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## INFLUENCE OF THE PRIMARY AND SECONDARY OXIDATION INHIBITORS ON THE OXIDATION STABILITY OF THE MINERAL BASE OILS

Branka DUGIĆ KOJIĆ<sup>1\*</sup>, Pero DUGIĆ<sup>2</sup>, Tatjana BOTIĆ<sup>3</sup>, Goran DUGIĆ<sup>4</sup>

<sup>1,4</sup>Oil Refinery Modriča, Modriča, Republic of Srpska, gdugic@modricaoil.com;

<sup>2,3</sup>Faculty of Technology, University of Banja Luka, Republic of Srpska, pero.dugic@tf.unibl.or,  
tatjana.botic@tf.unibl.org

\*Corresponding author: branka@modricaoil.com

**Abstract:** Oxidation stability is one of the most important characteristics of both base oils and finished products. Based on this characteristic, it is possible to evaluate the ability of lubricants to provide a long usage time under different application conditions. In order to ensure the best possible resistance of the lubricant to oxidation, in the formulations of finished products it is necessary to add oxidation inhibitors that will protect lubricant against oxygen attacks. The rate of oxidation depends on the quality and type of the base oil, the used additive package, but also the type of oxidation inhibitor, as well as the conditions of use. The aim of this paper was to investigate the influence of primary and secondary oxidation inhibitors on the oxidation stability of mineral base oils. Two base oils of different viscosity gradations were used for the test, as well as two types of oxidation inhibitors, primary and secondary. Samples were inhibited with five different concentrations. A standard test method ASTM D 2272 was used to determine oxidation stability.

**Keywords:** oxidation stability, oxidation inhibitors, mineral base oils, primary and secondary oxidation inhibitors, standard method ASTM D 2272.

### 1. INTRODUCTION

The characteristics of the base oils influence almost all the parameters of the finished product. Almost all the lubricant characteristics can be modified by adding suitable additives [1]. Oxidation stability is one of the key characteristics of lubricating oils. The oxidation process occurs during application, even during standstill. In addition to the components included in the finished product, oxidation stability is influenced by other parameters such as: the temperature that accelerates the oxidation process; presence of water - at elevated temperatures, hydrolysis and separation of additives and

lubricants occurs; The presence of metal negatively affects oxidation stability as there is an exchange of the ions that catalyze the oxidation process [2,3]. The process of oxidation leads to the emergence of various products that lead to changes in the physical and chemical characteristics of the oil. It is very important to determine the limit of the oxidation inhibitor content, whereby further increase in concentration does not lead to product improvement in terms of prolonging the usage time. Oxidation is the main cause of the increase in viscosity, the formation of varnishes, the breakdown of the base oil film, the formation of rust and corrosion. Therefore, understanding and controlling

oxidation is the main preoccupation of the lubricant manufacturers. Antioxidants are key additives that are an integral part of the lubricant formulation. They are designed to "sacrifice" themselves, that is, they oxidize before any other component in the lubricant [4]. They protect lubricants from oxidation degradation and thus enable the lubricant to fulfill the necessary requirements for application in engines and industrial conditions [5].

## 2. LUBRICANTS

Liquid lubricants, whether motor or industrial lubricants, constitute an indispensable part of each engine. Their basic role is lubrication i.e. reducing friction between touching surfaces, in addition protecting against corrosion, draining heat and removing the residues [6].

Liquid lubricants consist of base oil which makes up over 90% of finished product and additives. Base oils also represent additives carrier and allow their application in a wide temperature range [7].

### 2.1 Additive

Additives are chemical compounds that are dissolved in base oil [8]. They are characterized by good thermal performance and low flushing [9]. Additives have three basic tasks:

- To improve the existing physical properties of lubricants (modifiers IV, antifoam, PPD)
- To improve the chemical properties (antioxidants)
- By adding additive lubricant gets new features (corrosion inhibitors, EP additives, dispersants) [8].

