



Comparison of The Oxidative Stability-Enhancing Effects of Aminic and Phenolic Antioxidants on The Oxidation Resistance Performance of Polyol Esters with Different Molecular Structures by RBOT

Kübra Kavut^{1,2}
Hanife Gülen Tom¹

Abstract

Polyol esters are biodegradable synthetic lubricant base oils that can be used as an alternative to mineral oils, polyalphaolefins and diesters in many lubricant applications. These esters are not only effective lubricants, but they also have lower viscosity relative to their molecular weight, thus their major use in industrial lubrication. Therewithal polyol esters are oxidatively stable and their stability can be improved by using antioxidants. Sterically hindered phenols with 2 and 6 positions substituted with tertiary alkyl groups like butyl on the ring such as 2,6-di-tert-butyl phenol antioxidants and aromatic amine antioxidant compounds like nonylated diphenylamine are antioxidants with wide applications in industrial lubricants. Oxidative stability of oils can be determined using the Rotary Bomb Oxidation Test (RBOT). This article is the first to examine the oxidative stability-enhancing effects of 2,6-di-tert-butyl phenol and nonylated diphenylamine antioxidants on neopentylglycol (2-OH groups), trimethylolpropane (3-OH groups), trimethylolpropane complex and pentaerythritol (4-OH groups) type polyol esters using the RBOT test method. This study ascertained that synergistic effect of DTBP and BNPA on the polyol ester formulations except TMPCX.

Keywords

Polyol esters, industrial lubricant, antioxidant, oxidative stability, RBOT

Article Info

Research Article

Received: mm.dd.2023

Accepted: mm.dd.2023

Online Published: mm.dd.2023

INTRODUCTION

Primarily mineral oil-based, polyalphaolefins, polyalkylene glycols and other petrochemical- derived synthetic esters are used as lubricant base stocks available in the market [1]. The content of the vast majority of lubricant formulations consists of approximately 70-99% base stocks. Lubricants, both new and used, can be quite deleterious to the environment due to wrong application, improper usage, incorrect disposal and simple spillage [2]. The base oils and additives employed in making various lubricants and greases and their oxidation products can prove toxic to biodiversity - plants, aquatic animals and human and other living beings. While there may only be a tangential effect of these pollutants on human

¹ BELGIN OIL, R&D Center, ²Marmara Uni., Metallurgy and Material Eng. e-mail: kubra.kavut@belginoil.com, ORCID: 0000-0001-5697-3432 hanife.gulen@belginoil.com, ORCID: 0000-0003-4599-5403,

beings in the short term, they are still pernicious to those subjected to prolonged exposure. Producing alternative lubricants that can ensure sustainability owing to the depletion of petroleum reserves is another reason for the need to develop new synthetic ester-based products [3]. While the search for natural, renewable, biodegradable and green products continues, the interest in working with various esters has increased in direct proportion to this search. Currently, there are five base stocks that are biodegradable to some significance: highly unsaturated or highly oleic vegetable oils (HOVOs), low viscosity polyalphaolefins (PAOs), polyalkylene glycols (PAG's), dibasic acid esters or diesters (DE's) and polyol esters (PE's) [1]. PE's, one of these ester types that can respond to expectations, are biodegradable and hydrolytically stable compounds suitable for use in a wide variety of applications including aerospace and automobile industries, fire resistant hydraulic fluid, marine hydraulic fluid, metalworking fluid, food grade fluid, rolling oils and transformer fluid applications [4].

Vegetable oils like sunflower oil, rapeseed oil, soybean oil, sunflower oil, olive oil, castor oil and palm oil are entirely explored for their high biodegradability and renewability in the development of sustainable biolubricant formulations. On the other hand, as the working environment of lubricant becomes more and more difficult, since vegetable oil-based lubricants have disadvantages such as low thermal and oxidative stability, low fluidity at low temperature and low viscosity range, they cannot meet the needs of industrial lubricants in the new trend. At this stage, synthetic ester oils have gained wide acceptance due to their good low-temperature and viscosity temperature performances and great friction-reducing and antiwear properties [5]. Synthetic esters most commonly used in current lubrication engineering applications can be listed in four categories, monoester, diester, polyol ester, and aromatic carboxylic ester, based on the number and position of ester groups in synthetic ester molecules [6], [7].

PE is obtained synthetically by the reaction of fatty acids and polyhydric alcohols, also called polyols. Palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1) etc. It is one of the commonly used fatty acids. As for the preferred polyols, they are trimethylolpropane (TMP), neopentylglycol (NPG), pentaerythritol (PET). PE's have relatively good thermal and hydrolytic stability compared to the natural vegetable oil form, due to the removal of β carbon after the glycerol molecular backbone is replaced by polyol. In addition, esters of the polyol ester class differ from many other esters in that they do not have β hydrogen on the carbon atom. This results not only in better oxidative stability at higher temperatures, but also better oxidative stability in formulations at lower temperatures. PEs appear in solid or liquid form, depending on the degree of -OH group substitution on the polyols and the type of reacted acid. PE are classified as Group V base oil according to the American Petroleum Institute (API) base oil classification [8], [9].

