



Study of Oxidative Stability of Lubricants Blended with *p*-Substituted Phenolic Antioxidants

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Received: 10 May 2018;

Accepted: 8 June 2018;

Published online: 31 July 2018;

AJC-19024

Hindered phenolic antioxidants with different substitutions at *para*-positions are evaluated for their oxidation inhibition activity in mineral oil lubricants. Additives are blended in API Group-II base oil and subjected to bulk oil oxidation test under the conditions of the IP-48 test method. The unoxidized (fresh) and oxidized oils tested for presence and concentration of oxidation products by determining the change in acid value, increase in kinematic viscosity and concentration of oxidation products by FT-IR spectroscopy in the oil to evaluate oxidation severity. Based on the results, it seems that lighter *para*-substituted additives are incapable of protecting the oxidation of oil in the presence of oxygen and high temperature. It was observed that the inhibition activity of additives greatly increases due to the presence of *para*-substituted electron donating groups. The electron donating groups coupled with thioether linkage further raises the inhibition activity which is probably because of peroxide decomposing activity along with radical trapping.

Keywords: Phenolic antioxidants, Oxidative stability, Lubricant blends, API base oils, Total acid number.

INTRODUCTION

Base oils are the primary constituents of lubricants. They along with performance additives form the lubricants. Different applications require specific properties of lubricants and accordingly, performance additives are selected. Oxidation stability is one of the most critical properties of lubricant for extended service life. In operating conditions, lubricants get exposed to high temperatures, air mixing and contact with metals. These conditions favour thermal and oxidative degradation of lubricants. Oxidative degradation of hydrocarbons in air involves free radical chain reactions [1], which progresses through four significant steps namely initiation, propagation, branching and termination.

Oxidation of lubricant leads to many problems such as viscosity increase, sludge and sediment formation, varnish, filter plugging, loss of foam control, rust formation and corrosion, etc. [2]. For the useful service life of lubricants, inhibition of oxidative degradation is vital. The only practical approach for oxidation prevention is the addition of "antioxidants" of sufficient activities and in sufficient concentrations to achieve the desired stability. The comprehensive reviews on antioxidant additives are reported by Valgimigli and Pratt [3]. Because of

the commercial importance of antioxidants, research into the development of new molecules and studies of their mechanisms has been done by various researchers [4-11].

Hindered phenols and aromatic amines are two essential types of antioxidants generally used for the protection of lubricants from oxidative degradation [12]. Excellent reviews of radical-trapping antioxidants (RTA) of phenolic [13] and non-phenolic compounds [14] is available in the literature. Various methods for determination of oxidizability of lubricating oils have been used since long back. In 1936, Dornte [15] had devised a circulatory system to measure the oxygen absorption rate at constant pressure as a measure of oxidizability of oils. This methodology became the milestone in the field of lubricant oxidation stability study. Several workers [15-17] had used this basic concept with further refinement in hardware and analytical techniques for the study of oil oxidation process and oxidation stability evaluation. Energy Institute (EI) publishes various international standard test methods as IP methods for petroleum and related products. One such method IP 48 [18] is widely used to evaluate the tendency of lubricants to deteriorate under specified oxidation conditions. This test method correlated to bulk oil oxidation conditions of engine oils.

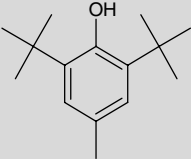
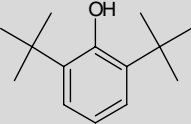
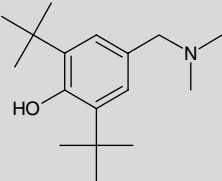
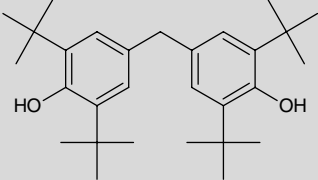
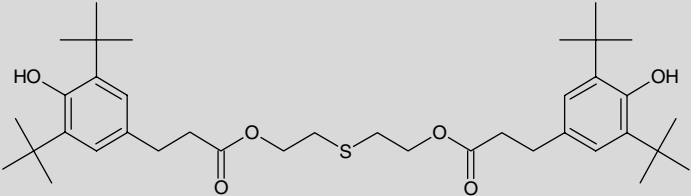
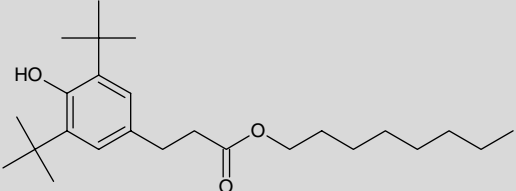
Several researchers have studied the effect of structure on the activity of phenolic antioxidants in different matrices such as biological systems [19,20], food and nutrition [21-23], polymers [24-26] and through theoretical approaches such as density functional models [27]. However, information from this literature cannot be directly extended to correlate the antioxidant activity in lubricants, especially in bulk oil oxidation conditions such as those encountered in IP 48 test conditions. Comparison of few additives in different oxidation conditions was reported earlier [28]. In the current study, the oxidation inhibition performance of nine *p*-substituted 2,6-di-*tert*-butyl phenol antioxidants has been investigated. These antioxidants were blended in Group-II base oil and the blended oils (lubricants) were subjected to bulk oil oxidation conditions as per IP-48 test conditions. The oxidation products were evaluated based on the increase in kinematic viscosity, total acid number and FT-IR analysis (area of carbonyl absorption peak) for the relative performance of the antioxidants.

