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# Examining the synthesis of organic material used as an oxidation inhibitor for all types of lubricating oils

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The following article introduces all types of industrial lubricating oils, their essential properties, primary compounds, and some additives. The subject that has been discussed in this review is an overview of additives that have an antioxidant role in a variety of industrial lubricants. These additives were first synthesized and then added to the oil by combining different percentages. After synthesis, compounds were identified by using data analysis methods, such as FTIR, NMR... and then mixed with different weight percentages with industrial Lubricating Oils. Some of its physical and chemical properties are studied after mixing, according to the ASTM standard.

**Keywords**: Lubricating Oil, ASTM Standard, Antioxidant Agent, Additive, Analysis

## INTRODUCTION

Lubricating oil that its origin is crude oil is relatively inexpensive material, which is used in very expensive industrial engines and machines, and has a direct effect on the efficiency and life of these devices. Therefore, the quality of the used oils must be perfectly appropriate in order to ensure the correct operation of machinery. But unfortunately, it has been seen that even the technical specialists do not pay enough attention on this matter. But this is not always the case, and the main consumer is not able to directly diagnose and evaluate the quality of the product. This is true in some cases where the efficiency and quality of a product and physical properties are related to its chemical properties, that is to say, to chemical reactions. Chemical reactions are generally slow, and therefore, it is not possible to detect their effects in the short term. In addition, maybe the effects of chemical activities interfere with other factors and cause the diagnosis of the cause that the resulting phenomena to be complicated [1].

According to the relationship between physical and chemical properties, petroleum products are the most complex, in terms of practical efficiency. Petroleum lubricating oils contain a variety of hydrocarbons and their derivatives, in particular, the components of lubricating oils are generally composed of very large molecules of $C_{15}$ to $C_{30}$. It can be seen that the composition and chemical structure of lubricating oils is variable and complex. Obviously, separating any of the oil compounds and determining their properties is simply not feasible. For this reason, for such products, nothing in the classical sense of chemical properties can be defined, and indeed, what is said under these titles is the average of the properties for each single component of the oil, and since the ratio and type of these components change in different oils, physical and chemical properties of oils are not fixed [2].

Lubricating oils are also more complex than other petroleum products in another sense. Lubricating oils must perform a variety of tasks, in their various applications, and must have certain properties for this purpose. What is obtained from crude oil, under the title oil is called base oil and it is only able to carry out some of the essential duties of engine oils and industrial machinery, and the rest of the properties are made by a series of special chemicals, which are called additives and are added to the oils in the range of about 3 to 10%. These chemicals also have wide varieties and they are added to the oils in varying ratios. Therefore, it should be noted that lubricating oils form a complex set in terms of chemical compounds.

Today, the material that is used under the name of the oil, for lubrication or other applications, such as hydraulic devices, thermal systems, electrical insulators, or metal cutting, should have many characteristics.

The general characteristics that any oil should have is the same basic characteristics that are intended from the outset, for example, to reduce the friction of parts in order to move two pieces, or tolerate and remove the heat by two systems, which is produced in various ways, and create some kind of sealing, which prevents the penetration of foreign particles, or vice versa, the other particles that are produced from abrasion are taken from the joint space of two pieces and removed from the work environment . In order to make a lubricant, which can handle

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all the necessary specifications in terms of performance, we mix the two main substances with each other in the name of base oil and additives.

The base oil is petroleum or synthetic, which is about 95-90% of oil based on the type of finished oil (in some cases it is less than this) and can meet the needs of oil, somehow and according to the application.

The essential ingredient of any finished oil is a substance called base oil, and after mixing with other substances, it becomes the oil of the product. Additives are a number of chemicals with special ingredients, which adding them in a certain amount to Base oil repairs and corrects oil properties. In addition, it gives a number of special features that are absent or weak in the base oil [3].

## TYPES OF LUBRICANTS

Lubricants, in today's industrial world can be classified into four categories of gas lubricants, liquid lubricants, semi-solid lubricants and, finally, solid lubricants.