Degradation of lubricants is inevitable and considered to be one of the primary problems limiting the service life of lubricants. Lubricant degradation can cause serious problems as high energy consumption, higher corrosion against metal surfaces and decreased oxidative stability. Also, degradation of lubricants often results in the formation of insoluble deposits or sludge during use and therefore an increase in viscosity. Degradation of lubricants can be

caused by a variety of factors, primarily thermal and/or oxidation, mechanical shear, additive depletion, and contamination. Among these factors, oxidation is considered the main cause of lubrication degradation. Besides, oxidation has a significant effect on other properties of lubricants, such as anti-wear performance. Lubricants must have superior oxidation stability to completely prevent or delay such problems. For this reason, antioxidants are the main additive that protects the lubricant from oxidative degradation by ensuring that the oil meets stringent requirements for use in industrial applications [10], [11]. Antioxidants interrupt the auto-oxidation process in different ways, according to their different structure and antioxidant mechanism. Oxidation inhibitors are classified into two groups: hydroperoxide decomposers and free radical scavengers, depending upon the mode of their controlling action. Hindered phenols and arylamine antioxidants as radical scavengers' function by donating hydrogen atoms to terminate alkoxy and alkyl peroxy radicals, thus interrupting the radical chain mechanism of the auto-oxidation process [12].

Hindered phenols are a group of (primary) antioxidants that function by scavenging mechanism through hydrogen donation in which the target molecules are peroxy radical intermediates. They are active over a wide range of temperature and they can provide a long-term stability of the lubricant with minimizing viscosity change and discoloration. Synergistic effect may result using a combination of hindered phenols and secondary antioxidants such as thioethers and phosphites. The sterically hindered phenols (I) with 2 and 6 positions on the ring substituted by tertiary alkyl groups (like butyl) are very active antioxidants reacting with the peroxy radical intermediates. The product of the first reaction (II) is also reactive functioning as the scavenger of the peroxy radicals [13]- [16].

Aromatic amine compounds are more active than the hindered phenols and are available in a wide range of molecular weights and forms. However, aromatic amines contribute more in discoloring the final product (formulated lubricant) compared to the hindered phenols, especially at higher temperatures or exposure to light. As active hydrogen donors, they can easily transfer the hydrogen atom on nitrogen to peroxy radicals [17], [18]. The typical group in this class of antioxidants is called alkylated diphenyl amines that are substituted amine antioxidants synthesized by the reaction between diphenylamine and alkylating agents. This group of antioxidants is used in lubricants as well as synthetic polymers and rubber vulcanizates [19].

There are a number of ways that the oxidative stability of an oil may be measured; some common ways are: oxidative stability index (OSI) [20], rotating bomb oxidation test (RBOT) [21], differential scanning calorimetry (DSC) [22], Indiana stirring oxidation test (ISOT) [23] and the thin-film micro-oxidation test [24]. While the petroleum industry requires a testing with much severe conditions than the food industry, the RBOT and micro-oxidation are the recommended tests, because of the environment in which they are used [25]. A reliable method for following and measuring the stability of a functional fluid is the RBOT, in which a large amount of catalyst is placed with the sample under oxygen pressure. The bomb is pressurized to 620 kPa with the test material and stirred at 150 °C. The test is complete once the pressure

in the bomb drops by 175 kPa after reaching a maximum pressure, which is designated as the RBOT time, usually reported in minutes [21].

The study examining the enhancing effect of bis(nonylphenyl)amine (BNPA), a nonylated diphenylamine compound, and 2,6-di-tert-butyl phenol (DTBP) antioxidants on the oxidative stability of TMP and TMP Complex esters is presented in our previous study [26]. However, since there is no detailed study examining the effects of these two antioxidant compounds on the oxidative stability of all polyol esters, a series of formulation studies were carried out in this study and oxidation induction times were investigated. Oxidation stability measurements were performed according to the ASTM D2272 method, using a rotary bomb oxidation tester, and the results were evaluated.

1. Material and Method

1.1. Material

Four kinds of esters were investigated in this study. Trimethylolpropane trioleate (TMPTO), a synthetic ester with a viscosity of 68.40 mm²/s at 40°C, and was supplied by Croda International Plc. TMP Complex ester (TMPCX) with a viscosity of 68.40 mm²/s at 40°C was supplied from Temix Oleo. Neopentylglycol Dioleate (NPGDO) with a viscosity of 24.00 mm²/s and Pentaerythritol Tetraoleate (PETO) with a viscosity of 65.00 mm²/s at 40°C was supplied by Oleon. 2,6-di-tert-butyl phenol (DTBP), one of the phenolic antioxidant derivatives we used in our studies, was obtained from SI Group, Inc. As another antioxidant, bis(nonylphenyl)amine (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 1 and Table 2.

