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Antioxidants Classification and Applications in Lubricants

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Abstract

Oxidation is a chemical reaction that occurs in lubricants upon exposure to an oxidizing agent such as oxygen and can be catalyzed by copper and iron. Antioxidants are a group of chemicals that can be used in the formulation of lubricants to stop or reduce the rate of oxidation. Based on the mechanism of action, antioxidants are categorized as primary antioxidants (radical scavengers), secondary antioxidants (Peroxide decomposers), and metal deactivators (complex-forming or chelating agents). Selection of the antioxidants in a formulation is a critical decision that depends on the base oil, application and other ingredients in the formulations. Presence of some other ingredients in the product with antagonistic behavior may suppress the role of antioxidants; however, optimal application of antioxidants with synergistic behavior would increase the stabilization impact of the ingredients on the base oil.

Keywords: lubricant, bio-lubricant, antioxidant, oxidation, stability, synergism

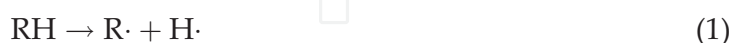
1. Introduction

Oxidation is an unwanted process which results in degradation of lubricants (containing hydrocarbons C_{20} - C_{70}) and generation of degradation products. Oxidation can start with the presence of oxidative agents such as oxygen to form a wide range of oxidation products with higher or lower molecular weight relative to the original oil depending on the progress of the process. Generation of lacquer and varnish, viscosity increase, sludge and deposit formation, and corrosion are some important consequences of oxidation. Copper and iron in metal parts, and harsh conditions such high pressure, high temperature, high friction and high metal concentration are factors that accelerate lubricant oxidation. In combustion engines, the generated heat from combustion process would be high enough to oxidize the lubricating oil unless antioxidants present in the formulation inhibit the progress of oxidation and the formation of degradation products.

Antioxidants are a group of additives that have the potential of prohibiting oxidation of base oil in the lubricants and the inhibition of oil breakdown and thickening [1, 2].

2. Mechanism of lubricants oxidation

Oxidation is a multi-step process mainly consisting of three stages: (a) initiation; (b) chain propagation; and (c) termination. In the initiation stage, an external factor (oxidizing agent) causes generation of a free organic radical ($R\cdot$) or an unpaired electron as part of the lubricant (RH) indicated below:



In the propagation stage, the free radical released during initiation stage is a highly reactive species with the potential of reacting with oxygen to form a peroxide radical. The peroxide radical is another reactive component with the potential of reacting with the lubricant or other components in the lubricant that can result in further decomposition of the lubricant and its components as follows:



Branching occurs as:



In the termination stage, the radical species generated during initial and propagation stages of oxidation would combine and form a stable organic compound and the free radicals are removed from the lubricating agent. The termination stage can be effective in attenuation or ending the oxidation process if no more radicals are generated during the initiation stage.



Altogether, two types of products can be produced during oxidation, namely oil soluble products (such as peroxides, alcohols, acids, esters, aldehydes, and ketones), and oil insoluble products with high molecular weight.

3. Measuring oxidative resistance

The chemical and physical properties of materials can be altered by oxidation. For instance, an increase in the acidity of the samples containing fats and oils can result in corrosion and

rusting. The lubricating properties of such systems can be affected by increasing the viscosity. Oxidation stability testing is essential, as follows: i) development of new products, ii) evaluation of potential new additives and iii) assessment of storage stability [3]. For the purpose of enabling development of valuable new products, it is important to assess the performance of various antioxidants in a lubricant to determine the required treatment-rate and the cost [4].

ASTM D-6186 is a standard method used to measure the performance of an antioxidant in a lubricating substance. In addition, pressurized differential scanning calorimetry (PDSC) is a suitable tool for measuring the oxidative stability. Accordingly, PDSC provides estimates of oxidative stability by detecting exothermic release of heat identified as auto-oxidation. Auto-oxidation is a process by which the antioxidant capacity of the lubricating system goes into the oxidative chain reaction when the effective ingredients are consumed. For example, the effectiveness of two antioxidants was compared using the PDSC test where each antioxidant was added at 2% level to treat the base oil. The results of oxidation induction time (OIT) for both samples heated at 135° for 7 days are shown in **Figure 1**. Many researchers rely on high-pressure differential scanning calorimetry (HPDSC) as an appropriate tool, especially for small samples, where bulk solution effects are minimized and it is facile to detect the interchange of the sample with its atmospheric oxygen. One of the main advantages of this tool is the repeatability of the test procedure with a reasonable reaction time [4–6].

Oxygen pressure vessel method or ASTM D942 (OPVOT) test performance can determine various antioxidants optimum treatment rate to make the most cost-effective formulation in a very short period of time [4]. Lubricants are formulated from a range of base fluids, either mineral or synthetic oils, in which chemical additives are dissolved. The base oil formulation and the nature of the chemical additives will affect on the physical and chemical properties of the lubricant [1]. The life span of the product can be changed using chemical additives for development of lubricants for specific applications. Gas chromatography (GC) and ESI are two significant methods which are used for the analysis of additives related to the additive age,

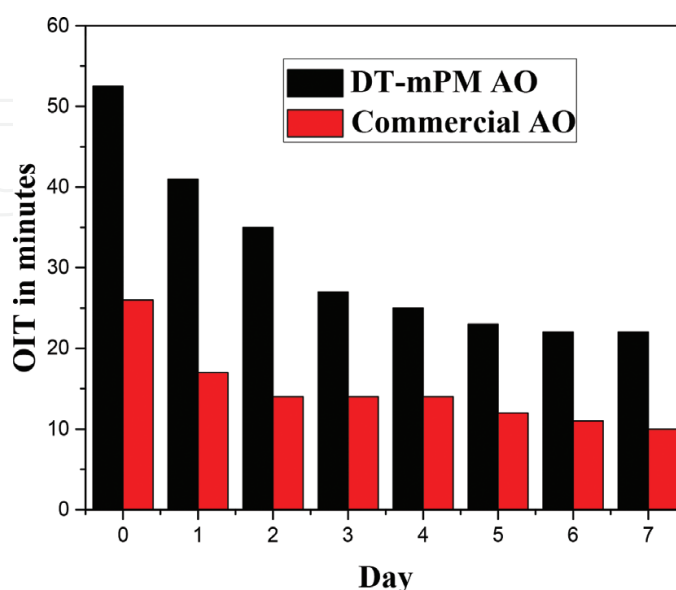


Figure 1. An alternative antioxidant known as DT-mPM displays a greater performance than a commercial antioxidant using PDSC study; AO: alpha-olefin [4].

