

STUDY OF ANTIOXIDANT ACTIVITY OF HINDERED PHENOLS IN BULK OIL AND THIN FILM OXIDATION CONDITIONS IN LUBRICANTS

K.T. Sutar^{1,*} and P.U. Singare²

¹ Department of Chemistry, Shri Jagdish Prasad Jhabarmal Tibrewala University, Vidyanagari, Jhunjhunu -333 001, (Rajasthan), India

² Department of Chemistry, Bhavan's College, Munshi Nagar, Andheri West, Mumbai-400058, (Maharashtra), India

*E-mail: sutar.kashinath@gmail.com, pravinsingare@gmail.com

ABSTRACT

Antioxidant activity of three substituted hindered phenolic antioxidants is studied in bulk oil oxidation and thin film oxidation conditions. Test conditions of The Institute of Petroleum test method IP-48 are used for evaluation of inhibition activity of antioxidants in bulk oil oxidation regime and Pressure Differential Scanning Calorimetry (PDSC) is used for thin film oxidation regime. Para position of phenolic antioxidant has a substitution of alkyl, ester and thioether linkage in these selected antioxidants. Antioxidant activity of thioether substitution is found better than ester and alkyl substitution. Ester substitution in para position has better inhibition activity than alkyl substitution. Relative Inhibition activity of selected antioxidants is similar in both bulk oil oxidation process (which is slower oxidation reaction) and in thin film oxidation (which is relatively faster oxidation reaction.)

Keywords: Antioxidants, base oils, hindered phenolics, bulk oil oxidation, thin film oxidation, IP-48, differential scanning calorimetry.

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INTRODUCTION

Oxidation is one of the main causes of deterioration of lubricant and decline in its service life. It is the prime reason for many lubricant problems such as deposit formation, thickening of oil, rust and corrosion, etc^{1, 2}. Therefore, oxidation inhibition is essential for lubricant to do its role for sufficiently long life. Various antioxidants are being extensively used in various lubricant formulations either alone or in synergies with other antioxidants.

Oxidative degradation of lubricants- in automotive engines- occurs in two main reactions- bulk oil oxidation and thin-film oxidation. Bulk oil oxidation generally takes place at a slower rate in a large oil body, such as in crankcase sump. Bulk oil oxidation results in an increase in the acid value of the oil, thickening of oil and eventually the formation of oil-insoluble polymers. The polymers may combine with other impurities (metals, ash, water, partially burnt fuel, etc.), with the mixture dropping out of the oil collectively as sludge. Thin-film oxidation is the faster reaction in which small quantity of oil is exposed to quite high temperatures and air (oxygen). Under such conditions, hydrocarbons of lubricants rapidly decompose to form polar oil oxidation products. These products built up rapid on the metal surface, leading to the formation of varnish. Thin film oxidation occurs on the cylinder liner.³

The oxidation of hydrocarbon is a free radical process and involves initiation, propagation, branching and termination as four major stages⁴. The oxidation process in the liquid phase can be catalyzed by metals or inhibited by various mechanisms. Due to thermal energy, homolytic decomposition of hydrocarbon forms alkyl radicals. These radicals react with oxygen to form peroxy radicals. Hydrogen-donating antioxidants (AH), such as hindered phenols compete with the organic substrate (RH) for peroxy radicals. This reduces the rate of propagation reaction and thus inhibits the oxidation process. Hindering the phenolic hydroxyl group with at least one bulky alkyl group in the ortho position appears necessary for high antioxidant activity. Steric hindrance decreases the ability of a phenoxyl radical to abstract a hydrogen atom from the substrate and thus reduces the formation of an alkyl radical capable of initiating oxidation⁵.

Field performance evaluation of formulated lubricating oil consumes a lot of resources and time. Before actual field evaluation of new oil in the fleet, it is essential to conduct a thorough investigation of the performance through laboratory tests. IP-48⁶ is one of the best suitable bulk oil oxidation tests whereas a thermal analysis technique such as PDSC⁷ is a quick and most suitable thin film oxidation test. DSC, TGA (Thermogravimetric Analysis) has been used widely by various researchers for evaluation of various antioxidants and mineral as well as biobased lubricant base stocks⁸⁻¹¹.

Pressure Differential scanning calorimeter (PDSC) is one of the important tools used to assess the oxidative stability of oil in thin film oxidation regime, by measuring Oxidation Induction Time (OIT), which is the time at which oxidation of material starts and is signalled by an abrupt exotherm. ASTM has developed a test method for measurement of OIT of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC). In PDSC, the pressure in the cell minimizes evaporation loss effects.

In this study, we have selected three hindered phenolic antioxidants, first with simple molecular structure, second with the substitution of electron donating functional group chain and the third one with thioether linkage in para substitution. These additives are blended with API Group II base oil. These blends are tested with IP 48 and PDSC to study the influence of substitution and molecular structure of antioxidant additives on oxidative stability of lubricant blends.