### 2.2 Antioxidants

New technologies and industrial materials require the use of better performance lubricants [10]. One of the most important characteristics of the lubricant is oxidation

stability because it is considered that it causes aging of lubricants, which results in oil tanning, formation of deposits, poor lubrication, etc [1]. Improvement of the oxidation characteristics is achieved by adding antioxidants to the lubricant formulation itself [11]. These are compounds that have the ability to control oxidation by preventing the interruption of the oil film and thickening, i.e. prevent the increase in viscosity, and ensure the performance of lubricants and longer service life [12]. Antioxidants are divided into two groups:

- Active components that remove radicals
- Active components that break down the peroxides

Active components that remove radicals are known as primary antioxidants. They donate a hydrogen atom that reacts with alkyl radicals or alkyl peroxy radicals, by stopping the chain reaction in the oxidation process. The primary antioxidant becomes a stable radical, the alkyl radical becomes hydrocarbon and the alkyl peroxy radical becomes alkyl hydroperoxide. The most well-known primary antioxidants are phenols and aromatic amines.

Secondary antioxidants include active ingredients that expose hydroperoxides. They react with oxygen or hydrogen peroxide, and in this way they promote their own oxidation. When the secondary antioxidant expires, accelerated oxidation of non-inhibited oils occurs. Secondary antioxidants include ZnDDP, phosphites and thioethers [5].

### 2.3. Oxidation mechanism

Oxidation is a multistage process involving the radicals process in three steps which, if left unconfirmed, will lead to the complete breakdown of the components in the lubricant [10]. The oxidation takes place through the reaction of the alkyl chain and the peroxide radical in three steps:

1. Initiation (initiation of chain reaction)
2. Propagation (duplication)
3. Termination (end of chain reaction) [5].

In the first step, the initiation step, external factors such as high pressure, heat or the presence of metals will activate the formation of free radicals obtained from organic components from lubricants. Either the bond within the organic sample between the two atoms is broken down to form a radical or the electron is taken from the molecule by an oxidized metal [10]. The ability of the homolytic breakdown of R-H to give free radicals is determined based on the strength of the C-H bond and results in stable radicals [5].



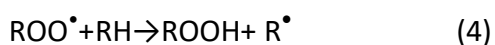
This reaction is relatively slow at room temperature, while the rise in temperature results in an acceleration of the reaction. Free radicals are highly reactive and can react with oxygen to form hydroperoxyl radicals [10]. As the initiation reactions continue, there is an increase in the peroxide content (ROOH and HOOOH), leading to secondary initiation (2), where peroxides are the sources of free radicals.



In the propagation phase, there is an irreversible reaction between alkyl radicals and oxygen, whereby an alkyl peroxy radical is formed. These reactions take place quickly, and the speed depends on radical change [5].

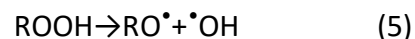


In the second step of propagation, hydrogen is released from the hydrocarbons by the alkyl peroxy radical, whereupon hydroperoxide and the second alkyl radical are formed again. Alkyl peroxy radicals are present at a higher concentration than alkyl radicals. The reason is that the oxygen is present at a higher concentration and reacts more quickly with the alkyl radical relative to the slower reaction of the alkyl peroxy radicals with the hydrocarbon [5].

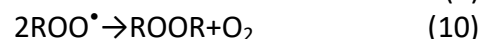


## 2.4. Peroxide decomposition

Alkyl hydroperoxides are extremely reactive, and at high temperatures, their decomposition results in additional radicals. They can undergo further isolation and propagation reactions, thereby increasing total oxidation. Alkyl peroxides and alkyl peroxy radicals are further expanded to neutral oxidation products such as alcohols, aldehydes, ketones and carboxylic acids [5].



The last stage of the oxidation process is the termination that stops the oxidation process when the radical is combined. Two alkyl radicals can be combined and form a hydrocarbon molecule. In addition, the alkyl radical may react with an alkyl peroxy radical to form a peroxide, or a reaction may occur between the two alkyl peroxy radicals in which the peroxide is formed by separating the oxygen. The more efficient this step is, the lower the degree of oxidation [5].



For this reason, the lubricant formulation also includes antioxidants, which stop the process of forming stable radicals. Antioxidants act either by decomposing peroxides or by reacting with free radicals.