composition and degradation of the lubricant [7–10]. Antioxidants are among the most important group of additives, that are normally composed of sterically hindered phenols or aromatic amines [1, 2]. The presence of oxygen and high temperatures within a tribological environment can be important factors for rapid oxidation of lubricants. The quantitative analysis of lubricant antioxidant additives in complex and native base oil matrices has been studied using ESI-MS and MALDI-MS [11, 12]. The rotating pressure vessel oxidation test (ASTM-D2272) is the most common method which can measure the RUL (Remaining Useful Life) of the oil's ability to resist oxidation.

Antioxidants are one of the most suitable additives to extend the lifetime of lubricants. Furthermore, antioxidants prevent the oxidative degradation of the lubricant oil thickening and the formation of sludge. Aromatic amines (e.g. dialkylated diphenylamine) and sterically hindered phenols (e.g. 2,6-di-*tert*-butylphenol) are two common antioxidants which are useful in lubricants stabilization to gain synergistic effects [3, 13]. A better understanding of the chemistry of antioxidants and their degradation mechanisms at the molecular level is crucial for developing more efficient lubricants. Lubricants based on mineral oils, are very complex mixtures; therefore, an analytical method with high sensitivity and selectivity to separate the components, and to characterize and quantify antioxidants and their degradation products has been established [14].

4. Activity and classification of antioxidants

Antioxidants are a series of compounds with the capability of controlling oxidation, and consequently preventing oil from breakdown and thickening (increasing viscosity), and helping better performance and longer life of an engine. Natural antioxidants are the chemical compounds that originally present in the mineral oil known as polycycloaromatics and sulfur and nitrogen heterocyclics, or with bio-oil, triglycerides and in biological systems known as tocopherol, astaxanthin, zeaxanthin, lutein, flavonoids, lycopene, etc. In the mineral oil refining process, severe conditions applied in the process strips the base oil of its natural antioxidants [1, 2]. Therefore, the lack of these important group of chemicals should be compensated by supplementation of the base oil using appropriate groups of additives. Three types of antioxidants are generally available, namely, radical scavengers (primary antioxidants), peroxide decomposers (secondary antioxidants), and metal passivators/deactivators [15].

Radical scavengers such as phenolic antioxidants, aromatic amines, and sulfur and phosphorus compounds that stop chain propagation by blocking or reacting with free radicals generated in the initiation stage of oxidation. Blocking of the radicals by the scavengers occurs through donation of hydrogen atoms that react with alkyl or peroxy radicals, leading to the formation of quinones or quinone imines [1, 2, 15].

Peroxide decomposers such as organosulfur (e.g. dialkyl sulfides and dithiocarbamates) and organophosphorus (e.g. triaryl phosphites and trialkyl phosphites) compounds have the conversion potential of hydroperoxides to non-radical derivatives such as alcohols [1, 2, 15].

Metal deactivators such as benzotriazole and N-salicylidene ethylamine acting as surface film-forming compounds or stable complex-forming agents (chelating agent) function by reducing

catalytic effect of metal ions on oxidation. Chelating agents function by trapping metal ions in their structure in the form of stable complexes to reduce the catalytic oxidation activity of the metal ions. Film-forming agents by covering the surface of the metals do not let them enter into the oil phase, and/or these agents may restrict the access of the corrosive species into the metal surface resulting in a reduced corrosive impact of the corrosive agents [1, 2, 15].

Due to the synergistic effect of the antioxidants, combinations of different types of antioxidants are used in lubricant formulations. This synergistic impact of the antioxidants has been proven in several research studies. For example, the results from a study by Davis and Thompson (1996) indicated that alkali metal carboxylic acids and substituted phenols would work as synergists for arylamine antioxidants in ester-based synthetics lubricants. Their results showed that the oil was stable and sludge free when tested at high temperatures at lab scale [16]. In another study by Sharma et al. [17], a synergistic effect was reported where zinc dialkyledithiocarbamate antioxidant was used with an anti-wear additive namely antimony dithiocarbamates in a soybean oil-based lubricant using a pressure differential scanning calorimetry (PDSC) and a rotary bomb oxidation test (RBOT) [17].

Different classifications are available for antioxidants. Based on the source, they can be classified as: (a) natural antioxidants, and (b) synthetic antioxidants. Based on the solubility, they are classified as: (a) oil-soluble antioxidants, and (b) water soluble antioxidants. Based on the mechanism of action: (a) primary antioxidants (radical scavengers), (b) secondary antioxidants (Peroxide decomposers), and (c) metal deactivators. Oil-soluble organic antioxidants are an important group for (hydrocarbon) lubricating oils that can be categorized as discussed in the following subsections.

4.1. Hindered phenolic compounds

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 (such as butyl) are very active antioxidants reacting with the peroxy radical intermediates (**Figure 2**). The product of the first reaction (II) is also reactive functioning as the scavenger of the peroxy radicals [15, 18].

The maximal activity of hindered phenolic antioxidants is attainable when both 2 and 6 positions of the aromatic ring are occupied by tertiary butyl groups; with one substituent replaced by methyl instead of tertiary butyl, the relative antioxidant activity may drop by 37.5% as shown in **Table 1** [18].