**1. Gas Lubricants**, in particular air, are used for lubrication in applications that high speed and low charge and the radial stability of the rotation axis is desired, or create abnormal temperature conditions or the presence of nuclear rays; Practical examples of gas and air applications as lubricants include ultracentrifugation lubricating, high speed precision rocking machines, dental drill wheels, and atomic reactor gas assemblies. Today, extensive research is being carried out on the use of gas and liquid vaporizers for applications such as high-speed spinning machines, gas turbines, jet engines and gyroscopes, and so on.

**2. Liquid Lubricants** are a wide range of fluids from pressurized liquid gases to a variety of synthetic oils. The application of liquid lubricants in lubrication is carried out in a hydrodynamic method with a thick layer or thin film of lubricant, and in this case, the most common type of lubricant is used.

**3. Semisolid Lubricants** include all types of greases and solid fats and waxes, in cases where the lubrication sealing is difficult for using liquid lubricant, or justifies light and non-continuous working conditions or lack of access in once lubrication for the mechanism lifespan and is used in ball bearings and roller bearings, which have a type of elastomer and hydrodynamic lubricant. Grease, which is the most commonly used semi-solid lubricant, consists of petroleum or synthetic oil and a filler or hardener.

**4. Solid Lubricants** are used for lubrication under special conditions, such as full vacuum or high charge and heat, and in cases where Boundary Lubrication is in use. Types of solid lubricants include graphite, mica, talc, molybdenum sulfide, lead oxide, sulfur fluoride and various types of plastics [4].

### *Properties of lubricating oils*

Lubricating oils should:

1. Have a good viscosity (viscosity - is a level of fluidity or non-fluidity), and perform the formation layer of oil, reduce friction and abrasion, as well as heat transfer and seaming, sealing and transferring forces.

2. Keep their viscosity within the degree of heat limits sufficiently to prevent damage to their duties. During the term, the viscosity index (VI) is said to have a high degree.

3. Resistant to the heat and oxygen (thermal decomposition and oxidation) sufficiently.

4. Prevent rusting, corrosion by acids and excessive abrasion of the parts (in cases where the base oil cannot form a thick layer and does not prevent abrasion).

5. Have detergents and dispersants, and prevent sediment deposits between the parts (sufficient fluid in the case of engines in the cold so that starting and continuing the movement would be easy).

6. Be in a good condition according to factors such as volatility, fire and the like.

7. Do not create foam during work.

8. Neutralize the adverse effects caused by the operation of the machine to the extent possible, (such as combustion of fuel in motors, mixing of steam in turbines, etc.).

9. The foreign pollutants, such as dust, rubbish, water and the like, should not be mixed with oil.

### *Lubricating oil compounds:*

The above properties should be made in some way in the oil. The important fact is that lubricating oils are composed of two main parts:

**1. Base Oil:** A substance that is obtained from crude oil after a refinery operation. Base oil, on average, accounts for 90% of the oil volume.

**2. The Chemical Substances, Called Additives**, which make up about 10% of the volume of the oils. There are only a limited number of essential oils in the base oil, and for lubricating oils have all necessary properties and can complete their tasks, additives are added to them [1-3].

### *Additives to lubricating oils*

With the increasing need for oil, there is a lot of research to develop and improve the operation of oils in order to lubricate and to transfer power.

Not only oils that are petroleum-based, but also synthetic oils, such as organic esters and silicone fluids and polyphenyl ether, also require additives to improve their lubrication, including:

**1. Oxidation Inhibitors**, which are mainly composed of organic compounds, including sulfur, nitrogen, phosphorus and some alkaline phenols. In practice, these compounds react with primary hydroperoxides due to oxidation of the oil, which results in the formation of a chain reaction and the formation of organic acid in the engine, in this way Babbit's corrosivity and supplies made from the zinc and copper bearings can be reduced to a minimum.