EXPERIMENTAL

Materials

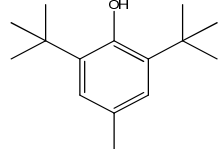
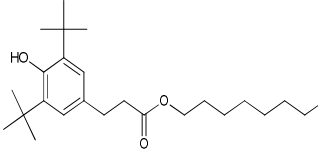
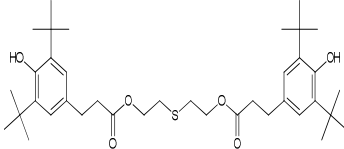
API Group II base oil was selected for this study as the majority of engine oils being blended with this type of base oil. The physicochemical test data of these base oils is given in Table-1.

Table-1: Physicochemical Data of Base Oil Selected for Study

Property	Method	Test results
Kinematic Viscosity @ 40°C	ASTM D445	32.016 cSt
Kinematic Viscosity @ 100°C	ASTM D445	5.6859 cSt
Viscosity Index	ASTM D2270	122
Sulphur Content	ASTM D5453	<0.01%
Nitrogen Content	ASTM D5762	<0.01%
Aromatic content	IS 13155	0.1%

Three different hindered phenolic antioxidants with different substitutions at the para position are selected for this study. Their chemical & structural formulae and physical properties are given in Table-2.

Table-2: Details of Hindered Phenolics Selected for Study

	AO-I	AO-II	AO-III
Chemical Name	2,6-bis(1,1-dimethylethyl)-4-methylphenol	Octyl-3,5-di-tert-butyl-4-hydroxy-hydrocinnamate	3,5-bis(1,1-dimethyl)-4-hydroxybenzenepropionic acid thiodi-2,1-ethanediyl ester
CAS No.	128-37-0	125643-61-0	41484-35-9
Structural formula			
Mol. Formula	C ₁₅ H ₂₄ O	C ₂₅ H ₄₂ O ₃	C ₃₈ H ₅₈ O ₆ S
Appearance	White crystalline solid	Colorless liquid	White powder
Melting Point	69-73°C	<10°C	78°C

Sample Preparation

Three different lubricant blends were prepared with base oil and antioxidant. 0.5 mass/% of antioxidant was dissolved in base oil by mechanical stirring at 600 rpm while heating at 60°C on a hot plate for 30

minutes. Samples were allowed to cool down to room temperature and stored in amber colored bottles to avoid any photochemical degradation. The blend composition matrix is given in Table-3.

Table-3: Blend Composition Matrix

	Blend -1	Blend -2	Blend -3
AO-I	0.5%	--	--
AO-II	--	0.5%	--
AO-III	--	--	0.5%
Base Oil	99.5%	99.5%	99.5%

IP 48 Oxidation

Oxidation test vessels were first cleaned by soaking in concentrated sulphuric acid for overnight and then washing with tap water and distilled water repeatedly. It was then dried in 100°C Glassware oven for at least three hours and then allowed to cool to room temperature before use. Empty test vessel with ground glass head was then weighed to nearest 0.1 gm weight. Approx. 40 ml oil sample then charged and then weighed the test vessel with the sample to nearest 0.1 gm. The vessel with the sample then charged in an oil bath maintained at 200 ± 0.5 °C. Air supply with a flow rate 15 ± 0.25 l/h is then connected from a compressor. Adjusted the air flow, once oil reaches the test temperature and then maintained the test conditions for $6h \pm 10$ minutes. Removed the oxidation tube from the bath and allowed to cool and stand at room temperature for 12 h. repeated the heating procedure after 12 hr. with air flow. After second 6 hr. cycle removed the oxidation tubes from bath and then cooled to room temperature. The oxidized oil is then tested for oxidative degradation.

The oxidation tubes are then weighed to nearest 0.1g to calculate the evaporation loss during oxidation. The oxidized oil was then subjected to following tests:

1. Change in Kinematic viscosity
2. Change in acid number
3. Carbon residue measurement
4. Measurement of oxidation products by FT-IR.

Kinematic Viscosity

Kinematic Viscosity at 40°C was measured with the Herzog Multi-Range Viscometer (HVM 472) which is fully automated equipment to measure the direct kinematic viscosity of transparent and opaque liquids using capillary viscometer. A test was conducted in accordance with ASTM D445¹².

Acid Number

The total acid number (TAN) of un-oxidized oil and oil oxidized in the IP-48 test was analyzed using the test procedure as per ASTM D 664¹³. The working procedure determines the sum of all acid compounds present in oil samples by an acid-base titration using standardized KOH as titrant. TAN is expressed in mg of KOH required per gm of the sample. Since samples are the non-aqueous type, they are diluted in a mix of toluene and isopropyl alcohol. The solvent for KOH is isopropyl alcohol.