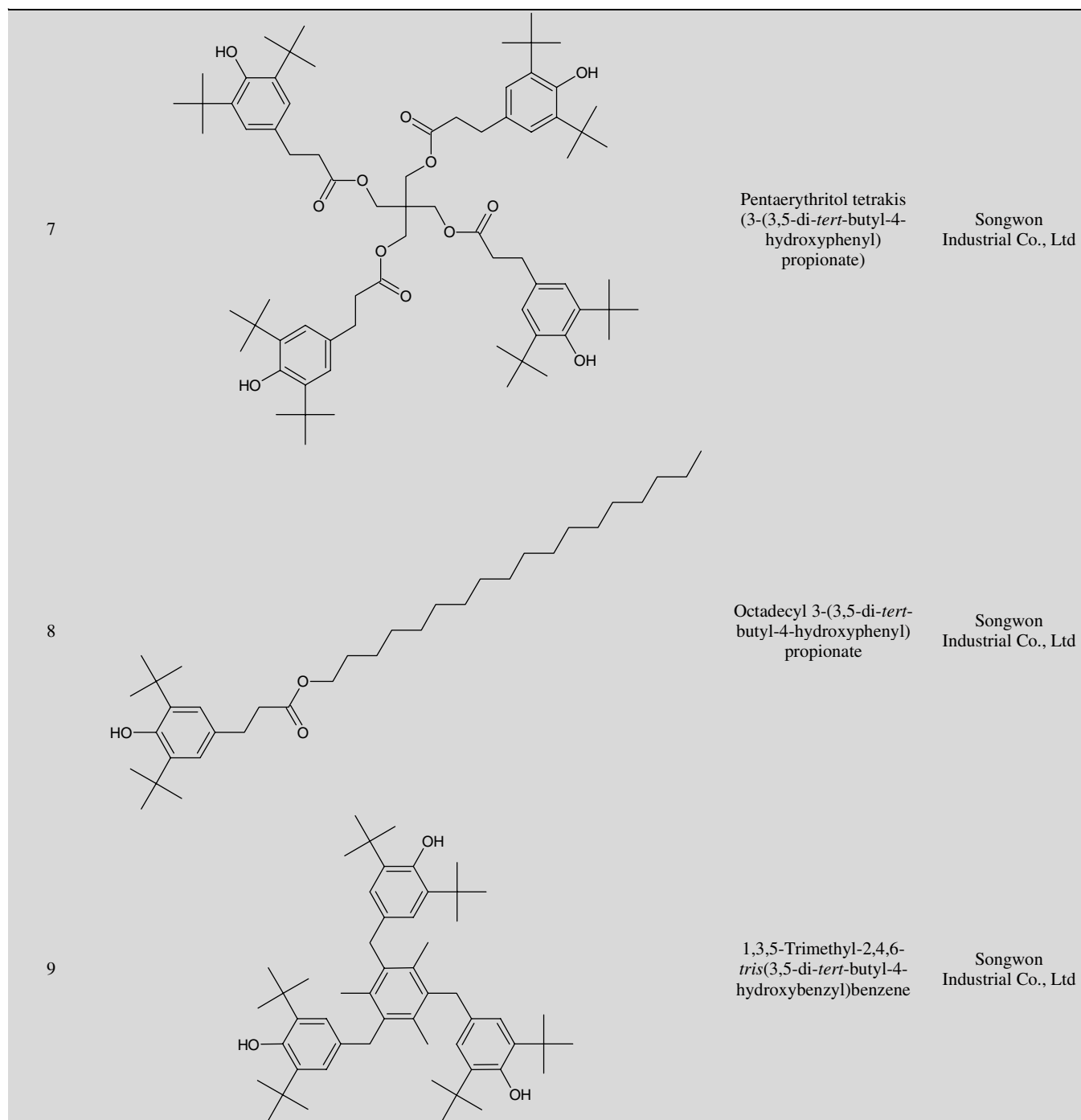
EXPERIMENTAL

Nine different commercially available sterically hindered phenols with different *para* substitution in 2,6-di-*tert*-butyl phenol were selected for this study. The details of these additives are given in Table-1. Commercially available ISO VG-32 viscosity grade API Group-II base oil was selected for making lubricant blends. All the laboratory chemicals such as isopropyl alcohol, toluene, potassium hydroxide, hydrochloric acid, *etc.*, used was of Analytical Reagent (AR) grade supplied by Merck Life Science (India). Ultrapure water generated from Milli-Q water generation system of Millipore Corporation was used for the preparation of reagents and solvent mixtures.

Sample preparation: Lubricant formulations were made by blending individual antioxidant additive at 0.5 % w/w treat rate in API Group-II base oil. Weighed additive sample (2.5 ± 0.01 g) by a direct transfer method in a dry, tared 500 mL capacity borosilicate glass beaker. The selected Group-II base oil was

TABLE-1
DETAILS OF ANTIOXIDATIVE PHENOLIC ADDITIVES USED FOR THE STUDY

Additive	Chemical structure	Chemical name	Source
1		2,6-di- <i>tert</i> -butyl-4-methylphenol	Oxiris Chemicals
2		2,6-di- <i>tert</i> -butylphenol	Oxiris Chemicals
3		2,6-di- <i>tert</i> -butyl-4-(dimethylaminomethyl)phenol	Oxiris Chemicals
4		4,4'-methylenebis(2,6-di- <i>tert</i> -butylphenol)	Oxiris Chemicals
5		3,5-bis (1,1-dimethylethyl) -4-hydroxybenzenepropanoic acid thiodi-2,1-ethanediyl ester	BASF India Ltd
6		Octyl-3,5-di- <i>tert</i> -butyl-4-hydroxyhydrocinnamate	BASF India Ltd



