SYNERGISM FOR THERMAL STABILITY AND OXIDATION INHIBITION, PERFORMANCE ATTRIBUTES IN ENGINE OILS

By

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COLLEGE OF ENGINEERING STUDIES

Submitted

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To

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Dedicated

to

My Parents

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Chapter 1 : Introduction and Literature Review

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DECLARATION CERTIFICATE

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment has been made in the text.

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CERTIFICATE

This is to certify that the thesis entitled **"SYNERGISM FOR THERMAL STABILITY AND OXIDATION INHIBITION, PERFORMANCE ATTRIBUTES IN ENGINE OILS"** submitted by **Mr. Shiv Kumar Vabbina** to University of Petroleum and Energy Studies, Dehradun for the award of the degree of Doctor of Philosophy is a bona fide record of the research work carried out by him under our joint supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

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Shiv Kumar Vabbina

Executive Summary

The need to reduce hazardous environmental impact has initiated the development of techniques and technologies in all industries around the globe. Transport sector is considered to be one of the frequently changing, first and foremost because of the efforts towards reducing hazardous emissions. Presently there are around 700 million vehicles running throughout the world which may touch 2 billion by 2050. Global emission of Carbon dioxide (CO_2) gas is increasing, which is driving all governing bodies around the world to tighten CO_2 emissions limits and therefore, fuel economy goals. Global CO_2 reduction becomes increasingly important. Bharat stage 6 standard (in 2020) will be considered to be a major change for vehicle manufacturers, as it needs 90-95 % reduced limits for regulated pollutants which are far below the limits that prevailed in 1990's. These proposed goals and limits are very hard to achieve for automobile industry and will drive the modifications in various technologies around the globe concerning three of its major areas viz., Engine, Fuel & Lubricant**.**

Development in different areas of engine design (modifying vehicle dynamics, engine weight reduction, downsizing, modification of power-train systems) have turned out to be decisive factors in meeting the ultra low emission requirements of present and future. Newer engines have become more compact and short in size. Vehicle and engine technologies to cope up with higher performance, lower emissions are getting more complex and sophisticated and is making engine more sensitive towards the fuel and lubricants qualities and properties.

The quality of fuels is regularly changing with changes in environmental regulations for emissions. Higher octane gasoline and higher cetane diesel permits the use of engine with higher compression ratios resulting in better fuel economy, cold start ability, lesser noise and lower emissions. Fuel Quality improvements for

decreasing CO_2 emissions have made many fuel producers to bring increased usage of renewable fuels around the world.

Engine technology developments towards downsizing and improvements in power trains have almost reaching to a stagnant level. Fuel quality improvements are also witnessing the same scenario. Use of alternate fuels is likely to see a greater demand in the future. As the fuel quality is improving day by day the engine oil needs to be adjusted to cope up with such improvements. This will obviously create new challenges for the engine oil formulations to be used in newer engines.

Engine oil has reduced residential time for the circulation and lubrication due to sump capacities of engine getting reduced. Engines will run hotter to generate more power; there will be reduced airflow for the cooling of engine parts. This means that stress on engine oil will be increasing manifold in newer engines. The working temperatures of modern engines are touching ~ 350 °C. The engine oil, therefore should be stable at such higher temperature, meaning engine oil used should have less volatility and good inhibition towards oxidation and also have to maintain a good film strength on the engine parts so that lower wear takes place. Engine oil should have optimum viscosity along the temperature profile of engine which means the oil should have high viscosity index and also the oil should be stable towards oxidation. Oxidation is the most significant form of chemical degradation of engine oil and additives present in it.

As emissions limits are getting reduced continuously and nearing to zero, accordingly the specifications for engine oil are changing regularly. Engine oil design factor, therefore, assumes an important role in meeting the environmental emission requirements of newer engines and on the other hand is challenging too.

Majority of the performance properties of the engine oil/lubricant are related to its thermal stability, oxidative stability and its capability to form film strength and to reduce friction between the moving parts. To mitigate these concerns oxidation inhibition and thermal stability of the engine oil along with good surface activity should be the primary focus for formulating an effective crankcase lubricant. Thus additives like antioxidants, friction modifier and viscosity modifier have high importance in developing crankcase lubricant.

This research endeavor aims to study the potential domains related to thermo-oxidative stability of engine oils for addressing the multifarious requirements of designs, operations and regulations of new generation automobile engines, along with studies on reducing friction and wear between engine parts.