Before titration of the sample, blank titration with 75 ml of solvent is measured. For TAN of the sample, weigh approximately 1 g of oil to nearest 0.1 mg in a 100-mL beaker and add 75 mL of solvent.

Carbon Residue Measurement

Micro Carbon Residue (commonly known as "MCR") is a laboratory test used to determine the amount of carbonaceous residue formed after evaporation and pyrolysis of oils under certain test conditions. The test suggests the oils coke-forming tendencies.

Tanaka's ACR-M3 automatic Micro Carbon Residue Tester was used for this analysis. Tests were conducted in accordance with ASTM D 4530¹⁴. About 1 gm sample is weighed accurately to 0.1 mg in a glass vial of 2ml capacity. Vials such weighed are then placed in vial holder, which is having the capacity to hold twelve

such vials. Holder with vials is placed in an MCR instrument oven chamber at room temperature and covered with a lid. The chamber is then purged with Zero Grade Nitrogen at 600 ml/min flow rate for 10 minutes. The Nitrogen flow rate then decreased to 150 ml/min oven heating started at a rate of 10° to 15°C/min up to 500°C. Oven maintained at 500±2°C for 15 minutes. Furnace power then shuts off and allowed to cool freely to room temperature under nitrogen flow rate at 600 ml/min. The vials are then weighed to nearest 0.1 mg and carbon residue percentage is calculated.

Measurement of Oxidation Products by FT-IR.

To estimate the degree of oxidation, and to estimate the remaining useful life of the lubricants, the FTIR test method has been developed by the Joint Oil Analysis Program (JOAP) and approved by ASTM as ASTM Practice E 2412-04 for lubricant condition monitoring by trending¹⁵. The ASTM method was revised as E2412-10¹⁶.

In the current study, Perkin Elmer's FT-IR Spectrum 100 is used with Zn-Se liquid sample cell of 0.1 mm path length and DTGS detector (inbuilt). The infrared transmittance spectrum of the oil sample is acquired in the range of 4000 to 550cm⁻¹ with sufficient signal to noise ratio, in Zn-Se cell.

DSC Model Q2000 from TA Instruments with Tzero PDSC cell was used for the studies. Aluminium and copper sample pans from TA instruments were used in the current study. High pressure in PDSC prevents the evaporation loss of lubricants and saturates the test sample with oxygen. This result in the speeding up of oxidation, as well as sharpening of the exotherm, as compared to normal DSC. PDSC experiments are conducted in an isothermal mode to measure oxidation induction time (OIT).

Isothermal PDSC was performed on 3 ± 0.2 mg of oil sample in open aluminium pan under pressure of 3500 kpa of high purity oxygen. Oxygen flow through the cell was regulated at 100 mL min⁻¹. Oil samples were heated from an ambient temperature of 180°C at the heating rate of 100°C min⁻¹. Once the temperature is stabilized at 180°C, pressurization of PDSC cell with oxygen, pressure, oxygen flow and temperature were adjustments were done within 2 minute time¹⁷. PDSC held at the isothermal mode until an exothermic peak of oxidation onset is detected. OIT of the sample was calculated by extrapolating the tangent drawn on the steepest slope of the corresponding exotherm curve to the baseline¹⁸.

RESULTS AND DISCUSSION

IP 48

Weight Loss Analysis

The weight loss occurs due to formation low molecular weight products and evaporation of these volatile species. Test results of weight loss of Blend 1, 2 and 3 are given in Table-4.

Table-4: IP 48: Weight Loss Analysis

Blend	The weight of Empty Test Cell, gm	The weight of Test Cell + Oil, gm	Sample Weight, gm	Final Weight, gm	Weight Loss, gm	% Weight loss
1	129.430	163.491	34.061	159.971	3.5	10.3
2	150.696	183.148	32.452	180.745	2.40	7.40
3	152.094	188.879	36.785	186.837	2.04	5.55

Change in Kinematic Viscosity (KV)

The Kinematic viscosity of samples before and after oxidation of oil was measured at 40°C in Herzog Multi-Range Viscometer (HVM 472). The ratio of viscosity after oxidation with that of before oxidation is reported as a change in viscosity. The rest results are given in Table-5.

Table-5: IP 48: Change in KV

Blend	Kinematic Viscosity @ 40°C, cSt		Change in Viscosity
	Sample Before Oxidation, V ₀	Sample after oxidation, V	V/V ₀
1	31.857	96.505	3.029

2	32.183	62.100	1.930
3	32.338	46.500	1.438

Change in Acid Number

The TAN values of the oxidized oil samples are given in Table-6.

Table-6: IP 48: Change in acid number

Blend	Sample Weight, gm m_s	KOH Normality, N C_{KOH}	Blank, ml V_{blank}	Endpoint, volume, ml $V_{last EP}$		TAN, mg KOH/gm	
				EP 1	EP 2	EP 1	EP 2
1	0.6608	0.0668	0.0590	1.7964	1.5929	9.85	8.70
2	0.9802	0.0850	0.0530	1.5317	1.3397	7.19	6.26
3	0.8810	0.0850	0.0530	0.8025	0.6974	4.06	3.49

Carbon Residue content

Carbon residue values for oxidized oils of Blend-1, 2 and 3 are given in Table-7.