2. Compositions such as Di-Tert-butyl Cresol and Phenyl-1-naphthylamine combined with well-refined paraffinic base oils are used for lubrication of steam turbines and hydraulic machines. For the difficult working conditions of internal combustion engines, zinc, barium and calcium thiophosphate compounds can be used.

3. Anti-abrasion agents that by forming a surface film minimize the rate of lubrication by the physical and chemical absorption of friction and abrasion. A variety of Anti-abrasion agents has oxygen, sulfur, chlorinated waxes, phosphorus and lead organic compounds. Tricresyl phosphate TCP and Zinc Dialkyl Dithiophosphate ZDDP are widely used to minimize abrasion in hydraulic pumps, gears, and transducers.

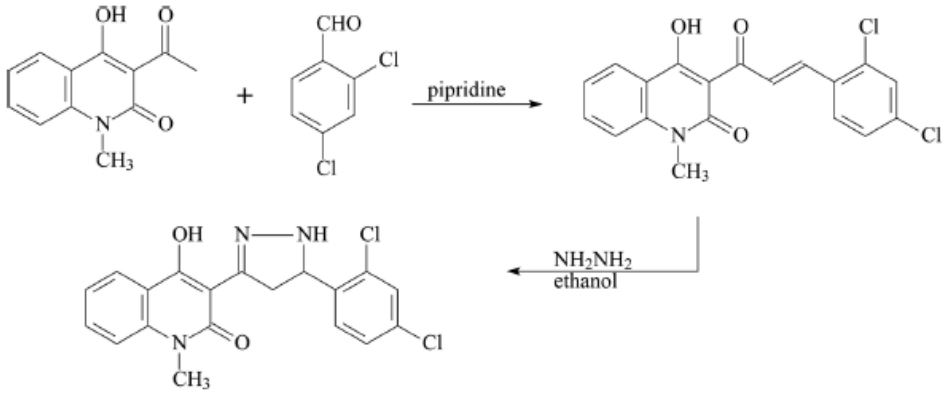
4. Cleaning materials in oil that prevent the deposition on combustion engine parts and make them suspended sludge in oil, in the form of Varnish, Carbon and lead deposits. Barium and calcium sulphonates and phenates compounds are used as a cleaning agent, in diesel petrol and diesel engine oils [3, 4].

In a study by Modather F. Hussein et al., they used 4-hydroxyquinolinone derivatives as antioxidant agents for a variety of lubricating oils. In their research, these compounds were first synthesized in the laboratory and then analyzed by spectroscopy. The compositions that they synthesized are:

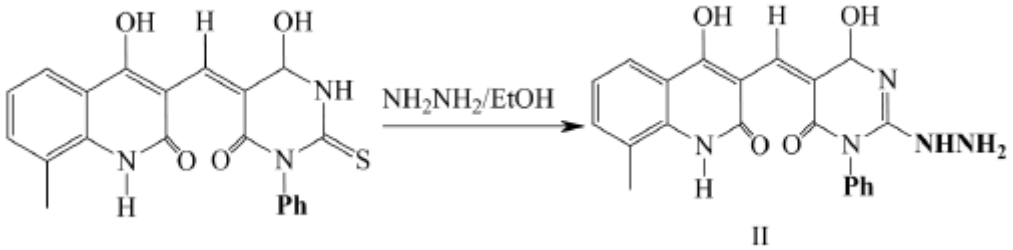
(1) 3- (5- (2, 4-dichlorophenyl) -4, 5-dihydro-1H-pyrazol-3-yl) -4hydroxy-1-methylquinolin (1H) -one,

(2) 5 - ((4-hydroxy-8-methyl-2-oxo-1, 2-dihydroquinolin-3-yl) methylene) -1-phenyl-2-hydroxyhydropyrimidine-4, 6 (1H, 5H) –dione

(3) 1-Butyl-4-hydroxy-3- (5-styryl-4, 5-dihydro-1H-pyrazol-3-yl) quinolin-2 (1H) –one




(1) 3-(5-(2, 4-dichlorophenyl)-4,5-dihydro-1H-pyrazol-3-yl)-4-hydroxy-1-methylquinolin- 2(1H)-one.

