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Determination of the Effects of Aminic and Phenolic Antioxidants on the Oxidation Resistance Performance of TMP and TMP Complex Esters by RBOT

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Abstract

Polyol esters are biodegradable synthetic base fluids that can be used an alternative over mineral oils, polyalphaolefins and diesters due to their excellent lubricity. Due to their thermal and oxidative stability, these esters can be used effectively in high temperature applications such as fire-resistant hydraulic fluids and in many industrial areas such as aerospace. Their stability/ aging-time can be improved with antioxidant additives. Sterically hindered phenols with 2 and 6 positions substituted with tertiary alkyl groups (as 2,6-di-tert-butyl phenol (DTBP)) and aromatic amine compounds (as bis(nonylphenyl)amine (BNPA)) are antioxidants with wide applications in industrial lubricants. Rotary Bomb Oxidation Test (RBOT) is the one of the most common used methods for determination of the oxidative stability of oil and lubricants. In this study, effects of DTBP and BNPA antioxidants on oxidative stability of trimethylolpropane trioleate (TMPTO) and trimethylolpropane trioleate complex (TMPCX) polyol esters were investigated using the Rotary Bomb Oxidation Test (RBOT) method. As a result of the studies, oxidation stability of TMPTO enhanced as amount of DTBP increased. It was ascertained that both antioxidant additives showed no effect on the unsaturated TMPCX, even when used separately or even together due to negative impact of unsaturated alkyl chains on oxidation stability.

Keywords

Polyol Ester, Antioxidant, Oxidation, RBOT

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INTRODUCTION

In conventional lubrication, mineral oil base stock, polyalphaolefins, polyalkylene glycols and other petrochemical derived synthetic esters are used as base oil [1]. The content of the majority of lubricant formulations consists of approximately 70-99% base oils. Base oils and additives used in the manufacture of various lubricants and greases, and the oxidation products formed after their use, can be toxic to biodiversity such as plants, aquatic animals and other living things. Although these substances have a tangential effect on humans in the short term, they are harmful with prolonged exposure. While the search for alternative

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lubricants that can provide sustainability and natural, renewable, biodegradable green products continues due to the depletion of petroleum reserves, the interest in working with various esters has increased in direct proportion to this search [2], [3]. There are five types of biodegradable fluids (with different percentages of biodegradability) in the literature, including vegetable oils with high unsaturation or high oleic content (HOVOs), low viscosity polyalphaolefins (PAOs), polyalkylene glycols (PAGs), dibasic acid esters (DE) and polyol esters (PE), which have been studied for use in lubricant formulations [4].

Vegetable oils such as sunflower oil, rapeseed oil, soybean oil, olive oil, castor oil and palm oil have extensive research area in the development of sustainable biolubricant formulations due to their high biodegradability and renewability. However, it is known that vegetable oil-based lubricants cannot meet the requirements of industrial oils in the new trend since they have disadvantages such as low thermal and oxidation stability, low fluidity at low temperature properties and low viscosity range and lubricant work environments are becoming more difficult. Low viscosity PAOs are another alternative for environmentally friendly lubricants and can be defined as low molecular dimers to tetramers. While low molecular weight causes undesirable high volatility for these fluids, it becomes an advantage at low temperatures where PAOs perform excellently. The absence of polarity of PAOs cause to problems of additive acceptability. On the contrary of PAOs, polyalkylene glycols (PAGs) have alternative ether linkages rather than essentially having a hydrocarbon backbone, making them highly polar. This high polarity has the disadvantage of being easily contaminated by moisture and this results in increased water solubility, which is detrimental for many lubricant applications. The solubility problem of organic additives in PAGs and the incompatibility of PAGs with conventional petroleum-based lubricants are other fundamental problems for this type. The main application area of biodegradable PAGs is fire resistant liquids. [1]. The high molecular weight of dibasic esters makes the volatility problems negligible and the ester bonds in the structure provide high solubility efficiency. Branching in the alcohol moieties results in very good low temperature performance. However, dibasic acid esters score poorly in recent biodegradability tests. Dibasic acid ester liquids have outstanding solubility and cleaning ability properties. Due to these properties, they can have a negative effect on some varnish or paint surfaces, which limits the use of dibasic acid esters. Thanks to these properties, the most basic area where dibasic acid esters find use is paint and coating applications [5].