Table-7: IP 48: Carbon Residue content

Blend	The weight of Empty Vial, gm	The weight of Vial + Oil Sample, gm	Sample Weight, gm	Final Weight, gm	Carbon residue, gm	% Weight Residue
1	2.9062	3.9423	1.0361	2.9125	0.0063	0.6080
2	2.9373	3.9795	1.0422	2.9405	0.0032	0.3070
3	2.9139	3.9424	1.0285	2.9161	0.0022	0.2139

Oxidation Products by FTIR

Oxidized lubricants show strong broad O-H stretching band in the 3230-3600 cm^{-1} region. The C=O stretching band of free acid at higher wave number at 1760 cm^{-1} . In addition to these, samples show characteristic C-O stretching in 1320-1210 cm^{-1} range and, in-plane O-H bending at 1440-1395 cm^{-1} . However, these absorptions are so weak to get detected significantly.

In FTIR Spectra of fresh oil Blend-2 and Blend-3, apart from normal phenolic O-H absorption at 3651 cm^{-1} , the strong absorption band at ~1744 cm^{-1} is observed due to C=O stretching whose force constant is increased due to the electron attracting nature (inductive effect) of adjacent oxygen atom of the C-O bond. C-S stretching vibrations in AO-III is weak and not detectable in the complex matrix, which otherwise could fall between 700-600 cm^{-1} .

ASTM E2412 provides test protocol for direct trending as well as by spectral subtraction. Direct trending suggests oxidation estimation by measuring area between 1800 and 1670 cm^{-1} . This measures the concentration of carbonyl compounds due to carboxylates and can be related to the concentration of oxidation products in the oil.

The test procedure as ASTM E 2412 was followed, however, instead of the area of the peak in the range of 1800 to 1670 cm^{-1} ; transmittance at the peak maximum in this wavenumber range is taken for further analysis. Generally, the peak in this range is broad due to the presence of various carbonyl-containing degradation products of the oil. These could contain lactones, esters, aldehydes, ketones, carboxylic acids. The transmittance of samples at peak maxima of carbonyl compounds (1718 cm^{-1}) was measured and values of optical density calculated to represent the concentration of the oxidation products generated.

The transmittance and optical density data of oil, before and after oxidation, is summarized in Table -8.

Table-8: Transmittance and Optical Density.

Blend	The transmittance of the oil before oxidation, I ₀	The transmittance of the oil after oxidation, I	I ₀ /I	Optical Density, A = Log (I ₀ /I)
1	0.5735	0.0056	102.41	2.01
2	0.5588	0.0078	71.64	1.86
3	0.5567	0.0466	11.95	1.08