## 2.5. Inhibition of oxidation

The mechanism of degradation of lubricants clarifies several possible counterproductive measures in order to control the degradation of lubricants. Blocking the power source is one way, but it is effective only for lubricants used in low shear and low temperature conditions. However, for most lubricants, it is more convenient filtering the catalytic impurities and decomposition of hydrocarbon radicals, alkyl peroxy radicals and hydroperoxides. This can be achieved by using active components

that remove radicals, components that decompose peroxides and metal deactivators.

There are two types of metal deactivators: chelating agents and film formation agents. Helate agents will form a stable complex with metal ions, reducing the catalytic activity of metal ions. Accordingly, deactivators can exhibit an antioxidant effect. The film-forming agents behave in two ways. First, they cover the metal surface, thus preventing the metallic ions from reaching the oil. Second, they minimize corrosion attacks on the metal surface physically limiting the access of corrosive species to the metal surface [5].

### 3. EXPERIMENTAL PART

#### 3.1. Materials and work methods

The experimental part consists of two parts. In the first part, the oxidation stability of the starting uninhibited mineral base oils was studied as:

- Mineral base oils BU1 and BU2

In the second part of the article, the oxidation stability of mineral base oils was studied, which were inhibited by two types of oxidation inhibitors, primary and secondary. Oxidation inhibitors are designated as:

- Primary oxidation inhibitor I1
- Secondary oxidation inhibitor I2

And the determination of the basic physical and chemical characteristics of mineral base oils was made using the standard methods of analysis shown in Table 1.

**Table 1.** Characteristics and test methods of the tested mineral base oils

Characteristics	Method	BU1	BU2
Viscosity at 40°C, mm <sup>2</sup> /s	BAS ISO 3104	21,681	32,58
Viscosity at 100°C, mm <sup>2</sup> /s	BAS ISO 3104	4,433	6,07
Viscosity index	BAS ISO 2909	122	136
Pour point, °C	BAS ISO 3016	-13	-9
Neutralisation number, mgKOH/g	ISO 6618	0,0052	0,0052

Table 2 shows the characteristics of the used oxidation inhibitors.

**Table 2.** Characteristics of oxidation inhibitors used in lubricant formulations

Characteristics	I1	I2
Viscosity at 40°C, mm <sup>2</sup> /s	-	100
Density at 20°C, mm <sup>2</sup> /s	1030	1120
Flash point, °C	≈127	>150
Neutralisation number, mgKOH/g	-	128

The inhibitor I1 belongs to the group of phenolic antioxidants, which are also commonly used in the formulations of liquid industrial lubricants. The most famous antioxidant from this group, with a single aromatic ring, is 2,6-ditert-butyl-4-methylphenol. It is used as an oxidation inhibitor for base oils, petrol and lubricants whose working temperature does not exceed 150° C [13].

The inhibitor I2 is based on zinc dialkildithiophosphate and belongs to a group of secondary antioxidants. ZnDDP is a multifunctional additive, i.e. In addition to being used as an antioxidant, it can also be used as an anti-wear additive and as a corrosion inhibitor [14].

There are several methods for determining the oxidation stability. The choice of the method itself depends on whether the base oil or finished product is tested, whether the control of the finished product or the development of a new product is carried out. In this paper, the ASTM D 2272 method was used to determine the oxidation state, method B.

50 g of the oil sample is poured into a glass vessel, and then the water and the spiral coil of the copper catalyst are added. The glass vessel is placed in a bomb equipped with a pressure gauge and filled with oxygen until the pressure on the pressure gauge reaches a value of 620 kPa (90 psi). The glass bowl inside the bomb is rotated at a speed of 100 rpm at a constant temperature of 150 ° C. The bomb is set at an angle of 30 ° relative to the surface. The oxidation stability measure is the time

(min) required to reach a certain pressure drop on the pressure gauge. Upon completion of the analysis, in the diagram where the pressure drop in relation to time was recorded, the maximum pressure and time at the point of the falling part of the curve is read, where the pressure of 175 kPa (25.4 psi) is lower than the maximum pressure. That is, the time that elapsed from the start of testing to the drop of 175 kPa (25.4 psi) in relation to the maximum pressure represents the lifetime of the sample. The time to sharp drop in pressure is usually the induction period, and if the time before the start of a sharp drop in pressure is longer, tested oil has a better resistance to oxidation. After completion of the oxidation stability test, the sample is filtered through filter paper and then poured into the separation funnel to remove the remaining water [15].