4.2. Aromatic amine compounds

This class of antioxidants is 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

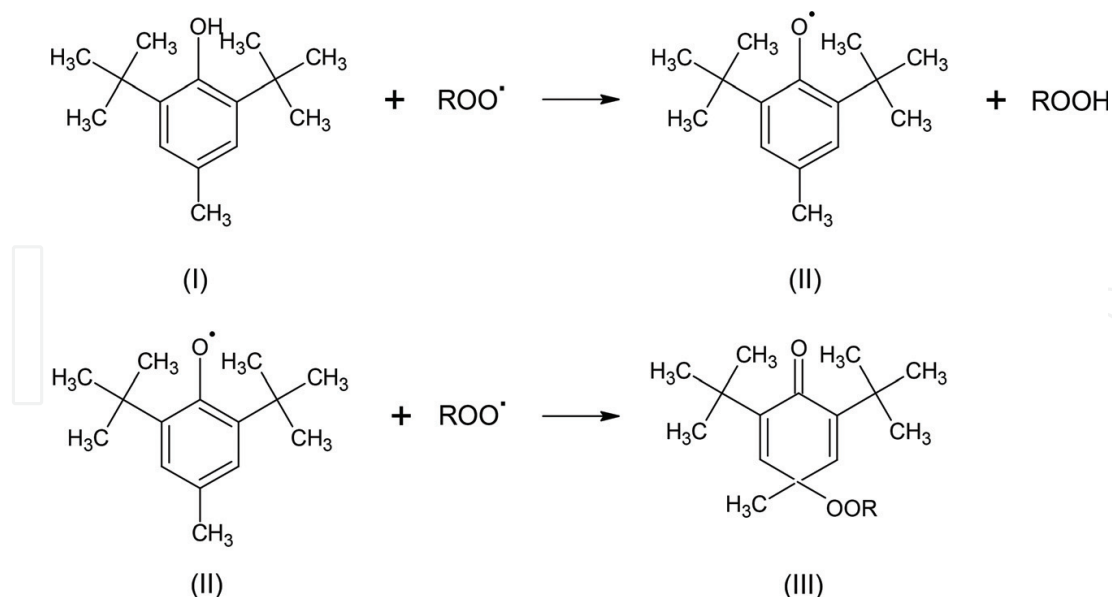


Figure 2. Mechanism of reaction of hindered phenols with peroxy radical.

Phenol structure	Relative antioxidant activity
	100.0
	62.5

Table 1. Relative antioxidant activity of phenolic antioxidants affected by the alkyl substituents at the ortho positions [1, 18].

the final product (formulated lubricant) compared to the hindered phenols, especially at higher temperatures or exposure to light [19]. 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 are called alkylated diphenyl amines that are substituted amine antioxidants synthesized by the reaction between diphenylamine and alkylating agents. This group of antioxidants are used in lubricants as well as synthetic polymers and rubber vulcanizates [22]. The mechanism of action of aromatic amines can simply be presented as follows **Figure 3**:

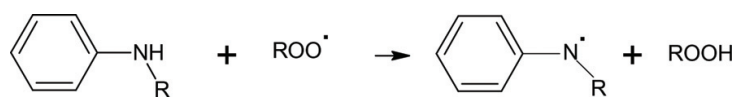


Figure 3. Mechanism of action of aromatic amines on peroxy radicals [resketched from 1, 2, 19].

The mechanism of the sequential reaction of the alkylated diphenylamine under low temperatures (<120°C) is shown in **Figure 4** [1, 23]. At the end of this reactions resulting in the elimination of four peroxy radicals, two compounds are generated, namely; 1,4-benzoquinone and an alkylated nitrosobenzene.

Comparing a diphenylamine molecule with sterically hindered monophenols, the former has the scavenging potential of four peroxy radicals, while the sterically hindered monophenols have the potential of elimination of 2 equivalents of peroxy radicals.

At higher temperatures (>120°C), after reaction of the antioxidant with the peroxy radical and formation of the nitroxyl radical in the second step, this compound would have the potential of reacting with (scavenging) a secondary alkyl radical leading to the regeneration of the original alkylated diphenylamine (**Figure 5**). It has been proven that the performance of the antioxidants based on diphenylamine depends on the substituents in the para position such that stoichiometric efficiencies of over 12 radicals per molecule have been reported in this regeneration process [1, 24].