In any lubricant, base oil is the major constituent which constitutes about 80-90% of it and has a greater role to play in thermal stability of engine oil, i.e., base oil used for optimizing should be less volatile in nature. To formulate improved lubricants, good quality base oils are pre-requisite. Base oil properties depend on its paraffinic, naphthenic & aromatic content. Physico-chemical data of all the four major base oil groups have been evaluated by different instruments like ^{13}C NMR Spectroscopy, IR Spectroscopy, Mass Spectroscopy, DSC, Selby Noack, etc., to select the best suitable base oil combination in this research base on the literature study and other parameters. Also the base oils compatibility with different antioxidants selected for study is helpful in further selecting the base oil (group III) among the other groups.

Engine oil should form good stable film strength on the moving parts so as to prevent the moving parts from wear and also reduce the friction. Next generation engine designs are developed for low viscosity fluids. Both friction modifiers and reduction in viscosity of engine oils can improve the fuel economy of automobiles. 3 Viscosity modifiers and 2 Friction modifiers have been studied elaborately by optimizing 9 different blends with various combinations of VM & FM with additive package in group III base oil. These blends are then tested for film thickness and frictional properties in EHD and SRV tribometer instruments. These results are correlated with the thermo-oxidative properties of the blends optimized and further selection of best VM/FM combination is done. The selected VM and FM are evaluated by GPC and ^{13}C NMR techniques to get additional information for the research carried which is discussed in the last chapter of the research.

The best VM/FM combination selected with antioxidants selected and additive package is added in group III base oil for developing energy efficient engine oils. 2 phenolic and 4 aminic antioxidants are selected for the purpose and various optimization of engine oils (8 blends) have been prepared. These blends are studied extensively in various laboratory tests of interest mainly for thermo-oxidative stability. TGA, DSC, PDSC, TFOUT are used extensively in the research for screening out few best combinations which have high thermal and oxidative stability as required for modern generation engines. The various parameter evaluated includes weight loss, onset oxidation temperatures, heat capacities and oxidation induction times.

Based on the results obtained 2-3 combinations out of 8 optimized blends are further validated against an industry standard engine oil for performance attributes of the engine oil by simulating real environments of actual operating engines. These performance attributes includes the deposit forming tendency, frictional properties and evaluation in an engine test program. For deposit forming tendency two types of deposits are evaluated in the research, frictional property is evaluated by SRV tribometer and engine test utilized is Sequence IIIE.

Synergism of thermal stability and oxidation inhibition characteristics is explained in the concluding chapter from the results obtained in this study and is correlated against the various laboratory evaluations and chemistry of additives. Also the behavior of antioxidants selected is justified with the mechanism of action. Futuristic approach to the research is also discussed at the last.

List of Symbols

bhp	Break Horse Power
cc	Cubic Centimeter
cst	Centistokes
g/km	Gram per Kilometer
g/l	Gram per Liter
ml/min	Milliliter per Minute
nm	Nanometer
psi	Pounds per Square inch
rpm	Rotations per Minute
w.r.t	With Respect To
w/w	weight by weight
^{o}C	Degree Centigrade
^{o}C/min	Degree Centigrade per Minute
^{o}F	Degree Fahrenheit
Hz	Hertz
J/g.^{o}C	Joules per Gram Degree Centigrade
kg/l	Kilogram per Liter
km	Kilometer
S/N	Sulphur and (or) Nitrogen
W/g	Watt per Gram (Heat Flow)

List of Abbrevations

ACEA	Association des Constructeurs Européens d'Automobiles
	(European Automobile Manufacturers Association)
API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
BEE	Bureau of Energy Efficiency
CAFÉ	Corporate Average Fuel Economy
CO	Carbon Dioxide
CO_2	Carbon Dioxide
CR	Compression Ratio
DI	Direct Injection
DIN	Deutsches Institut für Normung e.V
	German institute for Standardization
DOI	Digital Object Identifier

DPA	Di-Phenyl Amines
DPF	Diesel Particulate Filter
DSC	Differential Scanning Calorimeter
EHD	Elasto Hydro-Dynamic
EGR	Exhaust Gas Recirculation
EIA	Energy Information Administration
ESCA	Electron Spectroscopy for Chemical Analysis
EU	European Union
FAQ	Frequently Asked Questions
FM	Friction Modifiers
FTIR	Fourier Transform Infra Red Spectroscopy
FTM	Federal Test Method
GHG	Green House Gases
H_2S	Hydrogen Sulphide
HC	Hydrocarbons