added to the same beaker to make the total weight of contents to 500 g. The beaker was then placed on laboratory hot plate. The mixture was homogenized with laboratory stirrer. The speed of stirrer was adjusted to 500 rpm during stirring. Heating was started and energy controlled to heat the blend up to 60 °C. The stirring continued for another 30 min for homogenization of the blend. The lubricant blends were then allowed to cool to room temperature and then transferred to screw cap glass bottles and stored until further analysis.

Oxidation experiment: IP 48 Oxidation test bath of Petro-test Make (BAM oil bath) was used for conducting the test. The unit has an air compressor and flow-meters to generate and supply the dry air flow at a controlled flow rate. Schematic of IP-48 oxidation test setup is shown in Fig. 1.

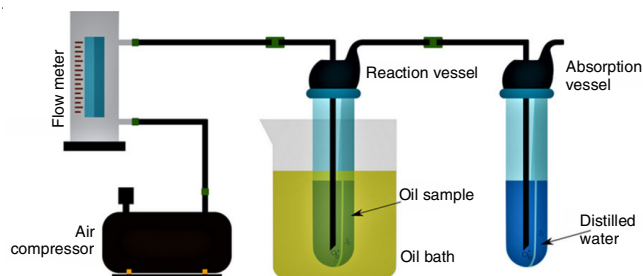


Fig. 1. Structural set up of IP 48 test

Oxidation test vessels (reaction vessels) were cleaned thoroughly and dried before use. Oil sample (40 mL) then charged in the reaction vessel. The reaction vessel with the sample then

charged in an oil bath maintained at 200 ± 0.5 °C. Supply of dry air with a flow rate 15 ± 0.25 L/h is then connected from a compressor specially designed for this test. The test conditions were maintained for $6 \text{ h} \pm 10$ min. After 6 h, reaction vessels removed from the bath and allowed to cool to ambient temperature for 12 h. The test was repeated again for second cycle of 6 h cycle. The reaction vessels removed from the bath at the end of cycle from bath and allowed to cool to room temperature.

Oil sample analysis: The oxidized oil was then tested for oxidative degradation using test parameters like a change in kinematic viscosity, total acid number (TAN), measurement of oxidation products by FT-IR analysis.