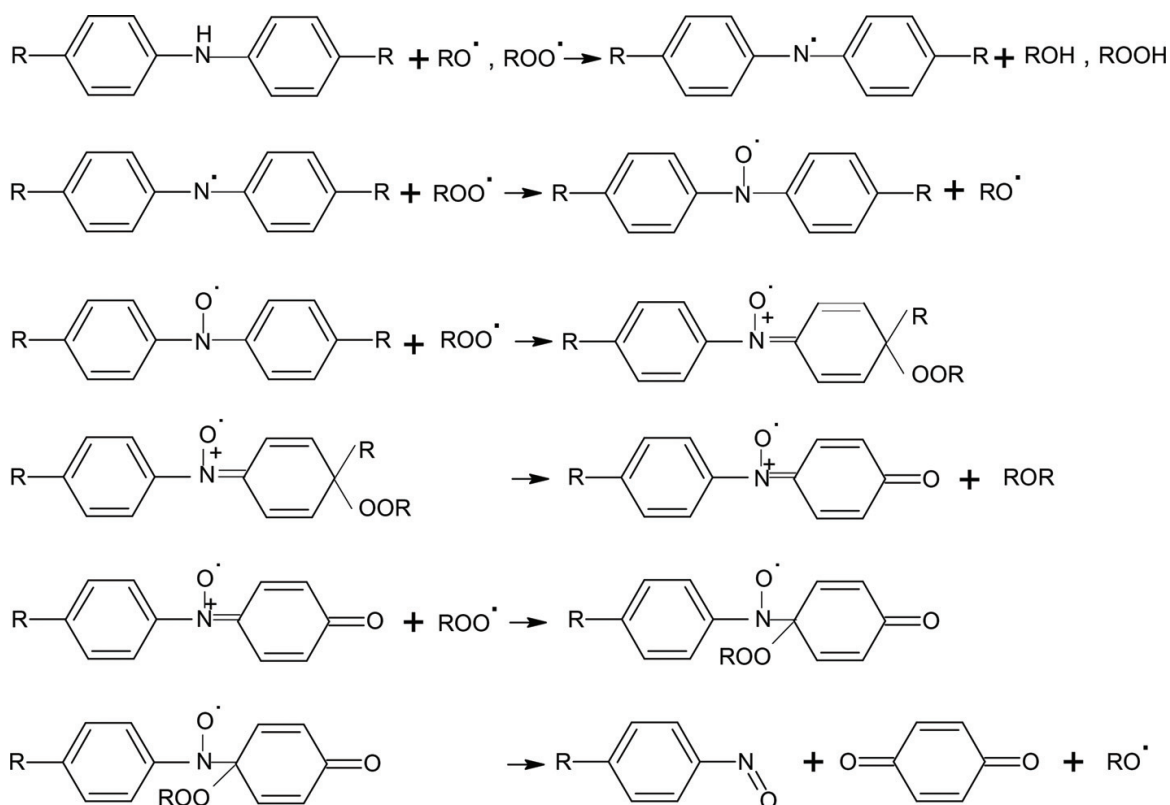


Figure 4. Mechanism of sequential reaction of alkylated diphenyl amine with peroxy radical at low temperatures (<120°C) [resketched from 1 and 2].

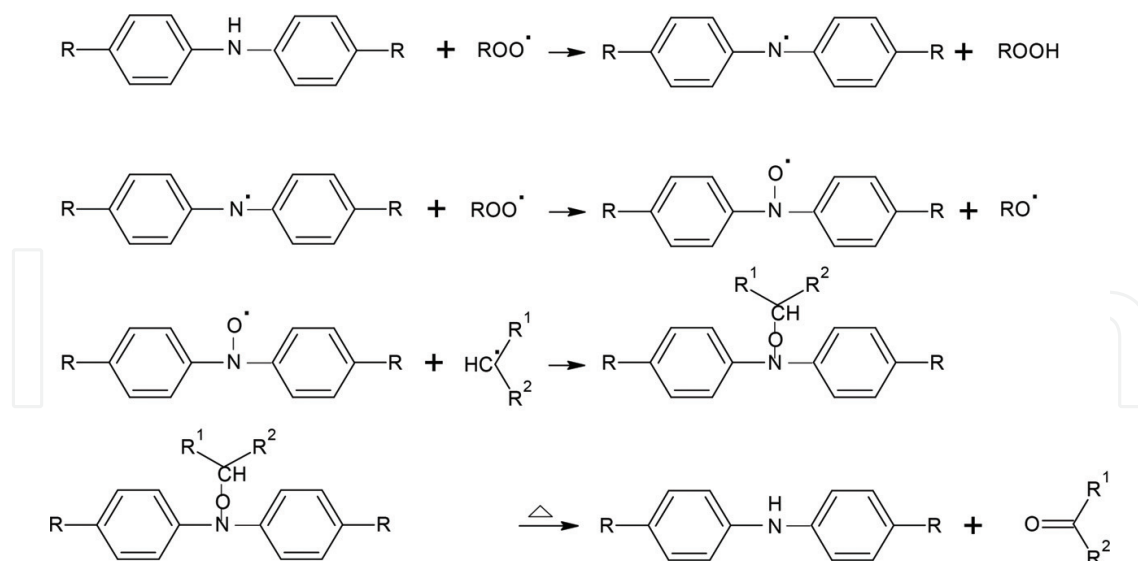


Figure 5. Mechanism of reaction of alkylated diphenyl amine with peroxy radical at high temperatures (>120°C) [resketched from 1].

The performance of aromatic amines on NO_x emissions from soybean biodiesel powered DI diesel engine has been investigated [25]. The results indicated that at 75% load for B100 fuel enriched with DPPD (N,N'-diphenyl-1,4-phenylenediamine) and NPPD (N-phenyl-1,4-phenylenediamine) as effective antioxidants, reductions of 28.36 and 20.96% were obtained with NO emissions, respectively. For B20, less reduction of NO was achieved with DPPD and NPPD additions compared to B100. The effectiveness of the both antioxidants in B100 and B20 fuels was proved for NO emissions.

In another study by Hess et al. [26], incorporation of antioxidants including butylated hydroxyanisole and butylated hydroxytoluene at 1000 ppm concentration in B20 resulted in the reduction of NO_x gases in a single-cylinder engine as shown in **Table 2** [26]. According to

Fuel	Change in NO _x from B20 combustion (%)
B20 + 2-ethylhexyl nitrate	-4.5 ± 1.0
B20 + 2,2'-methylenebis(6-tert-butyl-4-methylphenol)	+0.2 ± 1.0
B20 + citric acid	-0.7 ± 0.5
B20 + α-tocopherol	+0.3 ± 0.2
B20 + ascorbic acid 6-palmitate	-1.3 ± 0.9
B20 + tert-butyl hydroquinone	-0.3 ± 1.6
B20 + propyl gallate	-0.4 ± 2.8
B20 + diphenylamine	+0.7 ± 1.3
B20 + butylated hydroxytoluene (BHT)	-2.9 ± 1.5
B20 + butylated hydroxyanisole (BHA)	-4.4 ± 1.0

Table 2. The influence of additives on NO_x emission during combustion [26].

the results, the two aforementioned antioxidants were more helpful than other antioxidants but less effective than 2-ethylhexyl nitrate (EHN) which is an accepted NO_x-lowering agent.