Table 1. Molecular structure of the compounds used in the study.

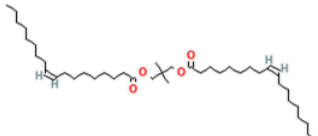
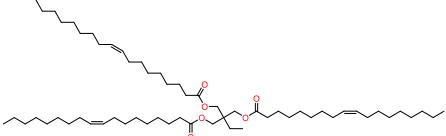
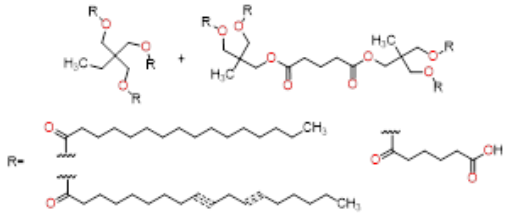

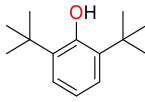
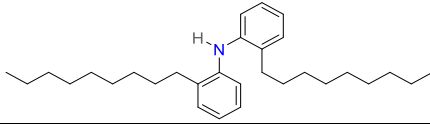
	
NPGDO	TMPTO
	
TMPCX	PETO

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

	
DTBF	BNPA

1.2. Formulation Model

The effects of DTBP and BNPA antioxidant compounds on oxidation stability performance of polyol and TMP Complex esters were investigated by formulating 36 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.

Comparison of The Oxidative Stability-Enhancing Effects of Aminic and Phenolic Antioxidants on The Oxidation Resistance Performance of Polyol Esters with Different Molecular Structures by RBOT

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	NPGDO (100:0)	19	TMPCX (100:0)
2	NPGDO + DTBP (99.75:0.25)	20	TMPCX + DTBP (99.75:0.25)
3	NPGDO + DTBP (99.5:0.5)	21	TMPCX + DTBP (99.5:0.5)
4	NPGDO + DTBP (99.25:0.75)	22	TMPCX + DTBP (99.25:0.75)
5	NPGDO + BNPA (99.75:0.25)	23	TMPCX + BNPA (99.75:0.25)
6	NPGDO + BNPA (99.5:0.5)	24	TMPCX + BNPA (99.5:0.5)
7	NPGDO + BNPA (99.25:0.75)	25	TMPCX + BNPA (99.25:0.75)
8	NPGDO + DTBP + BNPA (99.0:0.25:0.75)	26	TMPCX + DTBP + BNPA (99.0:0.25:0.75)
9	NPGDO + DTBP + BNPA (99.0:0.75:0.25)	27	TMPCX + DTBP + BNPA (99.0:0.75:0.25)
10	TMPTO (100:0)	28	PETO (100:0)
11	TMPTO + DTBP (99.75:0.25)	29	PETO + DTBP (99.75:0.25)
12	TMPTO + DTBP (99.5:0.5)	30	PETO + DTBP (99.5:0.5)
13	TMPTO + DTBP (99.25:0.75)	31	PETO + DTBP (99.25:0.75)
14	TMPTO + BNPA (99.75:0.25)	32	PETO + BNPA (99.75:0.25)
15	TMPTO + BNPA (99.5:0.5)	33	PETO + BNPA (99.5:0.5)
16	TMPTO + BNPA (99.25:0.75)	34	PETO + BNPA (99.25:0.75)
17	TMPTO + DTBP + BNPA (99.0:0.25:0.75)	35	PETO + DTBP + BNPA (99.0:0.25:0.75)
18	TMPTO + DTBP + BNPA (99.0:0.75:0.25)	36	PETO + 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 carried out 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.

3. Results and Discussion

3.1 Oxidation Induction Time

The oxidation induction time of NPGDO, TMPTO, TMPCX and PETO esters was 19, 16, 21 and 16 minutes, respectively. On the other hand, it was determined that the use of the DTBP antioxidant compound at minimum, medium and maximum rates proportionally increased the oxidation induction time in all esters except TMPCX. It was determined that the antioxidant compound DTBP did not increase the oxidation induction time of TMPCX ester. It was found that the antioxidant compound BNPA did not increase the oxidation induction time of all esters. Due to the synergistic effect of these two antioxidant compounds, it was determined that the oxidation induction time of other polyol esters except TMPCX increased significantly as a result of the combined use of DTBP (max. amount) and BNPA (min. amount). It was observed that the combination of maximum BNPA compound and minimum amount of DTBP compound increased the oxidation induction time of other polyol esters, except TMPCX, at a lower rate than the maximum amount of DTBP compound used alone (0.75%). 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 results of the oxidation induction time when DTBP and BNPA antioxidant compounds are used separately and together in all esters used in the study are shown in the graph in Figure 1, Figure 2, Figure 3 and Figure 4.