Kinematic viscosity: Kinematic viscosity measurements were performed according to ASTM D 445 method [29] using Herzog make automatic viscometer (Model Multi-Range Viscometer HVM 472). The Kinematic viscosity measurement was done at 40 °C. The kinematic viscosity of fresh oil (V_0) and oxidized oil (V) was reported in centistoke (cSt).

Total acid number (TAN): Total acid number of oxidized oil gives the idea of the concentration of acidic compounds in the oil. Total acid number of oxidized oil was analyzed using the ASTM D 664 method [30]. The oil sample was dissolved in the titration solvent prepared from toluene and isopropanol with a bit of water and titrated that solution with standard 0.1N alcoholic KOH. A glass electrode and reference electrode inserted in the solution and connected to a voltmeter/potentiometer. The titration end-point is reached when a clear inflexion point is found. The TAN value was then calculated from the end-point, normality of KOH solution and the weight of sample taken for titration. The TAN value was reported as mg of KOH required per g of the sample.

FT-IR analysis of oxidation products: Degradation of lubricants and additive depletion is generally measured in lubricating oil condition monitoring practice. FT-IR is one of the important tools used for such measurements. In the current study, Perkin Elmer's FT-IR Spectrophotometer (Model- Spectrum 100) was used with Zn-Se liquid sample cell of 0.1 mm path-length. The cell was cleaned using toluene followed by hexane and dried with dry nitrogen purging. The cell path-length was verified by fringe pattern measurement. The background spectrum of cleaned and dried cell was measured in the range of 4000 to 550 cm^{-1} . The oil sample was introduced into the sample cell manually through plastic syringe and. The transmittance spectrum of the oil sample was acquired in the range of 4000 to 550 cm^{-1} with sufficient signal to noise ratio.

RESULTS AND DISCUSSION

The change in kinematic viscosity calculated as the ratio of values of V to V_0 . The test results are shown in Table-2. Similarly, the total acid number values of the lubricating oil blends are given in Table-2.

FT-IR analysis of oxidation products: The FT-IR of all the samples was measured in a Zn-Se liquid cell of 0.1 mm path-length. The transmission spectrum of the base oil is shown in Fig. 2. Base oil FT-IR spectrum shows a typical absorption signals of hydrocarbon. Methylene group $\nu_{\text{asym}}(\text{CH}_2)$ signals were observed at 2909 cm^{-1} and $\nu_{\text{sym}}(\text{CH}_2)$ at 2850 cm^{-1} . These

TABLE-2
CHANGE IN VISCOSITY AND TAN VALUE OF
LUBRICANT BLENDS ON OXIDATION

Blend No.	Kinematic viscosity at 40 °C, cSt		Change in viscosity V/V_0	TAN (mg KOH/g)
	Sample before oxidation, V_0	Sample after oxidation, V		
1	31.857	96.505	3.029	9.85
2	31.708	100.680	3.175	9.91
3	32.008	68.260	2.133	7.29
4	32.313	57.130	1.768	6.75
5	32.338	46.500	1.438	4.06
6	32.183	62.100	1.930	7.19
7	32.252	104.280	3.233	10.97
8	32.120	62.710	1.952	6.20
9	32.400	73.736	2.276	7.90

are strong signals and merged due to signal saturation, as neat base oil IR scanning was done in 0.1 mm pathlength cell. Methyl group asymmetrical bending vibrations $\delta_{\text{asym}}(\text{CH}_3)$ absorbs at 1454 cm^{-1} , whereas symmetrical bending vibrations $\delta_{\text{sym}}(\text{CH}_3)$ absorbs at 1376 cm^{-1} . A strong absorption signal at 722 cm^{-1} is observed due to a methylene group in-plane rocking vibrations $\rho(\text{CH}_2)$. Relatively weak methylene twisting and wagging vibration absorption signals appear at 1304 and 1155 cm^{-1} , respectively [31].

The transmission spectra of lubricant blends (1-9) are shown in Figs. 3 and 4. All the additives show a typical sharp signal due to non-hydrogen bonded free O-H stretching vibration at 3650 cm^{-1} in the phenolic OH group. Additives 5 to 8 have a carboxylic acid ester functional group in their structure and typical carbonyl functional group $\text{C}=\text{O}$ of aliphatic ester is observed at 1744 cm^{-1} in these additives.