A study was carried out by Mukul et al. [27] to evaluate the importance of chemistry of antioxidants on the oxidative stability and thermo-oxidative properties of gear oil. They conducted the experiments on 4 oil blends, namely AO I (no antioxidant added), AO II (with an amine antioxidant (Irganox L57) added), AO III (with a phenolic antioxidant (Irganox L135) added), and AO IV (with both Irganox L57 and Irganox L135 added). In the high-pressure differential scanning calorimetry (PDSC) test at 160°C, the following order obtained for oxidation induction temperature (OIT) of the oil blends:

$$\text{AO II} > \text{AO IV} > \text{AO III} > \text{AO I} \quad (9)$$

A similar trend was also obtained for rotating pressure vessel oxidation test (RPVOT) results for the oil blends tested confirming a good correlation between the two test methods. However, a reverse trend of results for the oxidation level (%) of the aforementioned oil blends was achieved. According to the results, amine antioxidant resulted in a better performance compared to the phenolic antioxidant and synergism of the antioxidants did not have a significant role in delaying the oxidation reactions. The higher performance of amine antioxidant compared with the phenolic antioxidant on the thermo-stability of the lubricant could be its catalytic manner of reaction and regeneration over several cycles of scavenging and breaking of chain reactions of oxidation.

Thermal stability of polyol ester lubricant was affected by different types of antioxidants as reported by Mousavi et al. [28]. Among the systems studied, Phenyl-R-naphthylamine (PAN) showed a remarkable improvement on the thermal stability of the base oil (Figures 6 and 7) indicating less acid and less HMW products generation in this oil blend at high temperature (220°C). The greater area in Figure 7 is the representation of the generation of high-molecular weight products (HMW) due to oxidation and polymerization reactions.

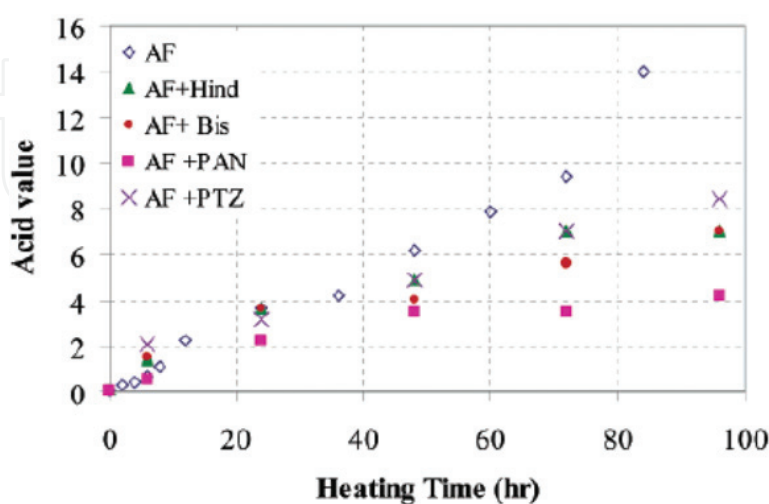


Figure 6. Acid values of original oil (AF) and inhibited oil (using different antioxidants) heated at 220°C over time. Reprinted with permission from [28].

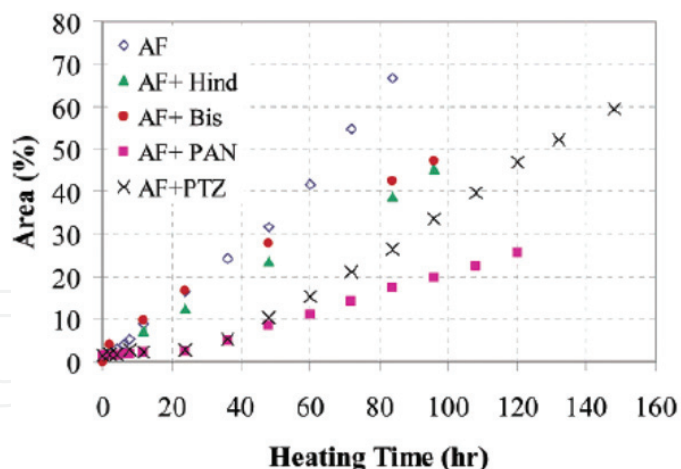


Figure 7. Peak area (%) obtained with gel permeation chromatography (GPC) for high molecular weight (HMW) chemicals generated at 220°C through oxidation/polymerization reactions. Reprinted with permission from [28].

4.3. Organosulfur compounds

Organosulfur compounds function as hydroperoxide decomposers by converting them into non-radical products. Acid-catalyzed decomposition is the most important mechanism of eliminating hydroperoxides in the lubricating system with acid catalysts sourced from organosulfur compounds, as reported by Hawkins and Sautter [29].

Compounds such as dialkyl sulfides (R-S-R) would react with hydroperoxide molecules converting them to sulfoxides as shown in **Figure 8**:

In the next step, assuming R is an alkyl, sulfoxide molecule can be converted (by heat) to sulfenic acid (RSOH) which is a very reactive acid, as outlined in **Figure 9**:

Since sulfenic acid is an unstable material, especially in the presence of hydroperoxide, it can be easily transformed to sulfinic acid decomposition occurs that can function as an acid catalyst in the decomposition of hydroperoxides at low temperature. At higher temperatures, sulfinic acid decomposition occurs by thermolysis and is converted to SO₂ that functions as the catalyst for hydroperoxide decomposition (**Figure 10**).

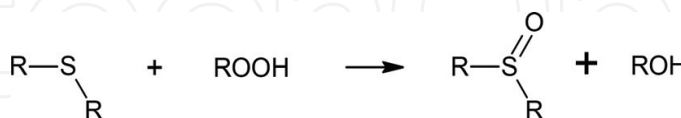


Figure 8. Conversion of hydroperoxides to dialkyl sulfoxide by dialkyl sulfide.

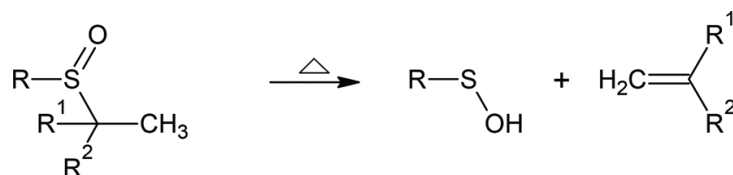


Figure 9. Generation of sulfenic acid from sulfoxide molecule.