Synthetic esters, which are most commonly used in current lubrication engineering applications, can be listed in four categories as monoester, diester, PE and aromatic carboxylic ester according to the number and position of ester groups in synthetic ester molecules [6], [7]. These esters are widely accepted in various lubricant applications due to their good low temperature operability, good viscosity temperature performances and excellent friction reducing and antiwear properties [8]. PEs, one of the ester types that can meet expectations, are biodegradable and hydrolytically and thermal stable compounds and they can be used in a wide variety of applications such as aerospace and automotive industries, fireproof hydraulics, marine hydraulic and metalworking fluids, food grade oils, rolling oils and transformer oils [9]. PEs are obtained by the reaction of polyhydric alcohols such as trimethylolpropane (TMP), neopentyl glycol (NPG), pentaerythritol (PET) with fatty acids such as palmitic acid (C 16:0), stearic acid (C 18:0), oleic acid (C 18:1). PEs have better thermal and hydrolytic stability compared to the natural vegetable oil form, due to the removal of the β carbon after replacing the glycerol molecular skeleton with the polyol. Esters of this class have not only better oxidation resistance at high temperatures, but also better oxidation resistance at lower temperatures, unlike many other esters, since they do not have β hydrogen at the carbon atom. PEs can be solid or liquid form depending on the degree of -OH substituent in the polyols and the type of acid reacting [10], [11].

Trimethylolpropane triesters, are synthetic lubricant base oils alternative to mineral oils, polyalphaolefins and diesters. TMPTO is being evaluated as a high-performance base fluid in industry (hydraulic fluids, two stroke engine oils and metalworking fluids). Recent studies show that the TMPTO exhibits high viscosity index, excellent low temperature properties and lubricity. Also, TMPTO is an environmentally friendly fluid that has attractive anti-wear properties. Therefore, it can be evaluated as potential lubricating base oil. For this aim, the knowledge of its thermal and tribological properties is of great interest [12].

Degradation of lubricants is inevitable and it is considered as one of the major problems limiting the service life of lubricants. Degradation of lubricant can cause serious problems such as higher energy consumption, higher corrosion to metal surfaces and lower oxidation resistance. In addition, another parameter that can cause serious problems is the formation of insoluble sediment or sludge during use, and therefore the increase in viscosity. Although the main cause of lubricant degradation is considered to be oxidation, it can also be caused by various factors such as thermal effect, mechanical shear, insufficient additive and pollution. Also, oxidation also has a significant effect on other properties of lubricants, such as anti-wear performance. To completely prevent or delay such problems, it is necessary to use antioxidants, the main additives that protect the lubricant from oxidative degradation, ensuring that the use of the oil in industrial applications meets the strictest requirements and that the lubricants have superior oxidation resistance [13], [14]. Antioxidants hinder the auto-oxidation process in different ways according to their different structures and antioxidant mechanisms. They are divided into two groups, hydroperoxide scavengers and free radical scavengers, depending on their controlling mechanism [15].

Hindered phenols (sterically) are a group of (primary) antioxidants that function by a scavenging mechanism through hydrogen donation, where the target molecules are peroxy radical intermediate. They are active over a wide temperature range and can provide long-term stability to the lubricant by minimizing viscosity change and color deterioration. 2,6-Di-tert-butylphenol (DTBP) is a very active antioxidant that reacts with peroxy radical intermediates. The product of the first reaction also performs as a reactive scavenger of peroxy radicals [16]-[19].

More active than hindered phenols, aromatic amine compounds are available in a wide variety of molecular weights and forms and contribute more to preventing discoloration of the final product compared to hindered phenols, especially under high temperature or light exposure. As active hydrogen donors, they can easily transfer the hydrogen atom on nitrogen to peroxy radicals [20], [21]. The typical group in this class of antioxidants is synthesized by the reaction between diphenylamine and alkylating agents. The major used bis(nonylphenyl)amine (BNPA) is an example of amine antioxidant compounds called alkylated diphenyl amines [22].

Oxidative stability index (OSI), rotary bomb oxidation test (RBOT), differential scanning calorimetry (DSC), Indiana mixing oxidation test (ISOT), thin-film micro-oxidation test, and turbine oil stability test (TOST) are some common methods for measuring oxidation stability [23]-[28]. RBOT is a reliable method for monitoring and measuring the oxidation stability behavior of a functional fluid. This method is a test method that takes place under oxygen pressure, in which a fixed amount of catalyst is placed in the bomb with the test material, the bomb is pressurized up to 620 kPa and the bomb is rotated at 100 rpm in a bath at 150°C. Oxidation stability is expressed as the time required for a given pressure drop of 175 kPa. Results are presented as a graph of pressure value in kPa versus oxidation induction time in minutes.