In this paper, the oxidation stability of the initial uninhibited samples of mineral base oils BU1 and BU2, samples of mineral base oils inhibited with different concentrations of oxidation inhibitors I1 and I2 were determined. In order to investigate the synergistic effect of primary and secondary oxidation inhibitors on oxidation stability, two series of samples were prepared which were inhibited by the combination of the oxidation inhibitors I1 and I2.

#### 4. RESULTS AND DISCUSSION

Two series of samples inhibited by inhibitors of oxidation I1 and I2 were added, which were added in concentrations from 0.1% m / m to 0.3% m / m, as well as a series of samples inhibited by the combination of inhibitors I1 and I2. Tables 3-5 give the results of tests of the characteristics of the mineral base oil BU1 and the formulated samples before and after the oxidation stability test.

Based on the results shown in FIG. 1, it can be seen that the BU1 inhibited inhibitor with oxidation inhibitor I1 reaches a maximum value at an inhibitor concentration of 0.25% m / m, while a mild decrease is observed at a concentration of 0.3% m / m.

For the BU1 sample inhibited with the oxidation inhibitor I2, the maximum consistency is reached at a concentration of 0.15% m / m, while further increase in the concentration does not result in an increase in the oxidation stability value, but a decrease. The reason for this may be that, in addition, the oxidation inhibitor I2 performs the function of the secondary inhibitor, it also performs the function as a corrosion inhibitor or is used as an anti-wear additive. The maximum value of oxidation stability in the BU1 inhibited inhibitor combination I1 and I2 is achieved at a concentration of 0.3% m / m. It can be assumed that higher levels of oxidation stability would result in further concentration increase.

**Table 3.** Characteristics of BU1 inhibited with inhibitor I1

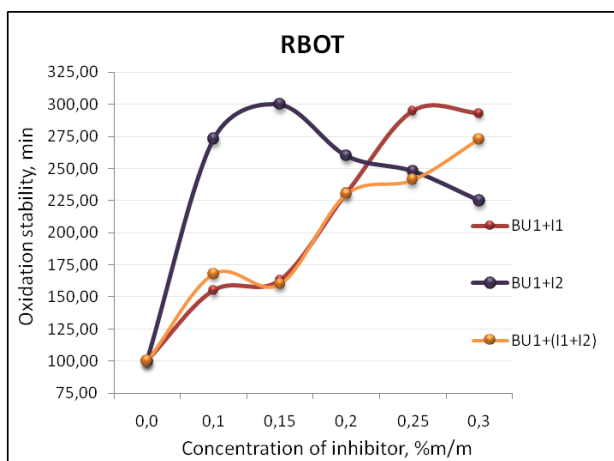
Characteristics	Oxidation inhibitor I1, %m/m					
	BU1	0,1	0,15	0,2	0,25	0,3
Before test						
Neutralisation number, mgKOH/g	0,0052	0,005	0,0054	0,010	0,0054	0,0055
After test						
Neutralisation number, mgKOH/g	1,40	2,43	1,52	1,32	1,31	1,30
Max. reached pressure, kPa	1292	1290	1288	1284	1253	1280
RBOT, min	100	155	163	231	295	293