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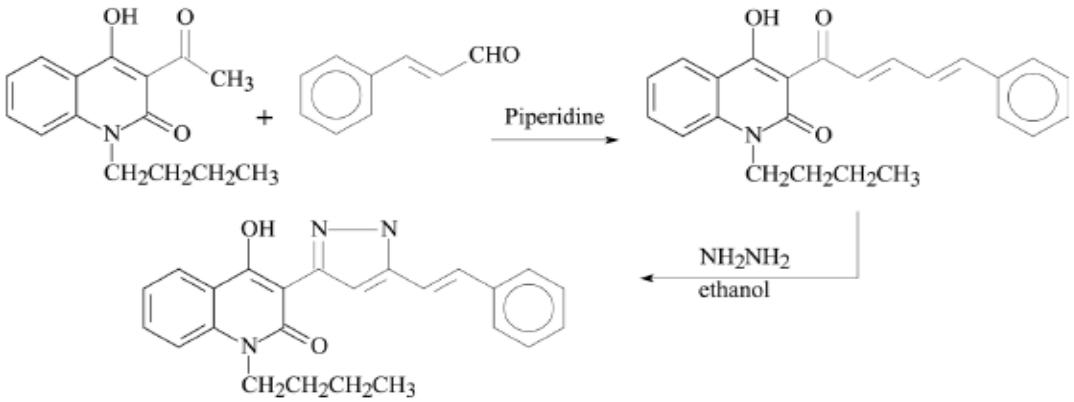
(2) 2-hydrazono-5-((4-hydroxy-8-methyl-2-oxo-1, 2-dihydroquinolin-3yl) methylene)-1-phenyldihydropyrimidine-4,6(1H.5H)-dione




(3) 1-butyl-4-hydroxy-3-95-styryl-4, 5-dihydro-1H-pyrazol-3-yl) quinoline-2(1H)

**Fig. 1**. Synthesis of three quinolinone-derived substances

Figure 1 shows the compounds and their synthesis.

After analyzing the compounds, their antioxidant effect was considered in lubricating oils. Therefore, an experimental data series was obtained by using ASTMd-942, ASTM d-664 test, which shows that the total acid number and the oxygen pressure drop of these compounds in lubricating oils, such as greases, are reduced, indicating the antioxidant effect of these compounds derived from hydroquinolinone.

In their study, it has been determined that the highest effectiveness of the antioxidant effect occurs when there is a combination of butyl and hydroxyl in quinolinone. These compounds prevent radical reactions during oxidation in oils and prevent the continuation and formation of radical oxidation reactions.

As shown in Figures 2 and 3, water lines exist when no additive is used in oil and, as expected, the amount of oxygen pressure drop and total acid number in the oil sample, G1 increases significantly, and the oxidized compounds are significantly reduced compared to G1 oil when using three derivatives from 4-hydroxyquinolinone, and this amount reaches its lowest level by adding the third derivative. The comparison of the three compounds above shows that the effectiveness and antioxidant effects of the third compound were greater than the other two compounds, and then the second combination of the first compound [5].