There is no detailed study in the literature investigating the effect of 2,6-di-tert-butyl phenol and bis(nonylphenyl)amine antioxidants on the oxidation stability performance of TMPTO and TMP complex esters. In this study, a series of formulation studies were performed to analyze the enhancing effect of both antioxidant compounds on the oxidation stability performance of TMPTO and TMP complex esters. Oxidation stability measurements were carried out using a rotary bomb oxidation test (RBOT) device according to the ASTM D 2272 method and the results were evaluated.

1. Material and Method

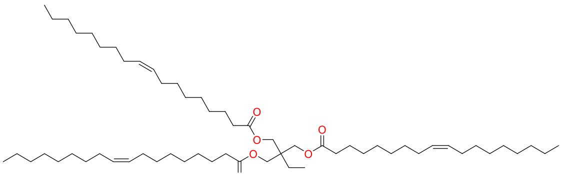
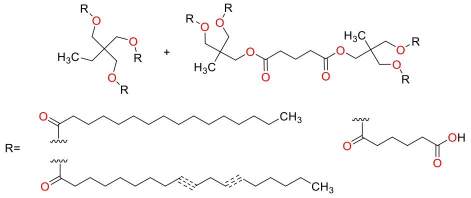
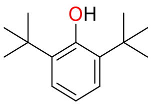
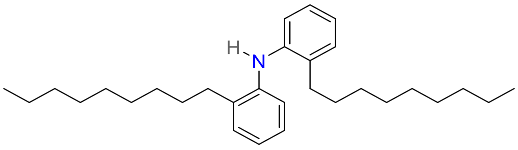
1.1. Material

One of the ester base oils used was Trimethylolpropane trioleate (TMPTO), a synthetic lubricant with a viscosity of 68.40 mm^2/s at 40°C and supplied by Croda International Plc. TMP Complex ester (TMPCX) with a viscosity of 68.40 mm^2/s at 40°C was supplied from Temix Oleo. DTBP, one of the phenolic antioxidant derivatives we used in our studies, was obtained from SI Group, Inc. As another antioxidant, BNPA, one of the aminic antioxidant derivatives, was supplied from LANXESS.

1.1.1. Chemical Structure of Compounds

The molecular structure of the compounds used in this study is shown in Table 2.

Table 2. Molecular structure of the compounds used in the study.

 TMPTO	 TMPCX
 DTBF	 BNPA

1.2. Formulation Model

The effects of DTBP and BNPA antioxidant compounds on oxidation stability performance on TMPTO and TMPCX ester were studied by formulating 18 different models. Use of these antioxidant compounds in different mass percentages and the synergistic effect of their combined use on the oxidation stability were evaluated with RBOT. The formulation model is shown in Table 3.

Table 3. Mass percent composition of TMP esters and antioxidants. Numbers in parentheses represent mass percent.

Sample No	Sample composition	Sample No	Sample composition
1	TMPTO (100:0)	10	TMPCX (100:0)
2	TMPTO + DTBP (99.75:0.25)	11	TMPCX + DTBP (99.75:0.25)
3	TMPTO + DTBP (99.5:0.5)	12	TMPCX + DTBP (99.5:0.5)
4	TMPTO + DTBP (99.25:0.75)	13	TMPCX + DTBP (99.25:0.75)
5	TMPTO + BNPA (99.75:0.25)	14	TMPCX + BNPA (99.75:0.25)
6	TMPTO + BNPA (99.5:0.5)	15	TMPCX + BNPA (99.5:0.5)
7	TMPTO + BNPA (99.25:0.75)	16	TMPCX + BNPA (99.25:0.75)
8	TMPTO + DTBP + BNPA (99.0:0.25:0.75)	17	TMPCX + DTBP + BNPA (99.0:0.25:0.75)
9	TMPTO + DTBP + BNPA (99.0:0.75:0.25)	18	TMPCX + DTBP + BNPA (99.0:0.75:0.25)

2. Measurements

The rotary bomb oxidation test is used to evaluate the oxidation stability of unused and in-service lubricating oils in the presence of water and a copper catalyst coil at a specified temperature and oxygen pressure. In this study, RBOT measurements were performed according to the ASTM D 2272 method. In each test, sample oil, demineralized water, and copper catalyst coil enclosed in a sealed glass container and it was placed in a pressure-resistant stainless-steel bomb equipped with a manometer. The bomb was loaded with 99.5% (v/v) oxygen until it reached a gauge pressure of 620 kPa and then it was placed in a constant temperature oil bath (150°C), and it was rotated axially at 100 rpm at an angle of 30° from the horizontal. The time (min) required to reach a 175 kPa drop in gauge pressure was taken as the oxidation induction time (OIT) of the test sample, and this time indicates the oxidation stability of the sample. The obtained oxidation induction time results in minutes were shown in Table 4.