The transmission spectra of oxidized oils along with Group-II base oil are shown in Fig. 5. The oxidized lubricant shows a strong O-H stretching absorption band in the region of $3600\text{--}3230 \text{ cm}^{-1}$. The band is broadened due to hydrogen bonding. The $\text{C}=\text{O}$ stretching band of free acid at higher wave number at 1760 cm^{-1} is generally observed, however, intermolecular hydrogen bonding of carboxylic acid, $\text{C}=\text{O}$ absorption weakens and hence it gets shifted to lower wavenumbers at $\sim 1720 \text{ cm}^{-1}$.

ASTM E 2412 [32] provides test protocol for direct trending as well as by spectral subtraction. Direct trending by this method suggests oxidation product concentration by measuring area between 1800 and 1670 cm^{-1} . Area of peaks in this region measures the concentration of all the carbonyl compounds and can be related to the concentration of oxidation products in the oil. In general, the peak in this range is broad due to the presence of various carbonyl-containing degradation products such as lactones, esters, aldehydes, ketones, carboxylic acids in the oil. Area calculation in the wavenumber window of 1800 to 1670 cm^{-1} may lead to error and hence area of carbonyl peak about 1720 cm^{-1} was calculated to the base, which indicates the total concentration of carbonyl compounds in the oxidized oil. The area of peak-related carbonyl substances in oxidized oil is given in Table-3.

Phenolic antioxidants act by converting alkylperoxy radicals into alkyl hydroperoxide. The sulfur-containing antioxidants