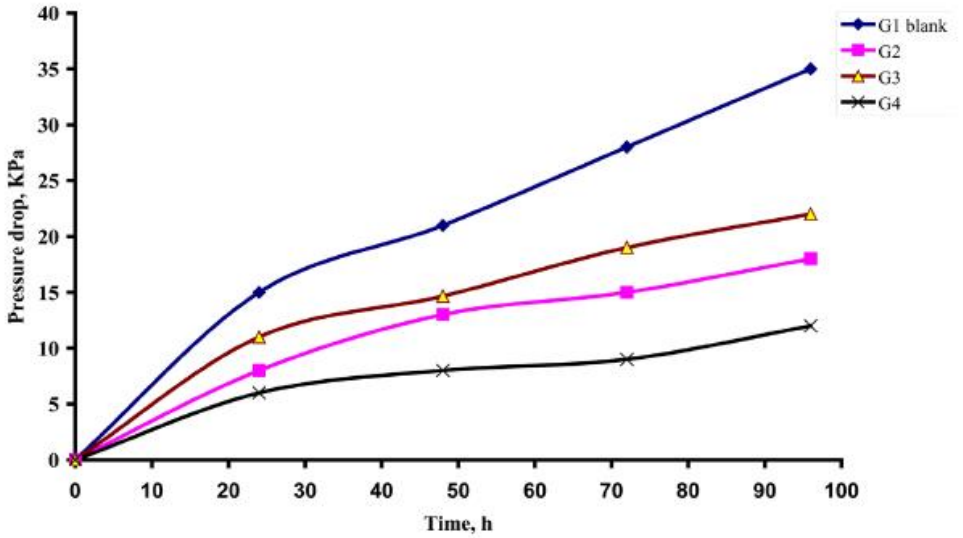



**Fig. 2.** Oxygen pressure drop in time, with and without the use of quinolinone-derived compounds.

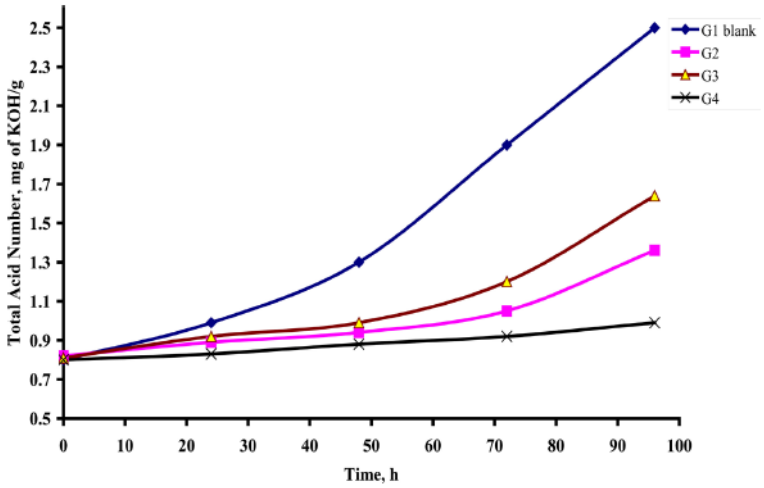



**Fig. 3.** Changes in acid number in time, with and without the use of quinolinone-derived compounds.

In another study, El Sayed al. [7], used polyphenols bound to heterocycles as an antioxidant agent in lubricating oils. Their synthetic compounds included the grouped olefins with heterocyclic compounds, which are methyl, amine, and carboxyl groups. In order to investigate the effect of these additives, the materials were added to lubricating oils of turbines with an ISO46 viscosity index. Then, they used ASTM standards to study the physical and chemical properties of the oils. Figure 4 shows the synthesized molecule of this type of antioxidant.