HCCI	Homogeneous Charge Compression Ignition
HOOT	Hot Oil Oxidation Test
HVI	High Viscosity Index
ILSAC	International Lubricants Standardization and Approval Committee
KV	Kinematic Viscosity
LHRE	Low Heat Rejection Engine
LNT	Lean NOx Traps
MHT	Moderately High Temperature
Mp	weight at peak height in between Mn & Mw
Mn	number average molecular weight
Mw	weight average molecular weight
NEDC	New European Driving Cycle
NMHC	Non-Methane Hydrocarbons
NMR	Nuclear Magnetic Resonance Spectroscopy
NOx	Nitrogen Oxides

OIT	Oxidation Induction Time
OOT	Oxidation Onset Temperature
OEM	Original Engine Manufacturer
PAO	Poly-Alpha Olefins
PCRA	Petroleum Conservation Research Association
PDSC	Pressure Differential Scanning Calorimeter
PM	Particulate Matter
RPVOT	Rotating Pressure Vessel Oxidation Test
SAE	Society of Automotive Engineers
SAPS	Sulphated Ash, Phosphorus and Sulphur
SCR	Selective Catalyst Reduction
SIAM	Society of Indian Automotive Manufacturers
SSI	Shear Stability Index
TEOST	Thermo-oxidation Engine Oil Simulation Test
TFOUT	Thin Film Oxygen Uptake Test

TGA	Thermo-Gravimetric Analyzer
THC	Total Hydrocarbons
TRR	Top Ring Reversal
VCR	Variable Compression Ratio
VGT	Variable Geometry Turbocharger
VHVI	Very High Viscosity Index
VI	Viscosity Index
VVT	Variable Valve Timing
US	United States

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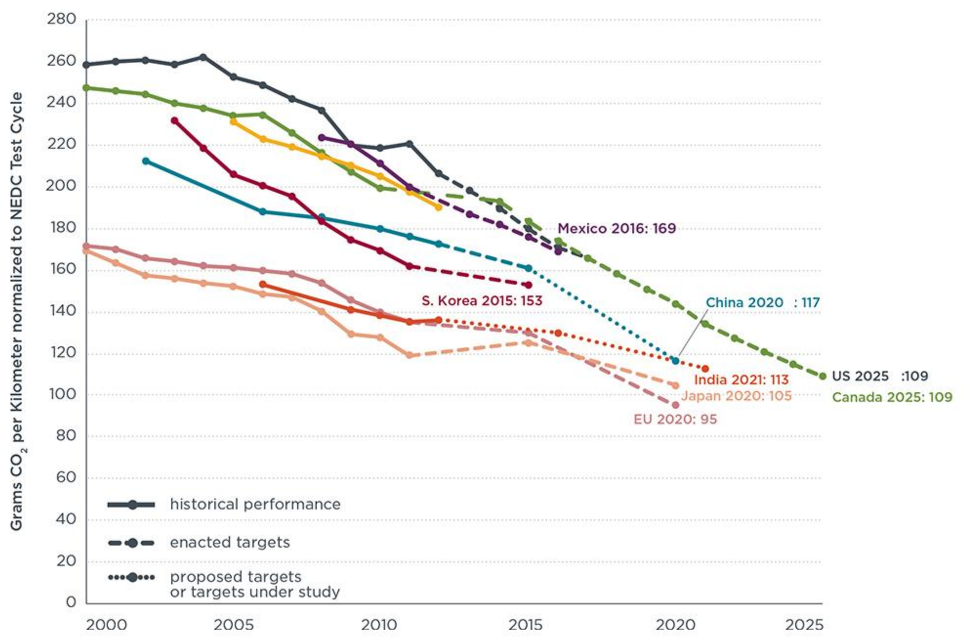
Chapter 1

Introduction and Literature Review

1.0 Introduction

The need to reduce hazardous environmental impact has initiated the development of techniques and technologies in all industries around the globe. Transport sector is considered to be one of the frequently changing, first and foremost because of the efforts towards reducing hazardous emissions. Global emission of Carbon dioxide (CO_2) gas is increasing, which is driving all governing bodies around the world to tighten CO_2 emissions limits and therefore, fuel economy goals. Governing bodies around the world are also reducing the limits of emissions of other harmful pollutants like sulphur, particulate matter and nitrogen oxides (NO_x). Stringent environmental emission regulations are made globally around the world due to global warming.

