATED PALM OIL

Compound	Palm oil	PmO 1	PmO 2	PmO 3	PmO 4
Rotary bomb test method, minutes, ASTM D 2272	20	45	63	80	85

Table 11
OXIDATION RESISTANCE OF ADDITIVATED MINERAL BASE OIL ISO VG 32

Compound	Mineral oil ISO VG 32	M 32.1	M 32.2	M 32.3	M 32.4
Rotary bomb test method, minutes, ASTM D 2272	65	180	270	370	420

Table 12
OXIDATION RESISTANCE OF ADDITIVATED MINERAL BASE OIL ISO VG 46

Compound	Mineral oil ISO VG 46	M 46.1	M 46.2	M 46.3	M 46.4
Rotary bomb test method, minutes, ASTM D 2272	60	175	260	360	410

Results and discussions

Evaluating all the results presented in the tables 9 – 12, the following comments could be figured:

- the efficiency of the antioxidant additive composition based on sulfur-containing hindered phenol in combination with suitable aminic antioxidant component is higher in the case of palm oil comparing with soybean oil, as could be seen in the figure 1;

- the efficiency of the additive is very similar for the both ISO VG 32 and ISO VG 46 mineral base oils, as is shown in the figure 2;

- for both, vegetable oils and minerals oils, after a certain concentration of the additive, rising of the additive concentration, practically don't bring a more consistent improvement of the oil oxidation resistance;

- the antioxidant additive is much more effective on mineral base oils in comparison with vegetable oils; that could be seen in the figure 3 - where is represented the behavior of soybean oil in comparison with ISO VG 32 mineral base oil as well as in the figure 4 - where is represented the behavior of palm oil in comparison with ISO VG 46 mineral base oil; that remark is in very good correlation with other literature data referring to the low additivation susceptibility of vegetable oils [7, 21, 22].

The different behavior of the additives mixed with the two types of oil category, vegetable oils and mineral base oils, can be explained based on their distinct chemical structure.

The data referring to mineral base oils oxidation process indicate a propagation mechanism by radicals; the antioxidant additive reacts with these radicals, inhibiting the oxidation [23, 24].

In the case of vegetable oil, the polar groups of triglyceride structure may interact with the additive, which also have a polar structure; so that, the efficiency of the

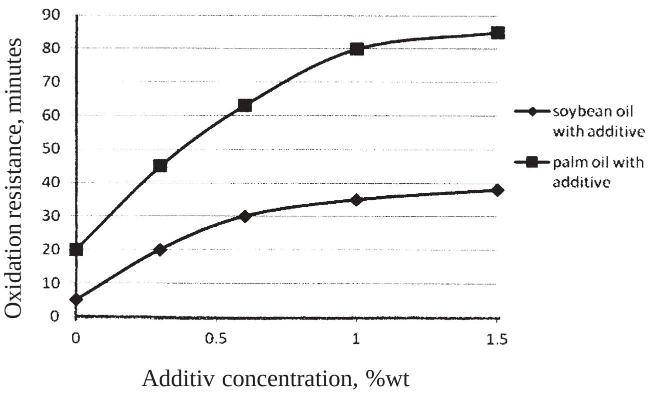

Fig. 1 Oxidation resistance of vegetable oils mixed with additive

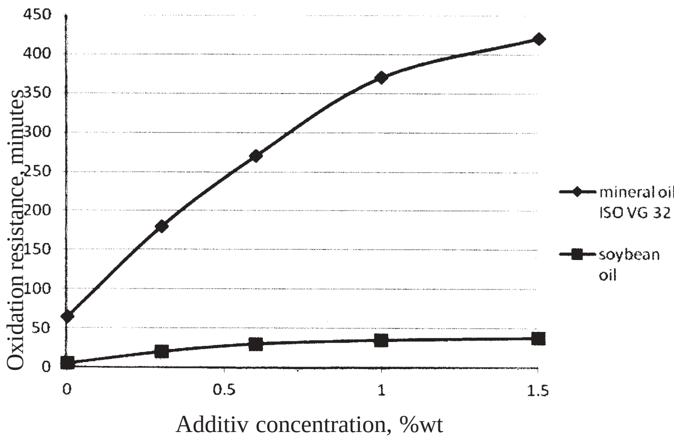

Fig. 2 Oxidation resistance of mineral oils mixed with

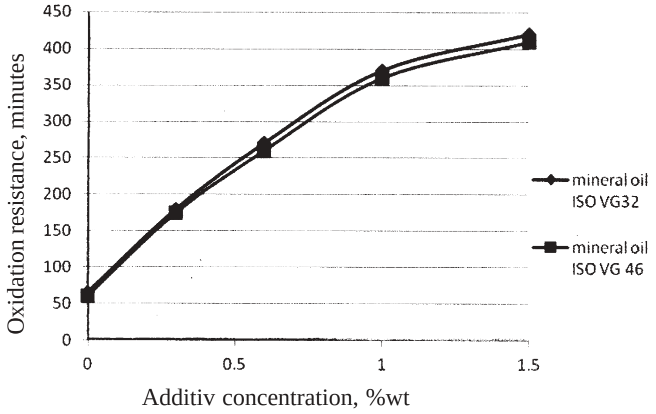

Fig. 3 Comparison between ISO VG 32 mineral oil and soybean oil

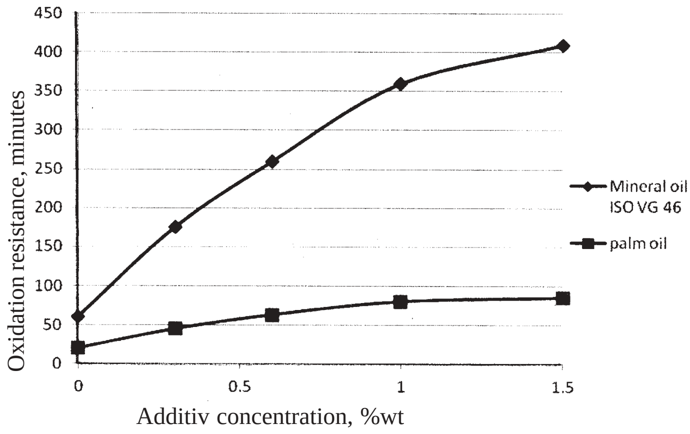

Fig. 4 Comparison between ISO VG 46 mineral oil and palm oil

additive, respectively the function of oxidation reaction inhibiting, is greatly diminished [21, 25].

Conclusions

The experimental study highlights interesting aspects concerning the behaviour of vegetable oils mixed with antioxidant additive. In order to have more conclusive information about the efficiency of the additives mixed in vegetable oils, other types of antioxidant additives will be tested in the next studies. Another direction of the future researches will be the oxidation resistance testing by long time testing methods that are less common, but more relevant.

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