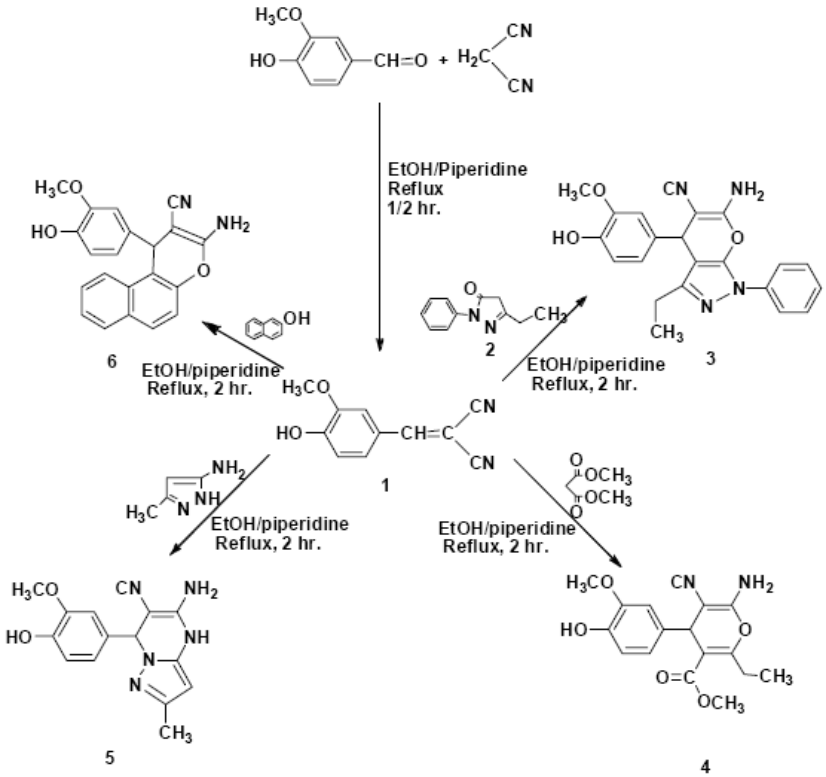



**Fig. 4.** The molecule and synthesis method of some polyolefins attached to the heterocyclic group

In a study by these researchers, it was found that the presence of this kind of polyolefin antioxidants in the oil mixture prevents free radical reactions. The best result was 16% w/w in the final mixture, which caused the stability of some of the compounds in the antioxidant and the reduction of radical reactions in the oil mixture, and, finally, increased oil stability with desired viscosity and better efficiency during industrial processes [6].

El Sayed et al. [7] also studied the effects of the imidazoles and triasols combination as antioxidant additives in industrial lubricants. In their research, 4 and 5-diphenylimidazole and 4 and 5-diphenyl 1, 2, 4-triazole and compounds with functional groups of thiobenzyl and thiomethyl were used as

antioxidants in industrial lubricants. The results of this study showed that the presence of thiomethyl groups of compounds increases the antioxidant effect in the presence of thiol groups. The reason for this is increased ability to take free electrons and increase antioxidant properties. On the other hand, thrysoles carry a phenolic hydroxyl group, which also increases the antioxidant strength of these compounds compared to other compounds without the presence of a hydroxyl phenol group. Finally, it has been shown in the results that group 4 and 5-diphenyl-2-thiomethylimidazole exhibit the highest antioxidant activity in them in combination with industrial oils [7].

Reda Fikry et al. [8] also studied the effects of cyanotic hydrazine and pyrazole compounds as antioxidant additive to lithium lubrication oils. They first synthesized materials:
(1) a- (2-amino-3-cyano-6-pyridyl) o-hydroxyl cinnamic hydrazide (Compound 1).
(2) ethoxymethyl-enamino derivative (Compound 2).
(3) 3-amino-5-hydroxyl-4-phenylazo-1H-pyrazole (Compound 3).

And then, they examined their physical and chemical structure using NMR, FTIR. After assuring the formation and correct synthesis, they mix these compounds with lithium oil and added to 0.1% of these compounds to the oil, and measured the amount of oxygen pressure and the acid number of the mixture. In their study, it was found that the combination of oils with these additives increases its resistance to oxidation and rapid decomposition of radical reactions. The data have shown that the efficacy of the compounds was as follows:

Compound 1> Compound 2> Compound 3

As it is clear from figures 5 and 6, when the organic compounds were added to the oil, the acid number decreased compared to the pure oil state, and this happened in the case of oxygen pressure drop. The reason for this is related to the bonding of hydrazide cyanide groups and their derivatives to free radicals, which are formed during oxidation reactions. As a result, the free radical reactions terminated by their binding, also The presence of phenolic and amino groups in these compounds, in form and orientation of the groups, causes the formation of radicals and creates a stable structure, and ultimately, reduces the acid number and the amount of oxygen pressure drop in the final mixture (the combination of oil with compounds) [8,9].