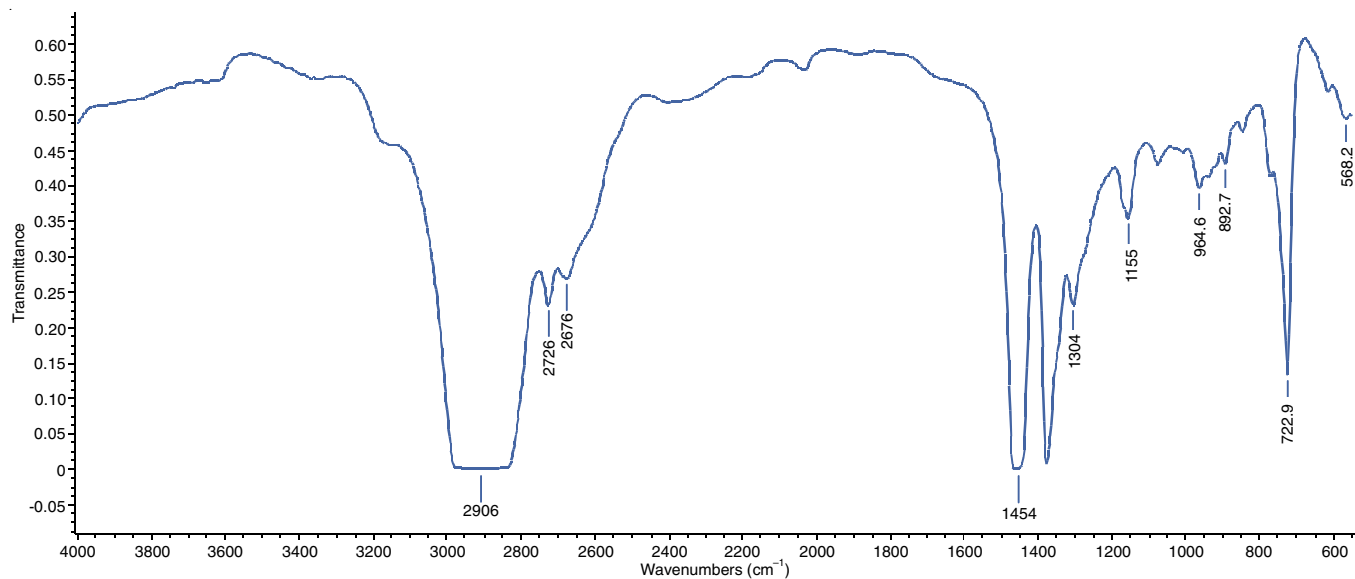


Fig. 2. Fourier transform infrared spectrum of Group II base oil

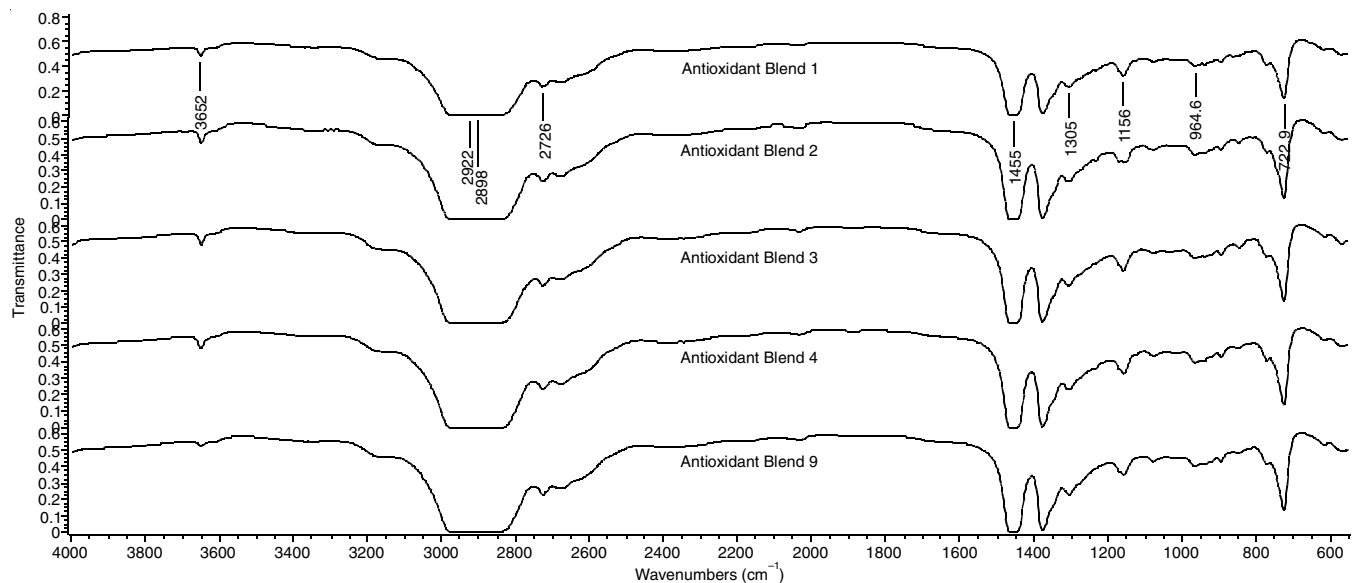


Fig. 3. Fourier transform infrared spectrum of lubricant blends 1 to 4 and 9

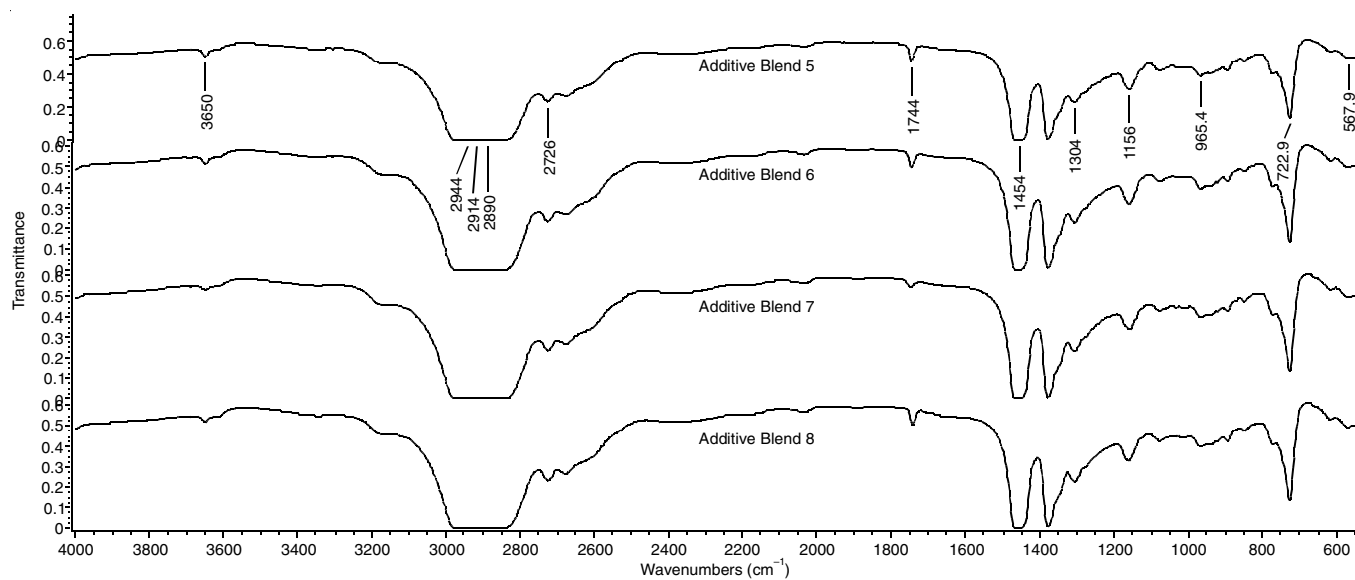


Fig. 4. Fourier transform infrared spectrum of lubricant blends 5 to 8

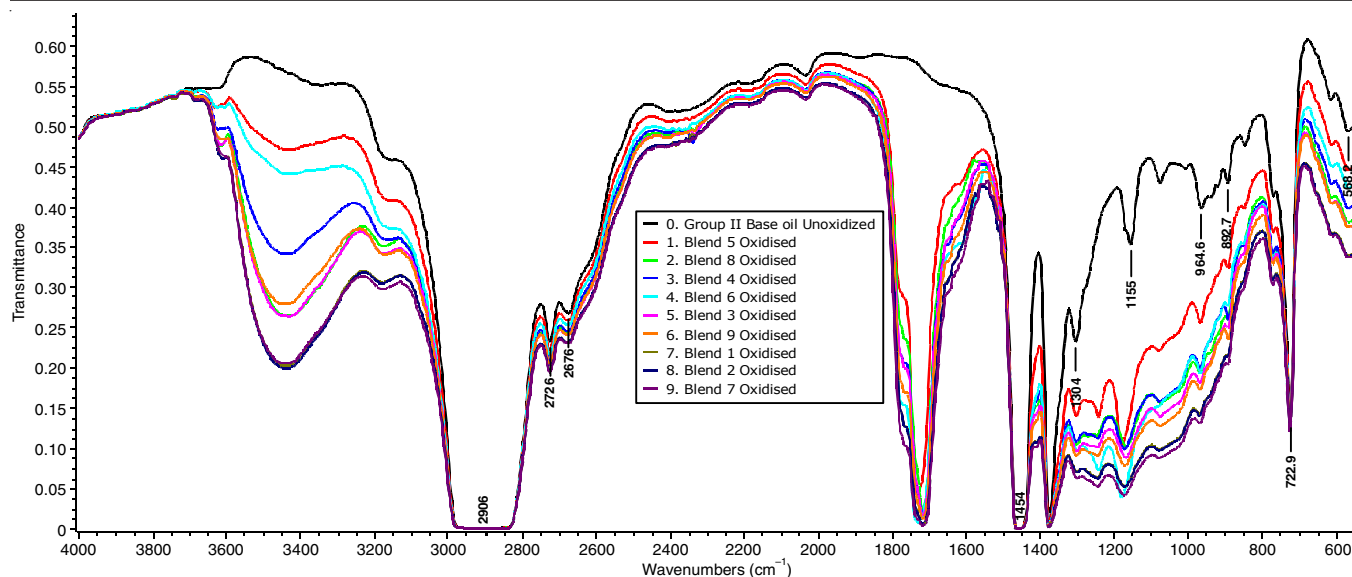


Fig. 5. Fourier transform infrared spectra of oxidized oils

TABLE-3
TEST RESULTS SHOWING FTIR PEAK AREA AT 1720 cm^{-1} RECORDED FOR DIFFERENT OXIDIZED LUBRICATING OILS

Blend No.	1	2	3	4	5	6	7	8	9
Area of peak	9416	9433	8398	8331	7036	9553	10237	7497	8903

prevent the initiation of autoxidation chains by removing hydroperoxide [33]. In an IP 48 test, oil is continuously getting exposed to dry air at relatively high temperature. Oxidation of oil leads to the formation of carbonyl compounds and the volatile degradation products get swept away with air flow. Measurement of acid value, kinematic viscosity change and area at 1720 cm^{-1} of oxidized oil indicates the degree of oxidation and. The acidity measured by potentiometric titration suggests the concentration of carboxylic acids, kinematic viscosity change suggests the degree of polymerization reactions in the later stage of oxidation. Area of the peak at 1720 cm^{-1} measurement is an indicator of carbonyl compound concentration.

Consolidated test data on the determination of acidity, kinematic viscosity change and concentration of oxidation products are summarized in Fig. 6.