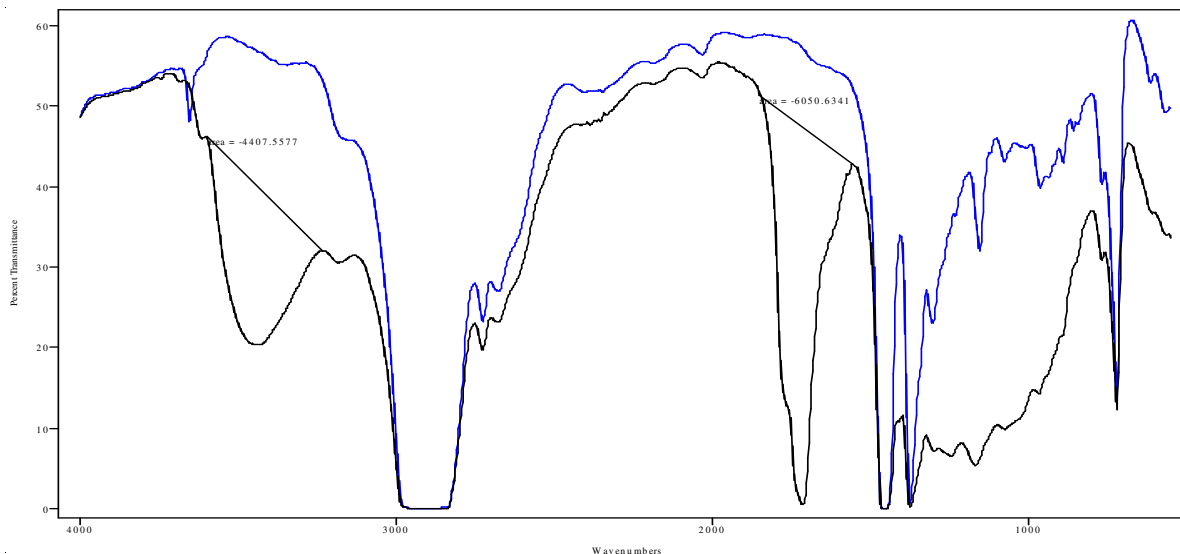


Fig.-1: Un-oxidized and Oxidized Oil Spectra with Blend-1

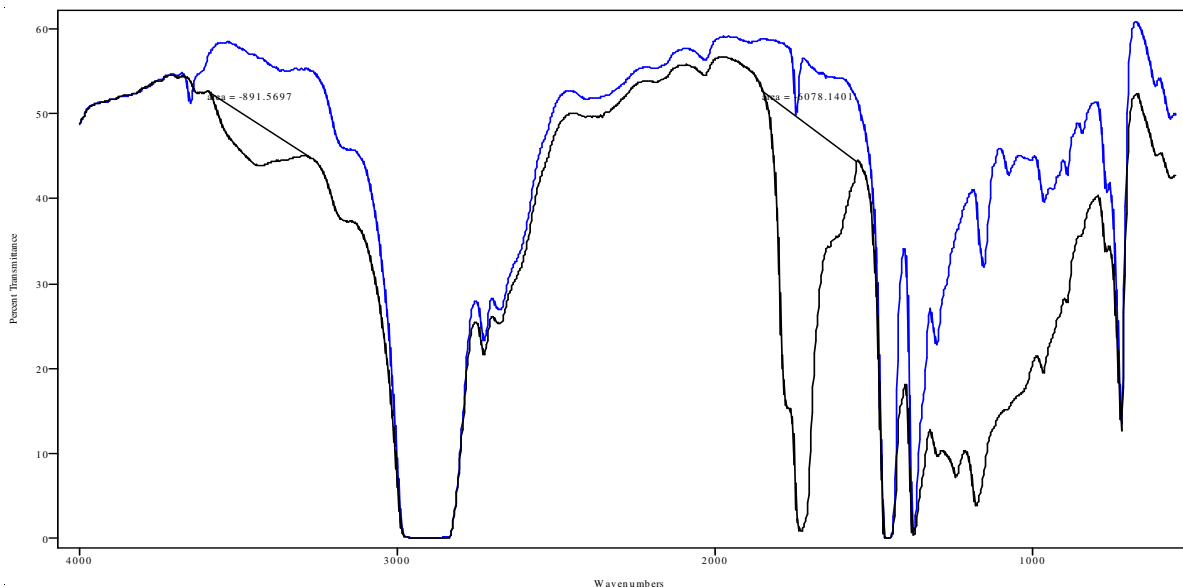


Fig.-2: Un-oxidized and Oxidized Oil Spectra with Blend-2

Comparative summary of IP -48 oxidation test data is given in Table-9.

Table-9: IP 48: Summary of Test results

Blend	% Weight loss	TAN, mg KOH/gm		Variation in Viscosity	Optical Density, A = Log (I ₀ /I)	% Weight Residue
		EP 1	EP 2			

1	10.3	9.85	8.70	3.029	2.01	0.61
2	7.4	7.19	6.26	1.930	1.86	0.31
3	5.6	4.06	3.49	1.438	1.08	0.21