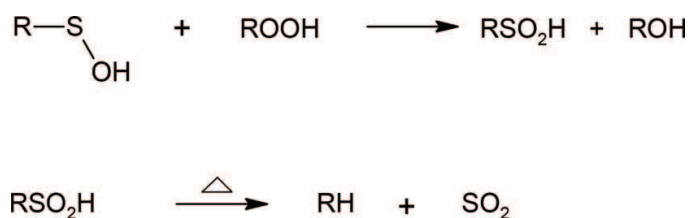


Figure 10. Conversion processes of sulfenic acid by hydroperoxide, and sulfinic acid by heat.

According to Bridgewater and Sexton [30], sulfur dioxide functions as a powerful Lewis acid such that one equivalent can decompose up to 20,000 equivalents of cumene hydroperoxide, i.e., $5\text{--}60 \times 10^{-6}$ mol/l of the sulfur compound decomposed over 50% of the 0.2 mol/l of cumene hydroperoxide in a 6-h period [30].

In addition to the sulfur-based acids mentioned above, sulfacids (RSO_xH) are also considered organosulfur antioxidants with a mechanism of reaction with peroxy radicals (**Figure 11**) and functioning as a primary antioxidant as below:

4.4. Organophosphorus compounds

Among organophosphorus compounds, phosphites are the main group of compounds that are used in the formulation of lubricants to overcome the oxidation reactions. They have the potential of reacting with hydroperoxides, peroxy and alkoxy radicals (**Figure 12**). Therefore, they can be effective on the stability of color and physical and rheological properties of the lubricant. In the reaction with hydroperoxide or peroxy radical, phosphite is oxidized to the corresponding phosphate, while the hydroperoxide and peroxy radical are reduced to a less reactive alcohol and alkoxy radical, respectively [1, 2].

If phosphite possesses a phenoxy group in its structure, it would eliminate peroxy and alkoxy radicals through reaction with them and also the generated phenoxy radical from this reaction would be a stable radical with the potential of elimination peroxy radicals (**Figure 13**). Stability of the generated phenoxy radicals due to their steric hindrance by the two alkyl groups on the ortho positions of the aromatic ring makes them appropriate antioxidant candidates in moist systems of lubrication [1, 2].



Figure 11. Reaction of sulfacids with peroxy radicals [resketched from [1, 2].

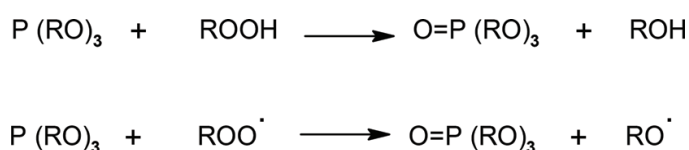


Figure 12. Reactions of phosphite with hydroperoxide and peroxy radicals [resketched from [1, 2].

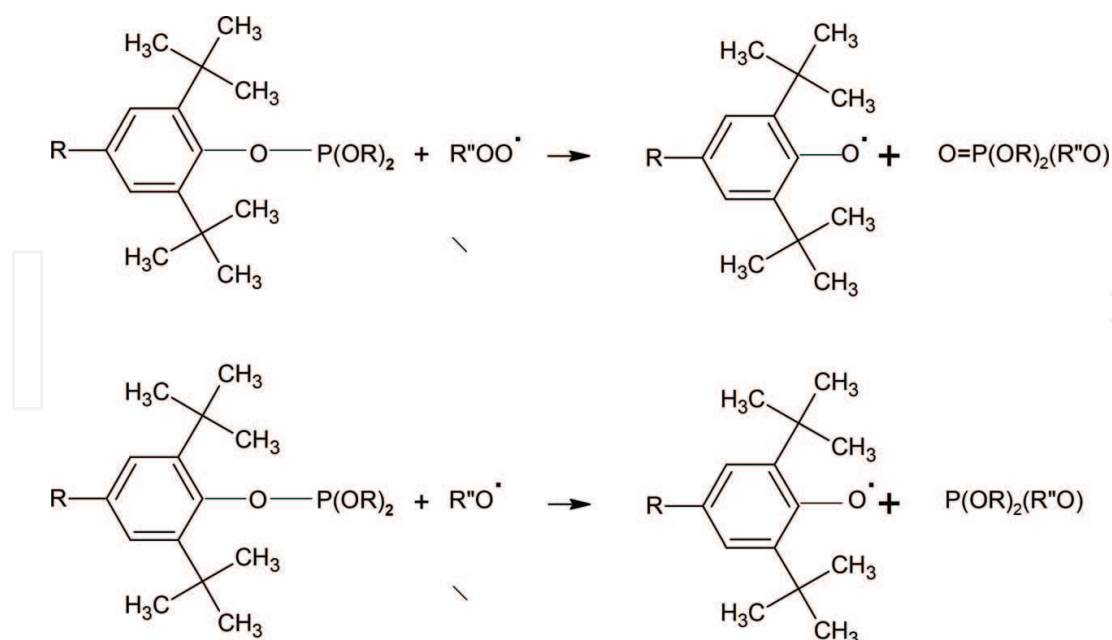


Figure 13. Reactions of phosphite (possessing phenoxy) with alkoxy and peroxy radicals [resketched from 2].

4.5. Sulfur-phosphorus compounds

Antioxidants with both sulfur and phosphorus elements are more efficient and effective than those with either sulfur or phosphorus. Metal dialkyldithiophosphates are a group of antioxidants in this class that have been widely used and have been synthesized by the reaction between phosphorus pentasulfide and alcohols (such as aliphatic, cyclic and phenolic, lauryl, octyl, methyl cyclohexyl, etc.) to produce dithio-phosphoric acids followed by a neutralization process using a metal compounds (such as zinc, barium, calcium and molybdenum compounds or oxides). Zinc dialkyldithiophosphate (ZDDP) is one of the well known compounds in this group that have been used as an effective antioxidant and anti-wear component in the lubricant industry for several years [2].