Presently there are around 700 million vehicles running throughout the world which may touch 2 billion by 2050 [1]. Global CO_2 reduction becomes increasingly important. One can see from the graph at Fig. 1.1 that up to 2005 the reduction in CO_2 was comparatively slow, but to meet the global stringent demands for the future generation the average rate of change over the next decade of years is expected to very fast (steep reduction in graph). Accordingly around the world the CO_2 reduction limits are specified in terms of mileage run of the vehicle. The introduction of these limits translates into an average fuel consumption reduction by 30% in a decade. This is very tough challenge to meet such emission requirements, while delivering improved performance with safety requirements. About 19.64 & 22.38 pounds of green house gas CO_2 is emitted from combustion per gallon of gasoline and diesel respectively [2]. In other words one can say that about 2.35 kg/l and 2.68 kg/l of CO_2 are generated in case of gasoline and diesel respectively.



Source : Carbon Dioxide Emission targets, International Counci on Clean Transportation
http://www.theicct.org/blogs/staff/improving-conversions-between-passenger-vehicle-efficiency-standards

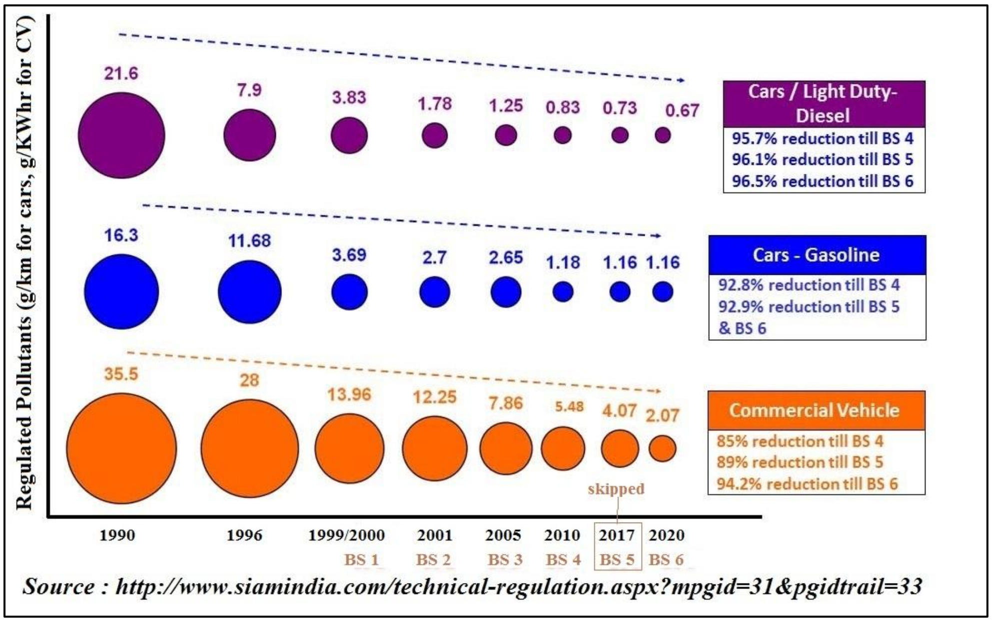
Figure 1.1 CO_2 reduction targets around the world.

India has set its reduction limit to 113 g CO_2/km by 2021. BEE (The Bureau of Energy Efficiency) & PCRA (Petroleum Conservation Research Association) in India recently announced mandates for fuel economy of passenger cars 18.20 km/l by 2016 and 22 km/l by 2021-22. In the European Union, a mandatory fuel economy standard is present to reduce emissions to 130 g CO_2 /km by 2015 and 95 g CO_2/km by 2020 [3]. United States CAFE (Corporate average fuel economy) regulation program had mandated fuel economy to the equivalent of 54.5 mpg for cars and light-duty trucks by Model Year 2025 [4].

Bharat Stage Emission standards [5] for automobiles in India are illustrated in the Table 1.1. Diesel run vehicles have more stringent CO emission limits, but they are allowed higher NOx emissions as illustrated in the table. Petrol-run vehicles though are exempted from particulate matter (PM) emissions through to the BS IV stage, but vehicles will have to satisfy the limit of 0.005 g/km for proposed BS VI stage which are far more stringent. However BS V stage has been skipped in India and will directly shift to BS VI from BS IV stage which is highly challenged target for automobile industry.

Table 1.1 Bharat stage emission standards [5], in g/km.