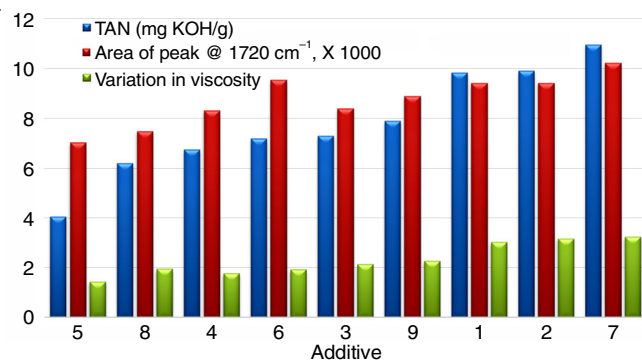


Fig. 6. Oxidative evaluation IP 48 test data

In antioxidant additives studied, the area of the peak at 1720 cm^{-1} and viscosity variation doesn't follow the same trend. It is found that lower the total acid number value, lower carboxylate peak and a lesser increase in kinematic viscosity indicates better oxidation inhibition activity.

It is also observed that peak area at 1720 cm^{-1} by FTIR compliments with total acid number value except for additive 6. This additive shows less total acid number value than additive 3, 9, 1 and 2 but more significant in the carbonyl absorption region of 1720 cm^{-1} . This additive has a lower area in the hydroxyl O-H stretching region of 3500 cm^{-1} , which indicates that oxidation products have more non-carboxylic products with C=O functional group's products than carboxylic acids and hence less acid value.

Additives 1 and 2 also have very less oxidation inhibition potential in the group of selected additives, however their performance is better than additive 7 in test conditions. Additive 1 has better performance as compared to additive 2 due to ease of hydrogen abstraction from phenolic hydrogen because of the electron donating methyl group in the *para*-position.

Additive 3 have electron donating amino methyl functional group in the *para*-position to a phenolic hydroxy group, which eases hydrogen atom abstraction from OH group. The performance is comparable to alkyl ester functional group in the *para* position as that in additive 6 and 8.

Additive 4 shows good inhibition potential due to better hydrogen abstraction potential and stabilization of phenoxy radical through benzene structure while additive 5 shows best overall performance in the selected additives. This performance attributes to the presence of thioether functional group in addition to the hindered phenolic functional group. It performs the dual function and reduces the polymerization chances by eliminating hydroperoxide. Hydroperoxide decomposers work as secondary antioxidants by decomposition of hydroperoxide intermediate [34], which results in the low acidic compound generation and less thickening of oil.

Additive 6 and 8 are 3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamate esters with the difference in aliphatic alcohol carbon chain length. Additive 8 has octadecyl carbon chain whereas

additive 6 have octyl carbon chain to ester functional group. Thus, additive 8 favours less acidity and area at 1720 cm⁻¹ but has higher viscosity increase as compared to additive 6. The overall performance of additive 8 is better as compared to additive 6. Thus, a longer carbon chain of alkyl group improves the performance of 3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamate ester in bulk oxidation conditions of oil.

Additive 7 shows the lowest oxidation inhibition potential in the test condition in a selected group of additives. The rate determining step of oxidation inhibition reaction depends on the ease of hydrogen abstraction from the phenol group, however transition step involves the two peroxy radicals. The second peroxy radical is trapped by addition at *para*-position through cyclohexadienone structure by charge transfer mechanism [35,36]. The structural features of additive 5 prevent this addition at *para*-position of hydroxy, which results in reduced inhibition potential of additive in bulk oxidation conditions.

Additive 9 shows better inhibition potential as compared to additive 1, 2 and 7, however, inferior performance as compared to additives with electron donating functional groups in the *para*-position, such as additives 5, 8, 4, 6 and 3.

Conclusion

The change in inhibition potential of antioxidants was observed due to the *para* substitution of 2,6-di-*tert*-butyl phenol with the different functional groups. The excellent oxidative protection of the lubricating oil was observed due to the presence of thioether linkage in *para* substitution of 2,6-di-*tert*-butyl phenol. The peroxide decomposing activity coupled with radical trapping was responsible for the best oxidative protection. It is expected that the present experimental data will be a useful to identify the appropriate oxidative inhibitor for the oils. However, further work on mechanistic studies of these antioxidants will be more helpful.

ACKNOWLEDGEMENTS

The authors are thankful to the authorities of Shri Jagdish Prasad Jhabarmal Tibrewala University, Jhunjhunu, India, N.M. Institute of Science, Bhavan's College, Mumbai, India and the Management of Bharat Petroleum Corporation Ltd. for granting permission to publish this work.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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