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	19	19	21
2	23	20	26
3	28	21	22
4	73	22	24
5	18	23	23
6	23	24	27
7	21	25	14
8	32	26	23
9	95	27	16
10	16	28	16
11	38	29	30
12	77	30	57
13	99	31	84
14	27	32	20
15	26	33	21
16	23	34	22
17	55	35	56
18	154	36	103

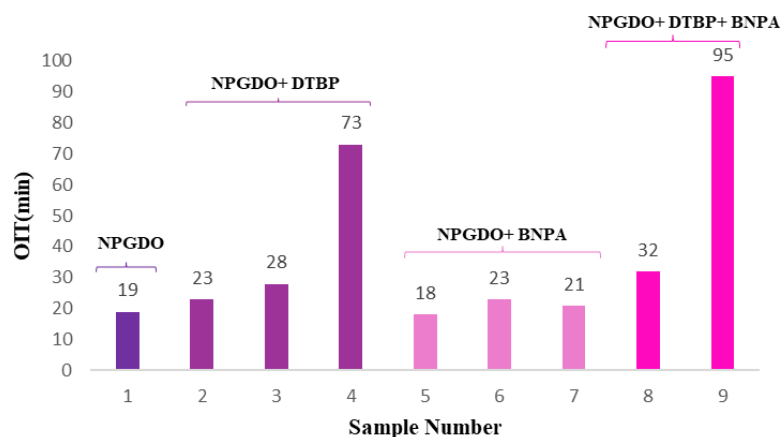


Figure 1. Oxidation induction time test graph of NPGDO-antioxidant compounds.

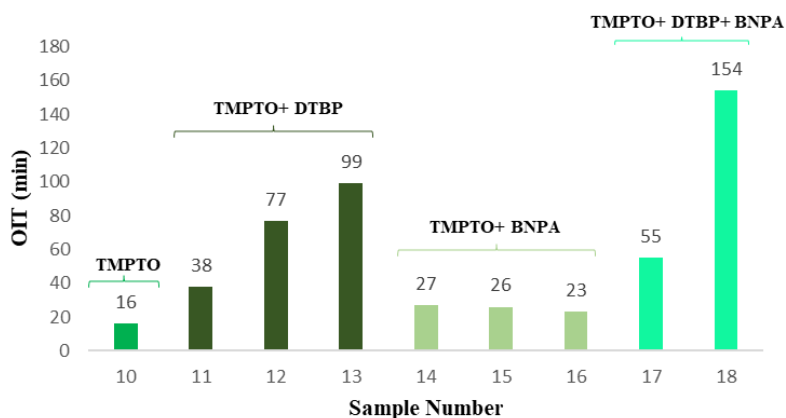


Figure 2. Oxidation induction time test graph of TMPTO-antioxidant compounds.

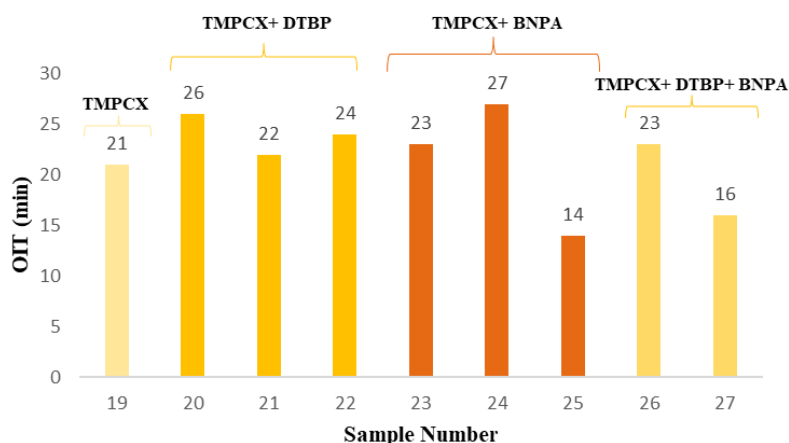


Figure 3. Oxidation induction time test graph of TMPCX-antioxidant compounds.