**Table 4.** Characteristics of BU1 inhibited with inhibitor I2

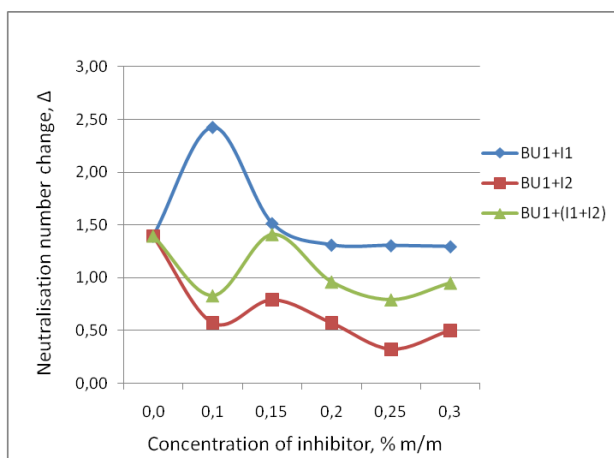
Characteristics	Oxidation inhibitor I2, %m/m					
	BU1	0,1	0,15	0,2	0,25	0,3
Before test						
Neutralisation number, mgKOH/g	0,0052	0,09	0,2	0,28	0,3	0,35
After test						
Neutralisation number, mgKOH/g	1,40	0,66	0,99	0,85	0,62	0,85
Max. reached pressure, kPa	1292	1273	1262	1255	1272	1262
RBOT, min	100	273	300	260	248	225

**Table 5.** Characteristics of BU1 inhibited with the combination inhibitors I1 and I2

Characteristics	Oxidation inhibitor I1+I2, %m/m					
	BU1	0,1	0,15	0,2	0,25	0,3
Before test						
Neutralisation number, mgKOH/g	0,0052	0,051	0,02	0,07	0,07	0,11
After test						
Neutralisation number, mgKOH/g	1,40	0,88	1,43	1,03	0,86	1,06
Max. reached pressure, kPa	1292	1271	1278	1276	1264	1275
RBOT, min	100	168	160	230	241	273



**Figure 1.** The dependence of oxidation stability of BU1 on the type and concentration of the oxidation inhibitor



**Figure 2.** Change of the neutralization value ( $\Delta$ ) before and after the oxidation stability test

It can be noticed that the biggest changes in the neutralization number occur in the sample

of HC base oil BU1 inhibited by the oxidation inhibitor I1, while for the sample of HC base oil BU1 inhibited with the oxidation inhibitor I2, the least of the neutralization number changes before and after the oxidation stability test. The values of the neutralization number change in the sample of the HC base oil BU1 inhibited with the combination of the oxidation inhibitor I1: I2 are between the values of the changes in the neutralization number of the HC base oil inhibited with oxidation inhibitor I1 and I2. A larger difference in the neutralizing number before and after the oxidation stability test, under the same conditions, means faster decay, i.e. poor oxidation stability.

Table 6-8 shows the results of the tests of the characteristics of the mineral base oil BU2 and the formulas samples, before and after the oxidation stability test.

From Figure 3 it can be noticed that for the sample of HC base oil BU2 inhibited with the oxidation inhibitor I1, the best oxidation stability value is achieved at a concentration of 0.3% m / m. Based on the diagram, it could be concluded that with further increase in inhibitor concentration, better oxidation stability times would be obtained, i. E. a trend of growth would continue. The maximum value of oxidation stability in a sample of HC base oil BU2 inhibited by oxidation inhibitor I2 is achieved at a concentration of I2 inhibitor of 0.15% m / m. With further increase in the concentration of inhibitors, poorer times for oxidation stability are obtained.

**Table 6.** Characteristics of BU2 inhibited with inhibitor I1.

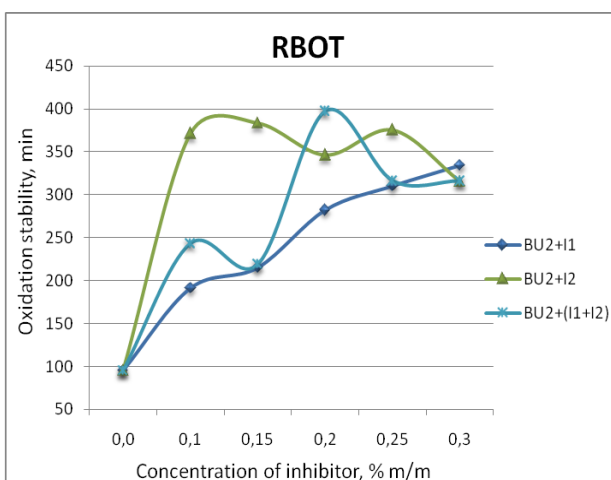
Characteristics	Oxidation inhibitor I1, %m/m					
	BU2	0,1	0,15	0,2	0,25	0,3
Before test						
Neutralisation number, mgKOH/g	0,0056	0,0055	0,0057	0,056	0,056	0,0057
After test						
Neutralisation number, mgKOH/g	1,40	1,59	1,79	1,59	2,84	1,47
Max. reached pressure, kPa	1292	1221	1254	1236	1262	1239
RBOT, min	100	191	215	282	310	334