Table 4. RBOT test results.

Sample No	RBOT test result (min)	Sample No	RBOT test result (min)
1	16	10	21
2	38	11	26
3	77	12	22
4	99	13	24
5	27	14	23
6	26	15	27
7	23	16	14
8	55	17	23
9	154	18	16

Moreover, graphs of pressure value in kPa versus oxidation induction time in minutes were also obtained. The graphs of the oxidation induction time versus the pressure value in kPa for the formulations obtained with TMPTO and DTBP-BNPA antioxidant compounds and TMPCX and DTBP-BNPA antioxidant compounds are shown in Figure 1 and Figure 2 respectively.

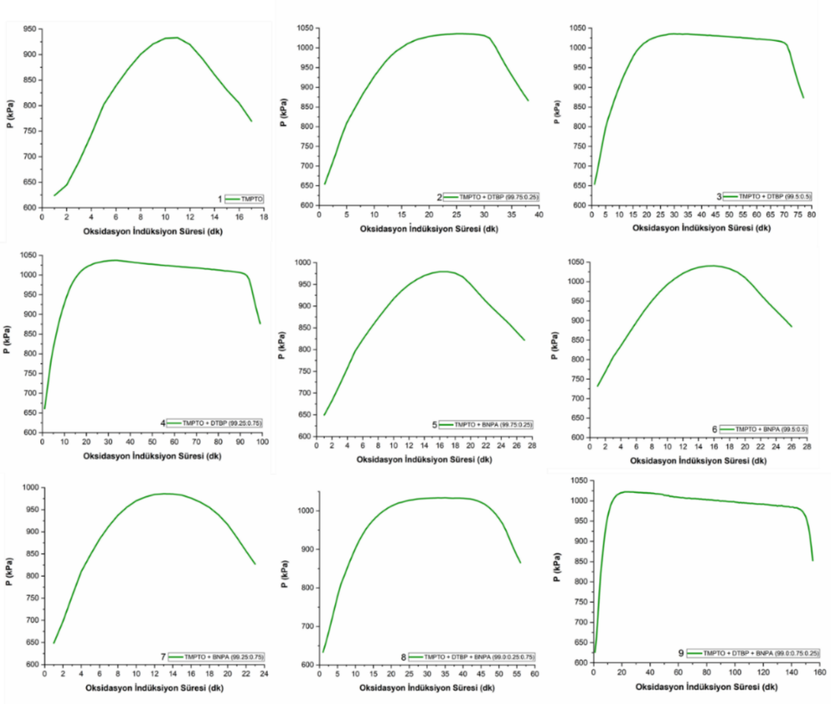


Figure 1. RBOT test graphs of TMPTO studies

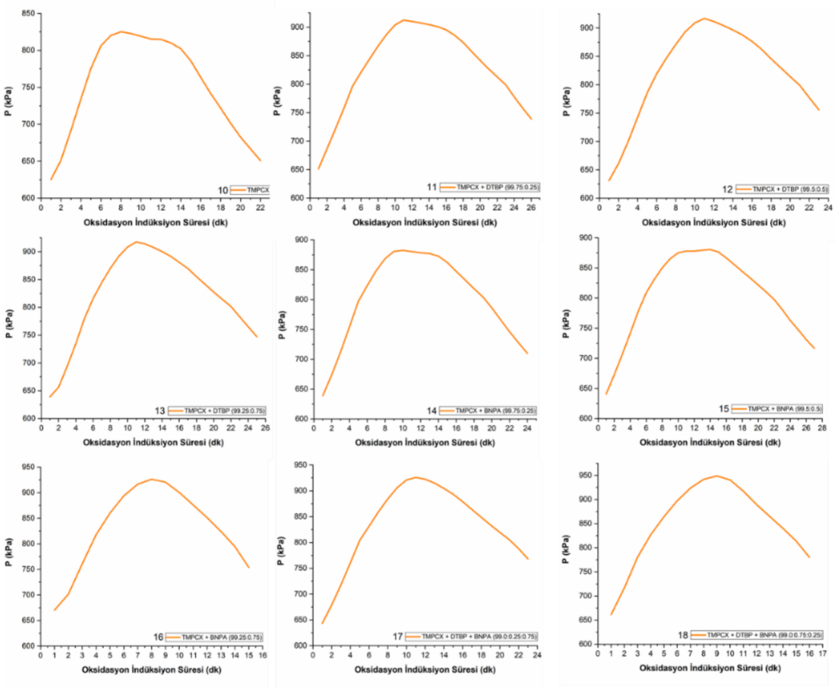


Figure 2. RBOT test graphs of TMPCX studies

CONCLUSION

The oxidation induction time of the TMPTO ester was 16 minutes. On the other hand, it was determined that the use of DTBP antioxidant compound at minimum, medium and maximum rates increased the oxidation induction time proportionally up to 99 minutes. It was ascertained that BNPA antioxidant compound did not enhance the oxidation induction time of TMPTO ester. It was found that the oxidation induction time increased up to 154 minutes when DTBP (maximum amount) and BNPA (minimum amount) compound was used together due to the synergistic effect of these two compounds. It was observed that the combination of BNPA compound at maximum and DTBP compound at a minimum amount increased the oxidation induction time at a lower rate compared to the maximum amount of DTBP compound. The results of the oxidation induction time in the use of DTBP and BNPA antioxidant compounds separately and together in different mass percentages in the TMPTO ester are shown in the graph in Figure 3.

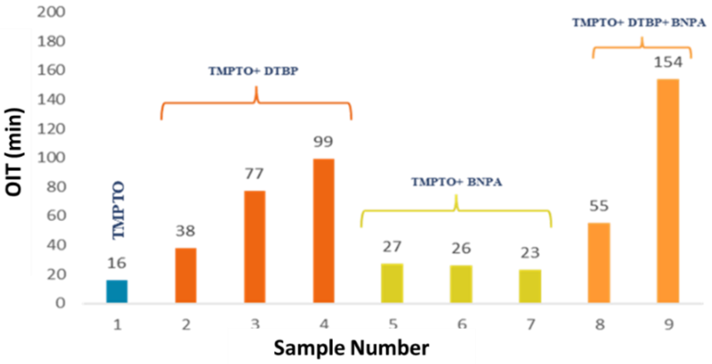


Figure 3. Oxidative indiction time test graph of TMPTO-antioxidant compounds.