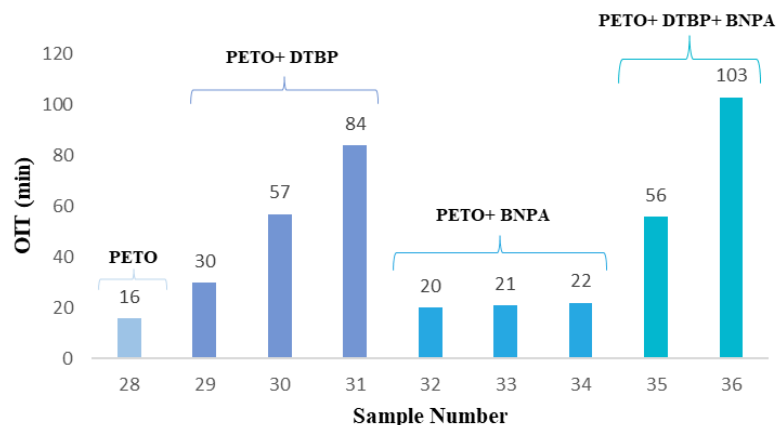


Figure 4. Oxidation induction time test graph of PETO-antioxidant compounds.

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 NPGDO, TMPTO, TMPCX and PETO with DTBP-BNPA antioxidant compounds are shown in Figure 5, Figure 6, Figure 7 and Figure 8 respectively.

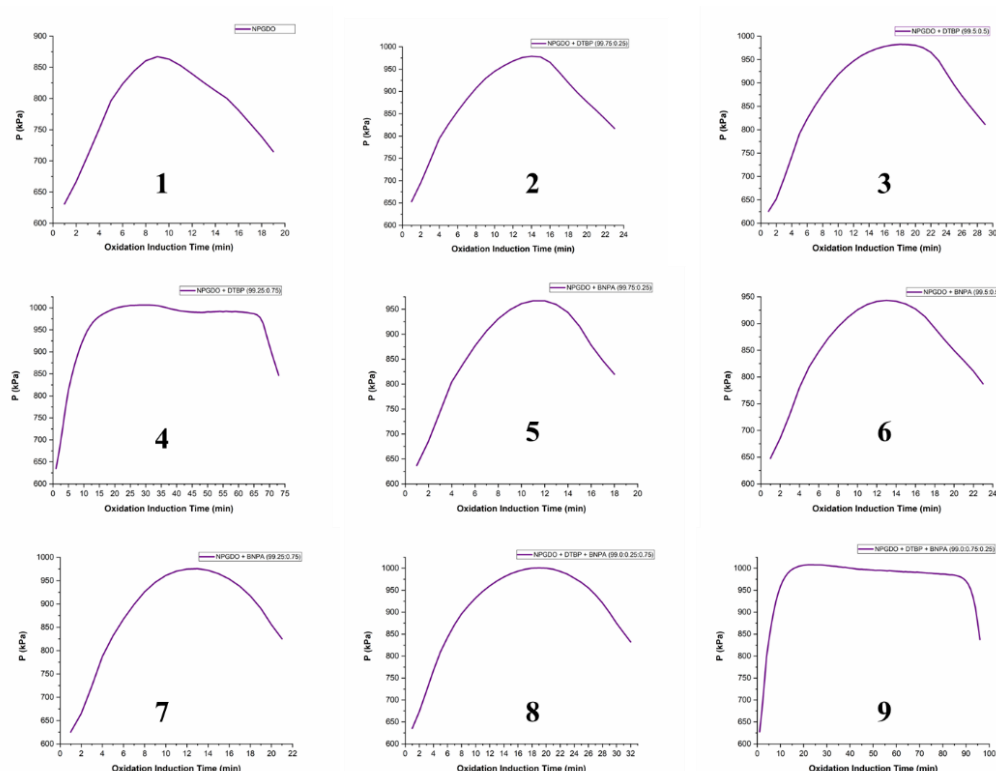


Figure 5. RBOT test graphs of NPGDO studies.

Comparison of The Oxidative Stability-Enhancing Effects of Aminic and Phenolic Antioxidants on The Oxidation Resistance Performance of Polyol Esters with Different Molecular Structures by RBOT