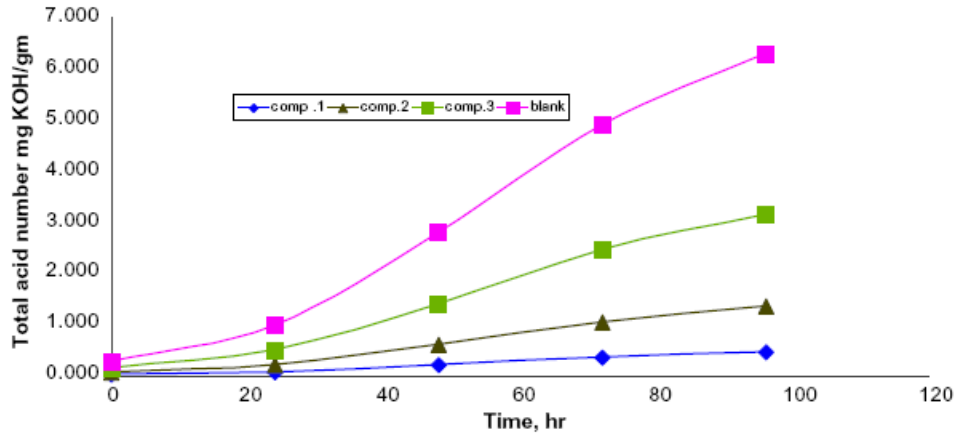



**Fig. 5.** Changes in acid number, by adding 3 compounds without it.

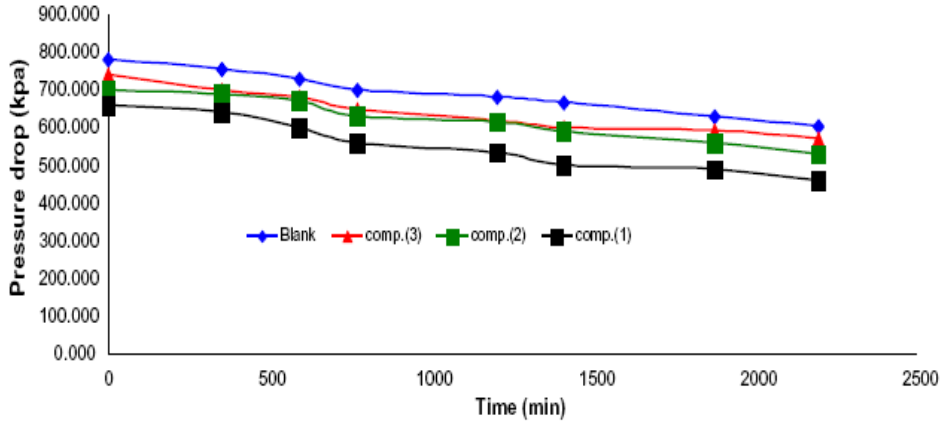



**Fig. 6.** Changes in oxygen pressure drop by adding 3 compounds without it.

## CONCLUSION

With increasing demand for oil, in order to lubricate, as well as to transfer power, a lot of research is being carried out to expand and improve the operation of the oils. Not only oils that have petroleum base, but also synthetic oils such as organic esters and silicon's fluids and polyphenyl ethers, also require additives to improve their lubrication. Oxidation inhibitors are mainly composed of organic compounds, including sulfur, nitrogen, phosphorus and some alkaline phenols. Among the various compounds of the organic groups, phenolic groups and imidazole, cinnamic hydrazine and pyrazole, were effective groups, which reduced the acid number and decreased the pressure of auxin in combination with oil, and finally, increased deterioration properties of oxidation.

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