4.6. Organo-zinc compounds (Zn dithiophosphate ZDTP/ZDP)

ZDTP/ZDP work as antioxidant and anti-wear agents protecting metals against corrosion in the lubricants formula. Therefore, they are considered multifunctional additives in engine oils and hydraulic fluids. The alcoholic group used in the structure of the compound is an important factor on the performance of the product, i.e. primary and secondary ZDTPs (with aliphatic alcohols) provide better results in terms of oxidation inhibition and wear protection compared to aryl ZDTP. The overall performance of ZDTPs would be affected by the presence of other additives in the formulation of the lubricating product [31–33].

In a typical antioxidant mechanism activity of ZDTP, an acid-catalyzed ionic decomposition of hydroperoxide may occur. First, ZDTP and hydroperoxide can form a basic ZDTP and then through some sequential reactions, hydroperoxides are decomposed. A typical example of the reaction between ZDTP and hydroperoxides outlined in [1] **Figures 14** and **15**:

ZDTP may also directly react with peroxy radicals leading to active inhibitors as shown below:



Figure 14. A typical reaction of ZNTP with hydroperoxides.



Figure 15. Reaction mechanism of ZDTP with peroxy radical.

The final radical $(RO)_2PS_2\cdot$ also has the potential of reacting with hydroperoxide and generating hydrogenated acid form of this compound with the functionality of an inhibitor.

4.7. Organo-copper compounds

Copper as a transition metal has been considered an oxidation promoter which may cause damage in the lubricant or lubricating systems; however, copper salts that are soluble in oil are reported to function as antioxidants [34, 35]. Limitation of loading copper within 100 to 200 ppm to obtain the optimal control of oxidation and wear is a drawback for copper-based antioxidants. Over this range, the performance of the anti-wear components in the lubricants would drop due to the reverse impact of copper. Organo-copper antioxidants are effective in ester and mineral oil lubricants at temperatures below 250°C.

Organo-copper compounds including copper naphthenates, oleates, stearates, and polyisobutylene succinic anhydrides have been reported to be synergistic with multi-ring aromatic compounds in controlling high-temperature deposit formation in synthetic base stocks [2].

According to some other studies, inclusion of oil-soluble compounds of copper in the range of 5 to 500 ppm resulted in improved performance of the automotive crankcase lubricants in terms of anti-wear, antioxidant performance and corrosion resistance [36].

4.8. Organo-molybdenum compounds

Molybdenum dithiocarbamate has been reported to function as an antioxidant and anti-wear component in the lubricants. However, it would lose its protective properties by time due to dropping its concentration below the critical level of activity [37]. The synergistic application of Molybdenum dialkyldithiocarbamate (MoDDC) with arylamines was tested to improve the durability and low friction performance of MoDDC over time. The DSC (differential scanning calorimetric) results have indicated that the oxidation and induction temperatures for a poly- α -olefin (PAO) lubricant would increase by the addition of MoDDC to the formulation. Also, MoDDC would have an antioxidative synergism with alkylated diphenylamine antioxidants (arylamines) such as octyl- and butyl-containing diphenylamine compounds.

5. Antioxidants/additives synergism and antagonism

Synergistic mixtures of antioxidants from different groups or classes are generally applied in the formulation of commercial lubricants to provide better stability toward oxidation. In

lubricating systems that involve a synergistic mechanism, free radical scavengers are the major antioxidant component, while the hydroperoxide decomposers function as auxiliary components for the free radicals [38]. It was reported that the oil-soluble organic molybdenum (organic molybdenum complex (MC)) and arylamine antioxidant (dioctyldiphenylamine (DODPA)) would have an excellent antioxidant synergism in an oil system (poly-alphaolefin synthetic lubricant (PAO)) as shown in the DSC thermogram (**Figure 16**). The OIT was increased from 221.4°C with DODPA as the sole antioxidant to 229.7°C with the combination of DODPA and MC as the synergistic antioxidants. Also, a lower acid generation and lower kinematic viscosities were observed after oxidation-corrosion test for the lubricant with antioxidant, especially in the lubricant with both DODPA and MC due to their synergistic impact (**Table 3**). As a consequence, a lower deposit occurs when both antioxidants are in the system (**Figure 17**) compared with the lubricants that contain DODPA solely.

In another study by Hu et al. [39] where a molybdate ester (ME) and dioctyldiphenylamine (DODPA) were used as antioxidants, a synergistic effect was reported between the two antioxidants.

Synergistic behavior of sulfonated calcium carbonate and an ashless antioxidant (N-phenyl- α -naphthylamine (T531)) in hydrogenated oil was investigated and the results suggested that anti-wear and antioxidant effect were synergistically improved in the system [40].

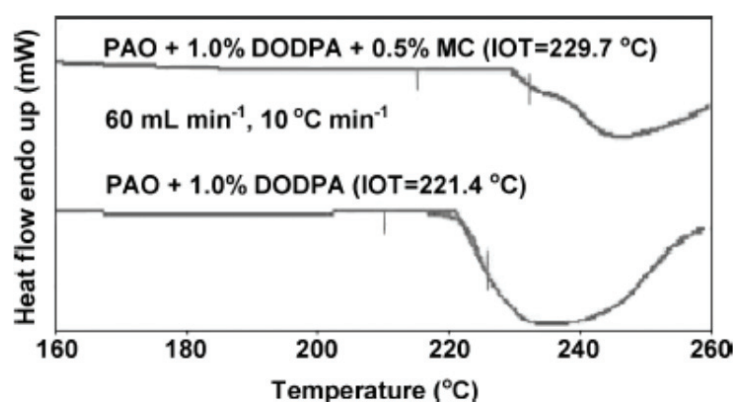


Figure 16. DSC thermograms of PAO oxidation in the presence of DODPA with or without MC [38]. Reprinted by permission of the Society of Tribologists and Lubrication Engineers, www.stle.org.