**Table 7.** Characteristics of BU2 inhibited with inhibitor I2

Characteristics	Oxidation inhibitor I2, %m/m					
	BU2	0,1	0,15	0,2	0,25	0,3
Before test						
Neutralisation number, mgKOH/g	0,0056	0,094	0,1	0,18	0,15	0,21
After test						
Neutralisation number, mgKOH/g	1,40	1,51	1,08	0,98	1,03	1,27
Max. reached pressure, kPa	1292	1242	1229	1283	1285	1278
RBOT, min	100	371	383	346	375	315

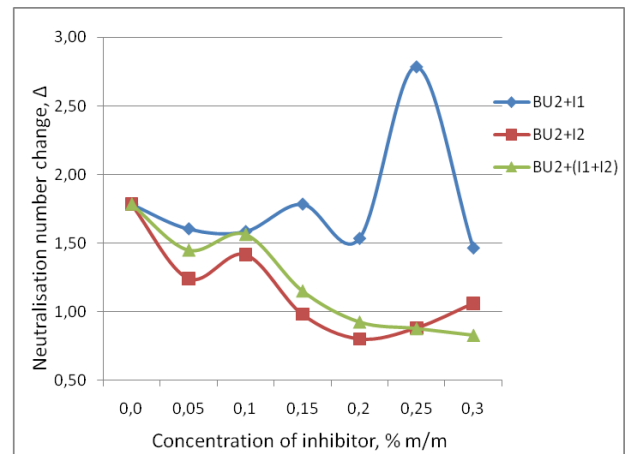
**Table 8.** Characteristics of BU2 inhibited with the combination of inhibitors I1 and I2

Characteristics	Oxidation inhibitor I1+I2, %m/m					
	BU2	0,1	0,15	0,2	0,25	0,3
Before test						
Neutralisation number, mgKOH/g	0,0056	0,027	0,03	0,077	0,095	0,094
After test						
Neutralisation number, mgKOH/g	1,40	1,59	1,18	1,00	0,97	0,92
Max. reached pressure, kPa	1292	1278	1293	1283	1282	1280
RBOT, min	100	243	219	397	316	316



**Figure 3.** The dependence of oxidation stability of BU2 on the type and concentration of the oxidation inhibitor

By combining the oxidation inhibitor I1: I2 in a ratio of 1: 1, the maximum value of oxidation stability is reached at a concentration of 0.2% m / m. From the diagram, it can be noted that the values of the oxidation stability of the sample of HC base oil BU 2 inhibited by a combination of two inhibitors in a ratio of 1:1 are between the oxidation stability values of HC base oil samples that are inhibited by the oxidation inhibitors I1 and I2, individually.



**Figure 4.** Change of the neutralization value (Δ) before and after the oxidation stability test

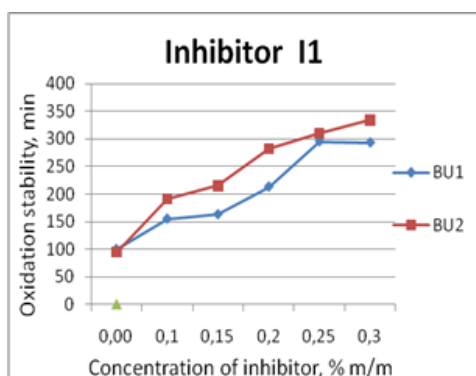
From Figure 4, it can be noticed that the largest changes in the neutralization number occur in the sample of the HC base oil BU2 inhibited by the oxidation inhibitor I1 at an inhibitor concentration of 0.25% m / m, while for the sample of HC base oil BU2 inhibited by the oxidation inhibitor I2 there was a slight change in the neutralization number before and after the oxidation stability test. The values of the neutralization number change in the sample of the HC base oil BU2 inhibited by the combination of the oxidation inhibitor I1: I2 are between the values of the changes in the neutralization number of HC base oil inhibited with oxidation inhibitor I1 and I2. A larger difference in the neutralization number before and after the oxidation stability test, under the same conditions, means faster decay, i.e. poor oxidation stability.