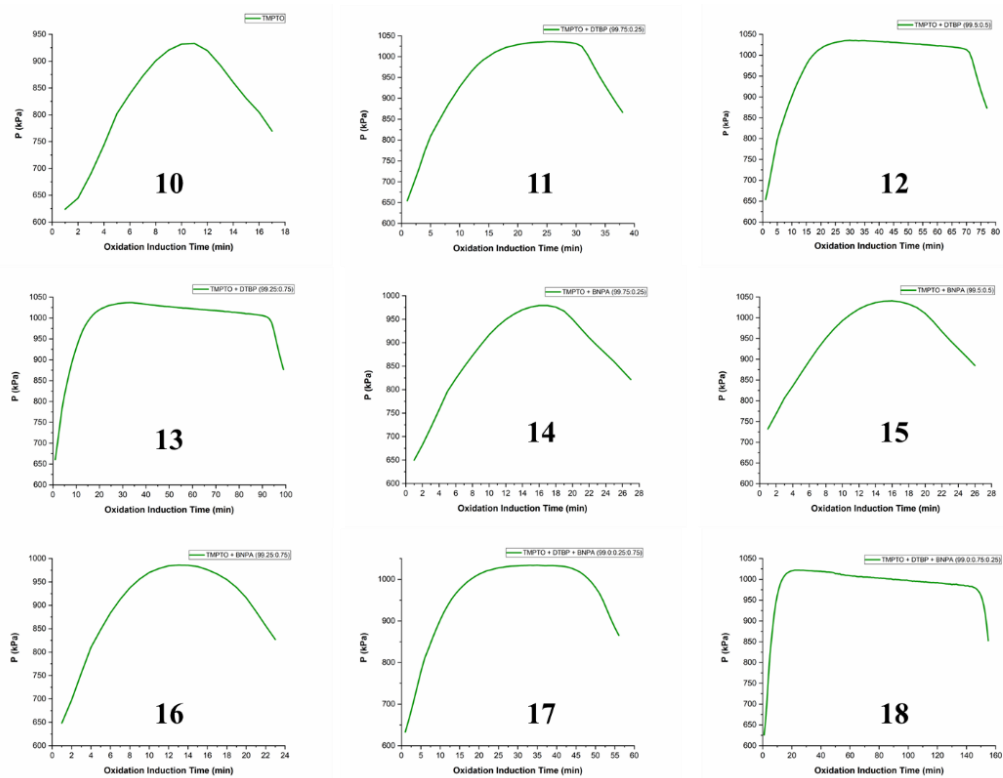


Figure 6. RBOT test graphs of TMPTO studies.

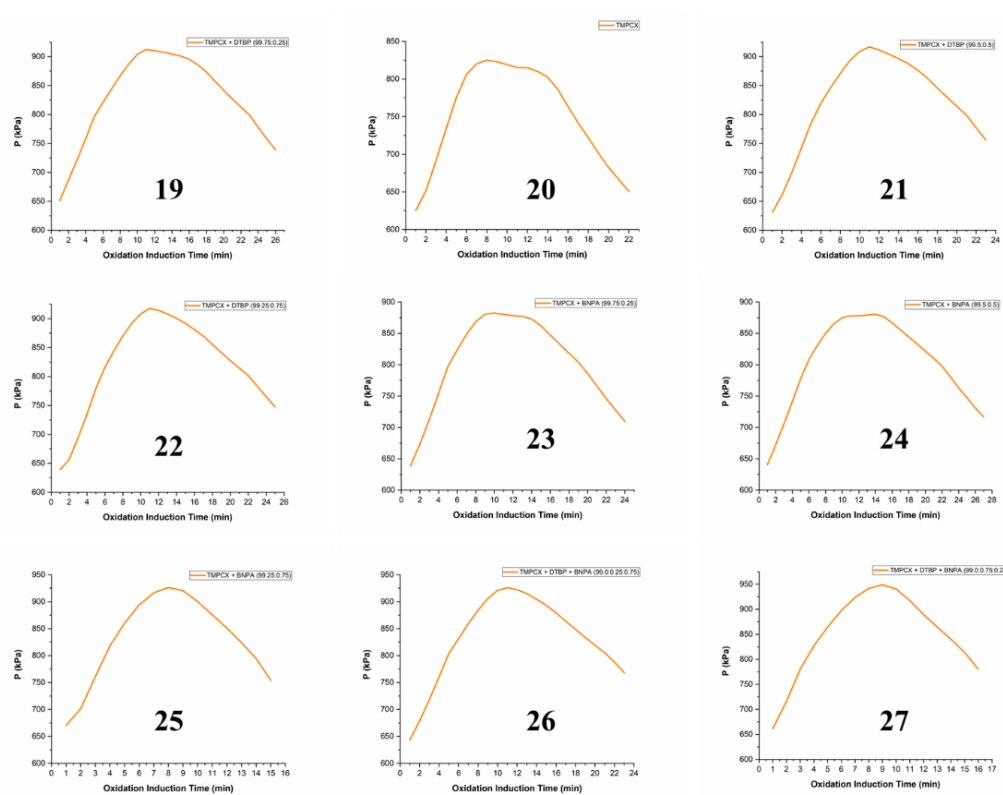


Figure 7. RBOT test graphs of TMPCX studies.