Lubricant	Δ TAN	Δ KV (%)
Polyalphaolefin (PAO)	8.2	216
PAO + 0.5% MC	5.6	180
PAO + 1.0% DODPA	3.6	36.8
PAO + 1.0% DODPA + 0.5% MC	2.1	15.3

Δ TAN: change in the total acid number; Δ KV: change in the kinematic viscosity.

Table 3. The change in total acid number and viscosity after 24 h in oxidation-corrosion test [38].

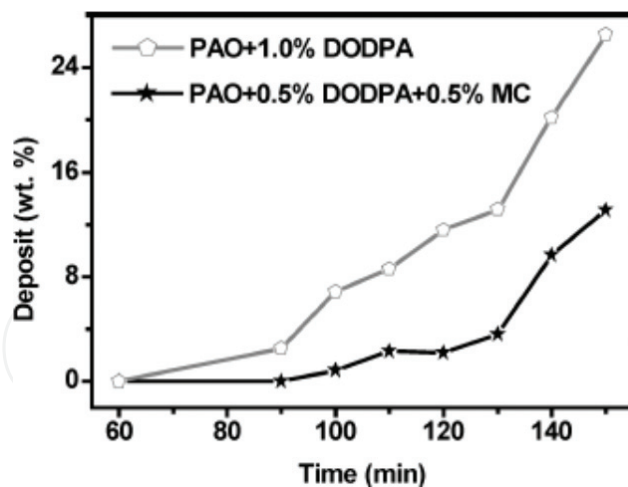


Figure 17. Deposit formation in PAO in the presence of DODPA with or without MC [38]. Reprinted by permission of the Society of Tribologists and Lubrication Engineers, www.stle.org.

In contrast to synergism, the presence of mixtures of antioxidants with other additives may have antagonistic behavior. Therefore, the combinations of the antioxidants along with other lube additives in a lubricating fluid need to be optimized to prohibit or minimize antagonism. It has been shown that anti-wear and antioxidant properties of ZDDPs have been adversely affected by some additives such as detergents and dispersants (sulfonates, phenates and salicylates). This undesired effect can be due to the competition of detergents and dispersants with ZDDPs by surface adsorption or restricted interaction of this component with the metal or the fluid phase [41].

6. Bio-based antioxidants and lubricants

Triglycerides from plant sources have been used as biolubricants with limited applications due to their low thermal and oxidative stability. As well, triglycerides have low volatility, high lubricity, low toxicity and good viscosity-temperature properties as their key advantages. Therefore, different antioxidants such as tocopherols, propyl gallate (PG), ascorbyl palmitate (AP), and some synthetic antioxidants (butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), mono-*tert*-butylhydroquinone (TBHQ), or 4,4'-methylenebis(2,6-di-*tert*-butylphenol) (MBP)) have been used to improve their resistance to the oxidative agents. In recent years, a great number efforts have been made to develop sustainable bio-lubricants and additives with the preference of non-toxicity, multi-functionality and compatibility to the present systems. Cellulose fatty esters have been developed as the lubricant additive, mainly for antioxidant applications. It has been modified to cellulose ferulate, cellulose lipoate and α -tocopherulate for antioxidant functionality [42, 43].

In a study by Singh et al. [44], cellulose laurate was synthesized for use as an effective biolubricant. The results indicated that the lubrication performance would increase with the degree of substitution (DS) in cellulose molecule and by increasing the concentration of cellulose laurate in the base oil which was *n*-butyl palmitate/stearate.

In another study [45], a multi-function additive as detergent/dispersant/antioxidant/anti-wear was developed from L-histidine (HDS) for bio-lubricant applications. Two types additives namely, Ca-HDS-L and Ca-HDS-M were synthesized by esterification with lauroyl chloride and myristoyl chloride, respectively. Using the products in a polyol base oil indicated that Ca-HDS-L worked as a better detergent and dispersant, but Ca-HDS-M functioned as a more effective antioxidant. The oxidative properties obtained by the two additives (ca. 1–3 g/l addition to the oil) are presented in **Table 4**.

Lubricant	TAN (soluble)	Total sludge (%)	Total oxidation products (%)
Polyol	2.019	32.454	34.416
Polyol +1000 ppm Ca-HDS-L	1.598	0.497	3.530
Polyol +2000 ppm Ca-HDS-L	1.514	0.022	1.300
Polyol +3000 ppm Ca-HDS-L	1.402	0.013	1.579
Polyol +1000 ppm Ca-HDS-M	0.476	0.065	2.423
Polyol +2000 ppm Ca-HDS-M	1.514	0.076	1.282
Polyol +3000 ppm Ca-HDS-M	1.458	0.021	1.183

Table 4. The effect of multi-function additives (Ca-HDS-L and Ca-HDS-M) on quality properties of a polyol lubricant in universal oxidation test (IP 306); TAN: Total acid number [45].

7. Future of antioxidants

Competent and creative research is still needed in the study of oil antioxidants. Some important questions as why one type of antioxidant is efficient in one kind of oil and inefficient in another is often puzzling. Lubricants can affect the environment to various extents; thus, the development of new environmentally friendly lubricant formulations is required. Moreover, new types of antioxidants are still being developed and further improvement in the design of high temperature antioxidants is required. Furthermore, several key issues in the field of lubrication and their relation to recent improvements are revealed as follows: corrosive properties of oily additives, shear strength and durability of high pressure agents, internal cohesion and viscosity of organic liquids, improvements in the viscosity index scale, and synthetic oils and their improvement [14].

In the future, along with improvement in lubricants performance, the service change lifetime also is intended to be extended. Polybutenes play a key role for control the viscosity in an extensive range of automotive and industrial lubricants. The disadvantages of using low-viscosity polybutenes are due to restrictions in volatility and oxidation resistance limit for base oil applications. ZnDTPs, hindered phenols, alkylated diphenylamines, organomolybdenum compounds and dithiocarbamates are antioxidants that are used for the protection of lubricants against oxidation. On the other hand, future antioxidants should be developed with consideration related the to environmental and emissions concerns, improved fuel/energy efficiency, higher performance standards, and new base stocks [1].

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