Since the presence of unsaturated alkyl chains on the ester significantly impairs the oxidation resistance of the esters, it was determined that there was no effect on increasing the oxidation resistance of both antioxidant additives on the unsaturated TMPCX ester, even when used separately or even together. The oxidation induction times measured as a result of the use of DTBP and BNPA antioxidant compounds in TMPCX ester separately and together in different percentages by mass, respectively, are shown in the graph in Figure 4.

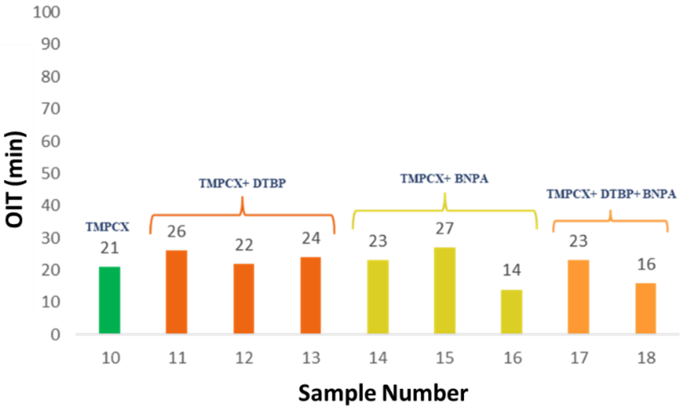


Figure 4. Oxidative induction time test graph of TMPCX-antioxidant compounds.

The present study was carried out to investigate the effects of 2,6-di-tert-butyl phenol and bis(nonylphenyl)amine antioxidants on the oxidation stability performance of TMP and TMP complex esters. At the end of study, the following conclusions can be drawn based on the above results.

1. Utilization of DTBP antioxidant compound at minimum, medium and maximum amounts increase the oxidation induction time of TMPTO ester proportionally. On the other hand, BNPA antioxidant compound does not increase the oxidation induction time of TMPTO ester.
2. Oxidation induction time increased more when DTBP (maximum amount) and BNPA (minimum amount) compound was used together due to the synergistic effect of these two compounds compared to the use of the DTBP antioxidant compound solely. Combination of BNPA compound at maximum and DTBP compound at a minimum amount increased the oxidation induction time at a lower rate compared to the maximum amount of DTBP compound.
3. The presence of unsaturated alkyl chains on TMPCX ester impairs the oxidation stability of the compound. Therefore, there is no effect on this ester to increase the oxidation stability even when both antioxidant compounds are used solely or together.

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