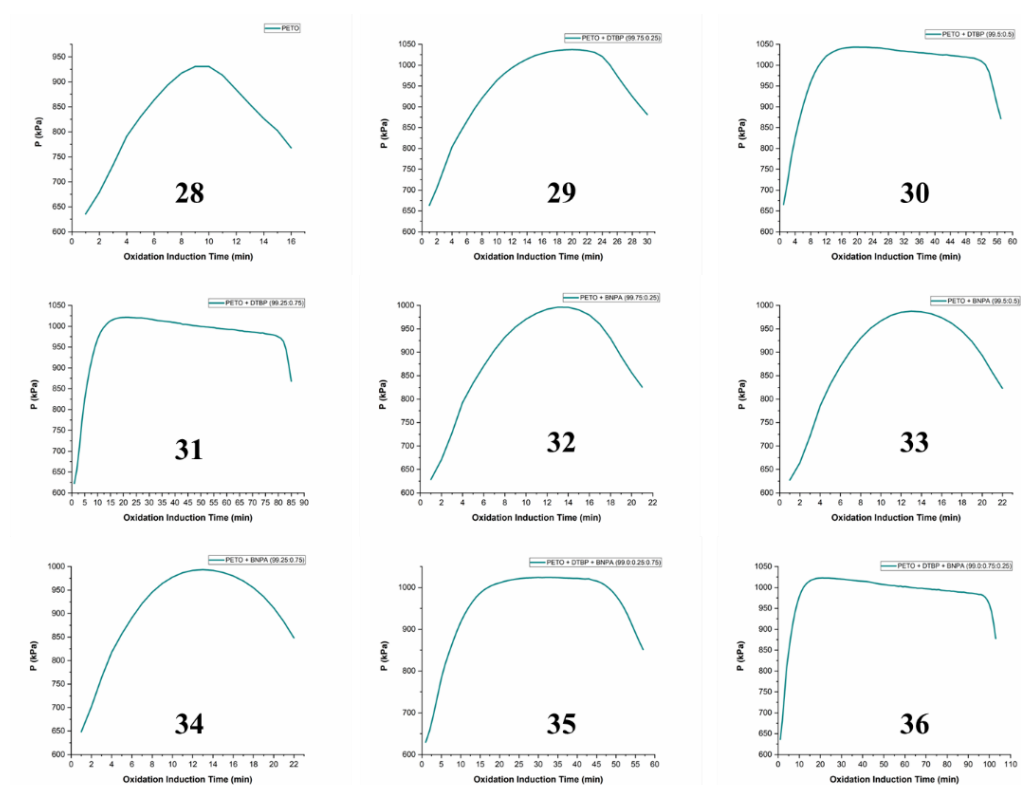


Figure 8. RBOT test graphs of PETO studies.

CONCLUSION

The present study was carried out to investigate the effects of DTBP and BNPA antioxidants on the oxidation stability performance of polyol esters. At the end of the study, the following conclusions can be drawn based on the results shared in the results and discussion section.

1. Utilization of DTBP antioxidant compound at minimum, medium and maximum amounts increase the oxidation induction time of all polyol esters except TMPCX proportionally. On the other hand, BNPA antioxidant compound does not increase the oxidation induction time of all polyol esters used in the study.
2. The oxidation induction time increased more when DTBP (maximum amount) and BNPA (minimum amount) compound were used together compared to the use of DTBP antioxidant compound alone in all polyol esters used in the study except TMPCX, due to the synergistic effect of these two antioxidant compounds. The combination of the maximum amount of BNPA compound and the minimum amount of DTBP compound increased the oxidation induction time to a lesser extent than the maximum amount of DTBP compound in all polyol esters used in the study except TMPCX.
3. Since the presence of unsaturated alkyl chains on the TMPCX ester disrupts the oxidation stability of the compound, studies conducted with this ester do not have an

increasing effect on the oxidation stability of the ester, even when both antioxidant compounds are used alone or together.

Acknowledgements

This study was carried out within the scope of the project coded S0411 and labeled ARISEN, financially supported by SMART Eureka.