In Figures 5 and 6, the influence of oxidation inhibitors on the oxidation stability of various mineral base oils is shown for each type of inhibitor separately.

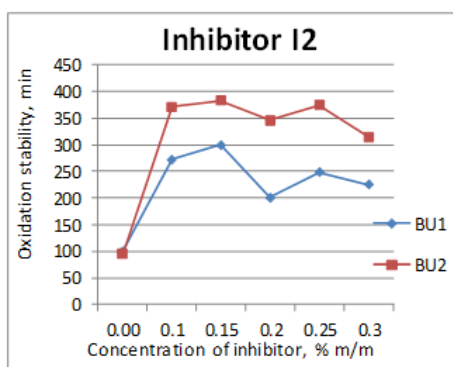
In the case of the inhibitor I1 (Fig. 5), similar

behavior is observed, i.e. a similar change in oxidation stability with an increase in the concentration of inhibitors. Figure 6 shows the effect of oxidation inhibitors on the oxidation stability of different HC base oils. It can be noted that the inhibitor I2 gives the best results in HC base oil BU2.

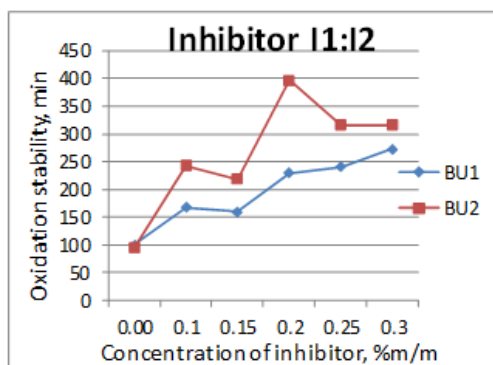
By combining the oxidation inhibitors I1:I2, the best oxidation stability values are achieved with HC base oil BU2. The worst oxidation stability values are achieved with HC base oil BU1.



**Figure 5.** Effect of inhibitor I1 on the oxidation stability of mineral base oils



**Figure 6.** Effect of inhibitor I1 on the oxidation stability of mineral base oils



**Figure 7.** Effect of combinations of inhibitors I1 and I2 on the oxidation stability of mineral base oils

## 5. CONCLUSION

Based on the conducted testing and analysis of the obtained test results, and in accordance with the set goals, the results of the research can be summarized in the following conclusions:

- The oxidation stability study of the base base oils without additives has shown that the best oxidation stability time has a mineral base oil designated as BU1 with an induction period of 100 min;
- The primary oxidation inhibitor I1 was better with mineral base oil BU2. However, even in this case, the maximum value has not been reached, and it can be assumed that with further increase in the concentration of the inhibitor it can obtain better oxidation stability.
- The ZnDDP-based inhibitor was best in combination with mineral base oil BU2. The maximum value of oxidation stability is achieved with a concentration of 0.1% m/m.
- In most, but not in all cases, the combination of the primary inhibitor I1 and the secondary inhibitor I2, achieved oxidation stability was between the individual action of the oxidation inhibitor. The longest induction period of 397 min was achieved with base oil BU2 with 0.2% m/m of inhibitor combination I1 and I2 in a ratio of 1:1.
- The increase in oxidation inhibitor I1 content also increases the oxidation stability of lubricants. While increasing concentration of inhibitors I2, a maximum value in the concentration range of 0.10 - 0.15% m / m is reached, and then it does not change or slightly decreases.
- As the optimal formulation of the finished product in industrial proportions, a base oil BU2 inhibited with 0.2% m/m of the inhibitor combination I1 and I2.

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