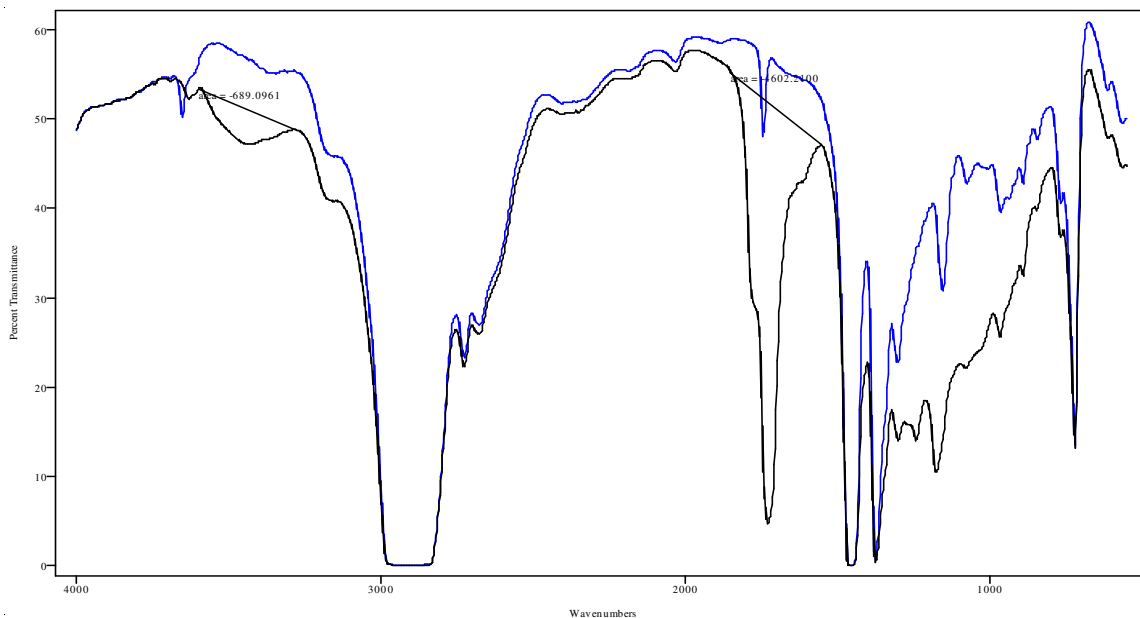


Fig.-3: Un-oxidized and Oxidized Oil Spectra with Blend-3

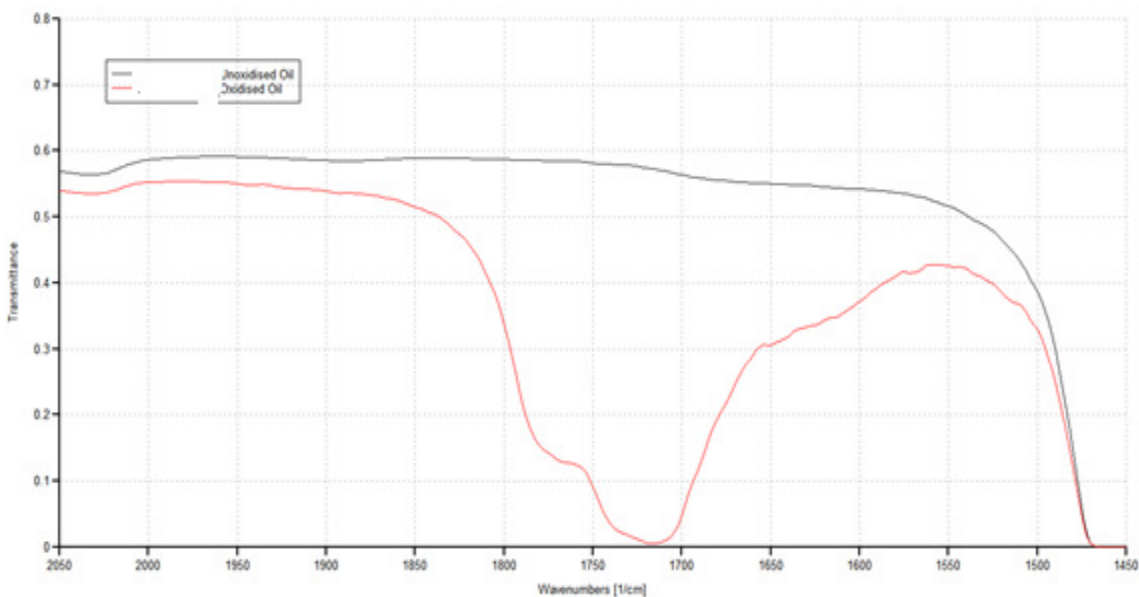


Fig.-4: FTIR Spectrum of Un-oxidized and Oxidized Oil Blend-1

Lower weight loss, lower TAN value, lower variation in viscosity, lower optical density and lower residue percentage denotes the better inhibition capacity of antioxidant.

The Antioxidant Activity by Isothermal PDSC.

The plot of Heat Flow (W/g) against runtime (minutes) for three Antioxidant Blends is given in below Fig.- 7 to 9.