Tier	Date	CO	NOx	HC+NOx	PM
Diesel					
BS II	2001-05	1.0	-	0.70	0.08
BS III	2005-10	0.64	0.50	0.56	0.05
BS IV	2010	0.50	0.25	0.30	0.025
BS VI	2020*	0.50	0.08	0.17	0.005
Petrol (Gasoline)					
BS II	2001-05	-	-	0.50	-
BS III	2005-10	2.30	0.15	0.35	-
BS IV	2010	1.00	0.08	0.18	-
BS VI	2020*	1.00	0.06	0.16	0.005



Source : http://www.siamindia.com/technical-regulation.aspx?mpgid=31&pgidtrail=33

Figure 1.2 % Reduction of emission limits since 1990.

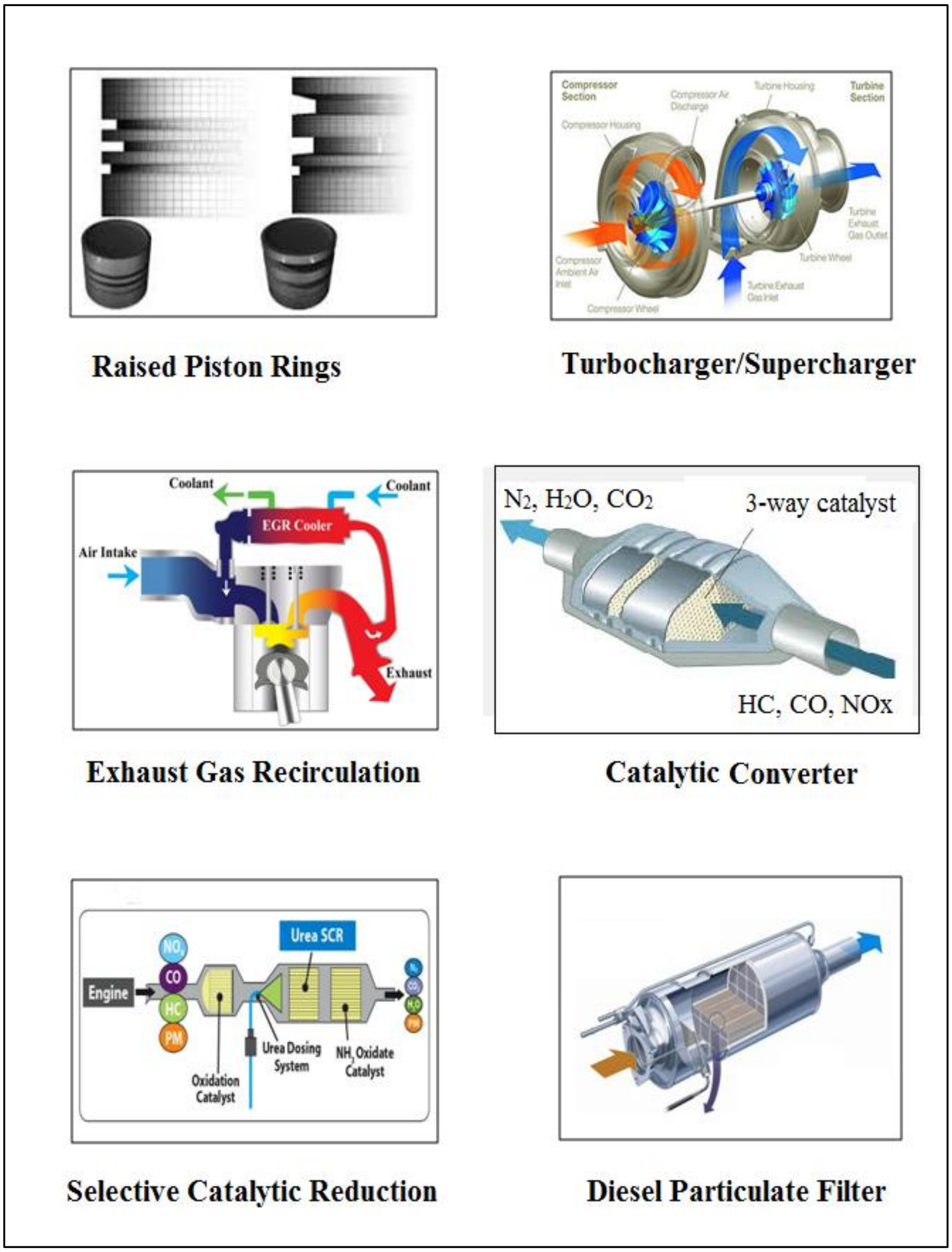
Fig. 1.2 shows that Bharat stage 6 standard (in 2020) will be considered to be a major change for vehicle manufacturers, as it needs 90-95 % reduced limits for regulated pollutants which are far below the limits that prevailed in 1990’s [6]. These proposed goals and limits are very hard to achieve for automobile industry and will drive the modifications in various technologies around the globe concerning three of its major areas viz., Engine, Fuel & Lubricant**.**