REFERENCES

- [1] Nagendramma, P.; Kaul, S. (2012). Development of ecofriendly/biodegradable lubricants: An overview. *Renew. Sust. Energ. Rev.* 16, 764-774.
- [2] Nowak, P.; Kucharska, K.; Kaminski, M. (2019). Ecological and Health Effects of Lubricant Oils Emitted into the Environment. *Int. J. Environ. Res. Public Health*, 16, 3002.
- [3] Mondal, P.; Basu, M.; Balasubramanian, N. (2008). Direct use of vegetable oil and animal fat as alternative fuel in internal combustion engine. *Biofuels, Bioprod. Biorefin.* 2, 155-174.
- [4] Bertin P.A.; Shaner, C.; Liu, N.; Mujkic, M.; Counter, K.; Brekan, (2015). J. E. P. O. Patent No. EP 3 172 294 A1.
- [5] Hu, C.; Ai, J.; Ma, Li.; Wen, P.; Fan, M.; Zhou, F.; Liu, W. (2021). Ester Oils Prepared from Fully Renewable Resources and Their Lubricant Base Oil Properties. *ACS Omega*, 6, 16343-16355.
- [6] Salimon, J.; Salih, N.; Yousif, E. (2012). Improvement of pour point and oxidative stability of synthetic ester basestocks for biolubricant applications. *Arabian J. Chem.* 5, 193-200.
- [7] Brown, M.; Fotheringham, J. D.; Hoyes, T. J.; Mortier, R. M.; Orszulik, S. T.; Randles, S. J.; Stroud, P. M. (1997). Synthetic base fluids. *Chem. Technol. Lubr.* 2, 34-74.
- [8] Chang, T. S.; Yunus, R.; Rashid, U.; Choong, T. S. Y.; Biak, D. R. A.; Syam, A. M. (2015). Palm oil derived trimethylolpropane triesters synthetic lubricants and usage in industrial metalworking fluid. *J. Oleo Sci.* 64(2), 143-51.
- [9] O'lenick, T.; O'lenick, T.; (2019) Polyol Esters in Personal Care Formulations Part 1 – Chemistry. *H&PC Today* 14(5), 40-43.
- [10] Duangkaewmanee, S.; Petsom, A. (2011). Synergistic and antagonistic effects on oxidation stability of antioxidants in a synthetic ester based oil. *Tribol. Inter.* 44(3), 266-271.
- [11] Li, W.; Jiang, C.; Xu, N.; Ma, R.; Wang, X. (2018). Tribological properties of polyol-ester-based lubricants and their influence on oxidation stability. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology.* 233(6), 1-8.
- [12] Wu, Y.; Li, W.; Zhang, M.; Wang, X. (2013). Improvement of oxidative stability of trimethylolpropane trioleate lubricant. *Thermochim. Acta*, 569, 112-118.
- [13] Kuo, H. C. Tribology – Lubricants and Lubrication. *InTech Open*, 1-322.

- [14] Davis, T.G.; Thompson, J.W. (1996). Synergistic antioxidants for synthetic lubricants. *Ind. Eng. Chem.* 5,76-80.
- [15] Sharma, B.K.; Perez, J.M.; Erhan, S.Z. (2007). Soybean oil-based lubricants: A search for synergistic antioxidants. *Energy & Fuels.* 21, 2408-2414.
- [16] Wasson, J.I.; Smith, W.M. (1953). Effect of alkyl substitution on antioxidant properties of phenols. *Ind. Eng. Chem.*45, 197-200.
- [17] Nishiyama, T.; Yamaguchi, T.; Fukui, T.; Tomii, K. (1999). Chain-breaking fused heterocyclic antioxidants: Antioxidant activities of phenothiazines compared to related compounds. *Polym. Degrad. Stab.* 64, 3-38.
- [18] Lucarini, M.; Pedrielli, P.; Pedulli, G.F.; Cabiddu, S.; Fattuoni, C. (1996). Bond dissociation energies of OH bonds in substituted phenols from equilibration studies. *J. Org Chem.* 61, 9259-9263.
- [19] Gatto, V.J.; Elnagar, H.Y.; Moehle, W.E.; Schneller, E.R. (2007). Redesigning alkylated diphenylamine antioxidants for modern lubricants. *Lubrication Science.*19, 25-40.
- [20] Akoh, C.C. (1994). Oxidative stability of fat substitutes and vegetable oils by the oxidative stability index method. *J. Am. Oil Chem. Soc.* 71, 211-216.
- [21] American Society for Testing Materials, 1998b. Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel, ASTM (D 2272-98). ASTM, West Conshohocken, PA, 1 -12.
- [22] Bowman, W.F.; Stachowiak, G.W. (1998). Application of sealed capsule differential scanning calorimetry. Part I: predicting the remaining useful life of industry-used turbine oils. *Lubr. Eng.* 54, 19-24.
- [23] Du, D.C.; Kim, S.S.; Chun, J.S.; Suh, C.M.; Kwon, W.S. (2002). Antioxidation synergism between ZnDTC and ZnDDP in mineral oil. *Tribol. Lett.* 13, 21-27.
- [24] Adhvaryu, A.; Erhan, S.Z. (2000). Oxidation and low-temperature behavior of unmodified and genetically modified vegetable oils: a step toward biodegradable lube. Abstract of American Oil Chemist Society, Annual Meeting, San Diego, CA, 25-28 April.
- [25] Cermak, S. C.; Isbell, T. A. (2003). Improved oxidative stability of estolide esters. *Ind Crops Prod.* 18(3), 223–230.
- [26] Kavut, K.; Tom, H.G.; Ozpercin, T. (2022). Determination of the Effects of Aminic and Phenolic Antioxidants on the Oxidation Resistance Performance of TMP and TMP Complex Esters by RBOT. *International Journal of Industrial Development Research* 2(8760), 1-10