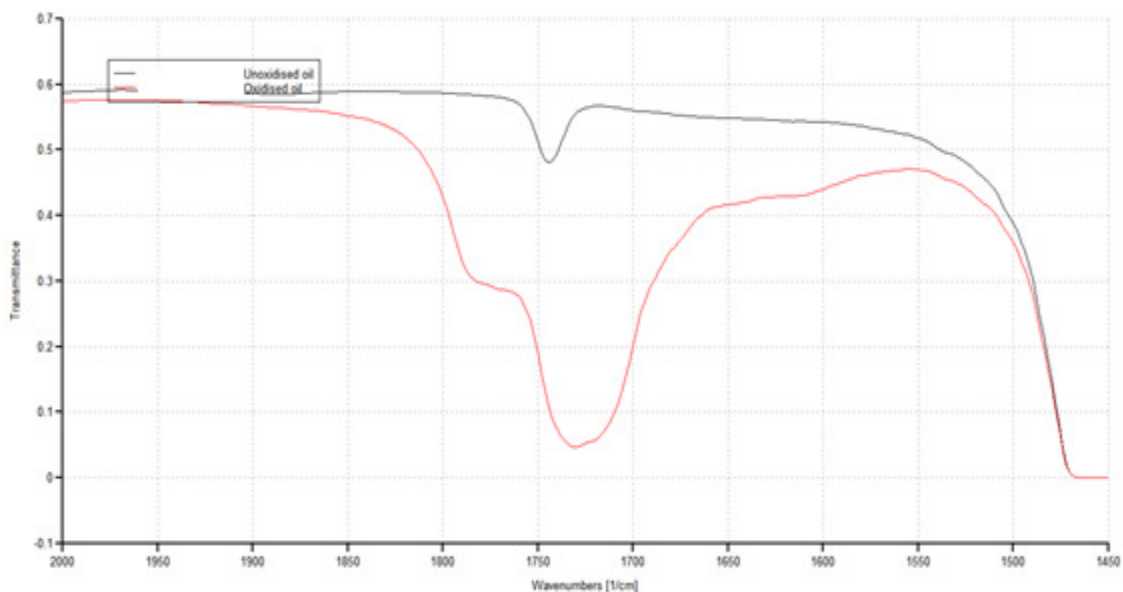


Fig.-5: FTIR spectrum of un-oxidized and oxidized oil Blend-2

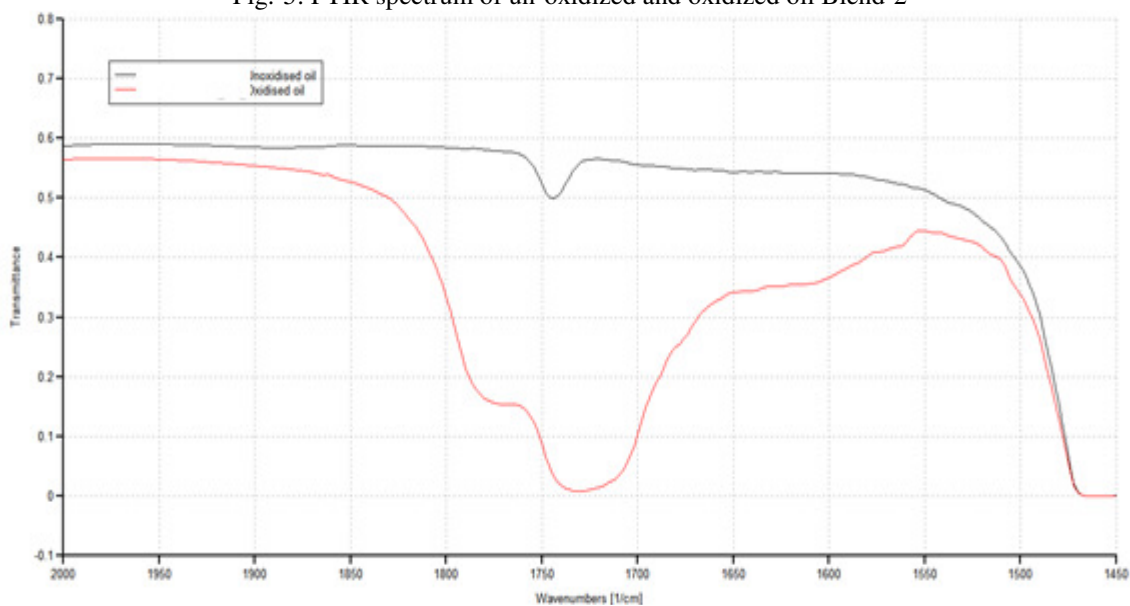


Fig.-6: FTIR spectrum of un-oxidized and oxidized oil Blend-3

The OIT values obtained by Isothermal PDSC for Blend 1-3 are given below:

	Blend-1	Blend-2	Blend-3
OIT, minutes	19.35	44.00	46.82

Higher the OIT in minutes denotes the longer the oil can withstand oxidation inhibition and longer the useful life.

CONCLUSION

From the test results of IP-48 and PDSC, it is concluded that:

1. The inhibitory activity of antioxidants in bulk oil, as well as thin film oxidation test observed, is AO-III > AO-II > AO-I. The relative activity of the selected antioxidants is similar in both the oxidation regimes.

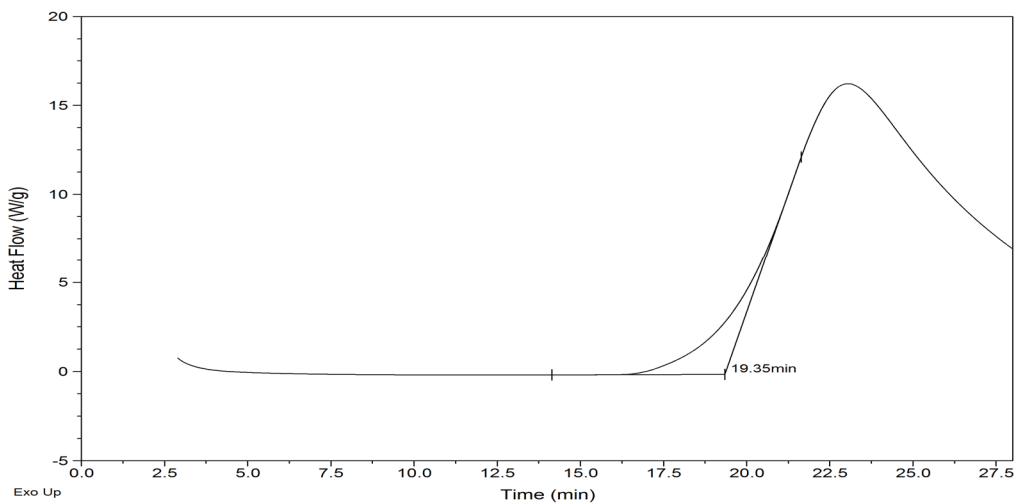


Fig.-7: PDSC Curve for Blend-1 at 180°C

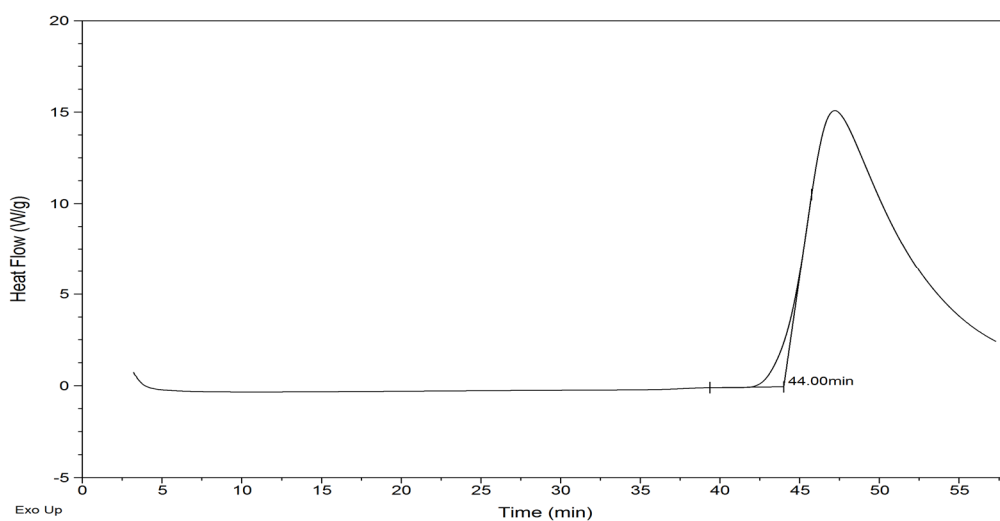


Fig.-8: PDSC Curve for Blend-2 at 180°C

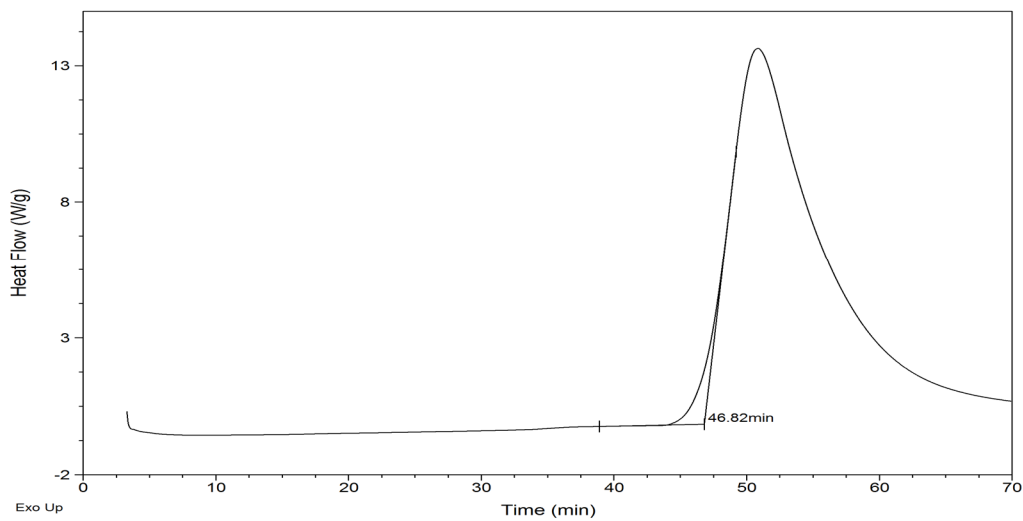


Fig.-9: PDSC Curve for Blend-3 at 180°C

2. Ester functional group in the para position of the phenolic -OH group give better stability of phenoxy radical as compared to the methyl function group. Hence antioxidant activity of AO-II is much better than AO-I in both the oxidation regimes.
3. AO-III antioxidant with thioether linkage is given highest oxidation stability amongst three blends. An ester of thiodipropionic acid is capable of decomposing stoichiometrically more number of hydroperoxide radicals formed in the initiation reaction of oxidation. AO-III is, therefore, exhibiting highest antioxidant activity in the selected AO samples.

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