The major issues for the Engines in coming days include reducing atmospheric pollution and adapting to the variety of fuels. Due to stringent environmental regulations for making the vehicular emissions already cleaner than the surrounding atmosphere, efforts are planned to reduce the greenhouse gases (GHG) emissions. Enhancement in air quality by decreasing the GHG emissions have made original engine manufacturers (OEMs) to modify their engines to decrease tailpipe emissions near to zero by dramatically improving the efficiency of power trains resulting in increased fuel economy. OEMs will be finding all possible solutions to improve fuel economy to decrease CO_2 emissions and in order to avoid the financial penalties as a result of emissions.

Development in different areas of engine design (modifying vehicle dynamics, engine weight reduction, downsizing, modification of power-train systems) have turned out to be decisive factors in meeting the ultra low emission requirements of present and future. Change in shape of vehicle to reduce the aerodynamic force as the vehicle is moving forward has considerably been helpful in this context. Engine and body weight reduction has been obtained by the use of lightweight materials like carbon fibers in the manufacturing of same. The size of the engine and hence the weight is getting reduced resulting in vehicles becoming lighter than past. Engine downsizing alone have been found to lower emissions up to 10 %, when compared to the base engine. It is important to understand the technological changes in engine from the past to present, on the part of OEMs to match the emission guidelines, some of which are illustrated in Fig. 1.3.

The *top ring position*s of the new generation engine pistons are raised. The top ring of piston which seals the combustion chamber absorbs the heat directly. Generally the temperature in this zone is around 350 °C. In past, the distance between uppermost ring groove and piston crown was typically 7.5 to 8.0 mm.

Currently this distance has been reduced to only 3.0 to 3.5 mm in some engines. This reduces the ample area on top of the ring that captures fuel vapor & prevents it from being fully burned once the air/fuel mixture gets sparked, hence the share of un-burned fuel remarkably reduced.. This helps in lowering the emission of un-burned fuel to the atmosphere [7].



Raised Piston Rings

Turbocharger/Supercharger

Exhaust Gas Recirculation

Catalytic Converter

Selective Catalytic Reduction

Diesel Particulate Filter

Figure 1.3 Changing engine technologies around the globe.

Use of t*urbochargers/superchargers & variable geometry turbocharger (VGT)* was done to increase the energy efficiency of engines. By this technology more air was sent in combustion chamber of the engine by the compressor powered by turbines which are run by exhaust gas from the engine. Thermal loading is reduced due to shorter burning period for the fuel resulting in enhancing the complete burning of fuels injected in the combustion chamber. This finally helps in producing more energy from smaller engines.

Use of e*xhaust gas recirculation (EGR) & cooled EGR* in new engines was done to lower emissions. In this system a portion of exhaust gas is sent back into the engine, thereby reducing NOx emissions. Additionally, hot exhaust gas circulated with fresh air reduces the energy needed for the air/fuel mix to burn efficiently. Most of the new generation engines need EGR systems to reduce their emissions.

Variable valve timing (VVT) is used in modern engines. VVT is the technology by which the operation of the valve is altered by changing the time of the lift and closing of inlet/exhaust valves of the IC engines. By this technology fuel economy is enhanced and better performance and emission reduction is observed.

Variable compression ratio (VCR) in the recent engines utilizes the change in the volume of the combustion chamber to meet the power of the vehicle. At low power levels of the engine higher compression Ratios (CRs) are used which results in fuel economy and at high power levels of the engine low CRs are used to prevent knocking. CRs can be adjusted to any range from 7:1 to 20:1 in this.

Use of d*irect injection (DI)* with high injection pressures are used recently. Fuel is sent directly into the combustion chamber at the end of compression stroke. By this technique higher fuel efficiency and power outputs are achieved. This also helps in the lean burning of fuel.

The use of *3-way catalytic converters* in the modern engines reduces emissions by the converting nitrogen oxides and carbon monoxide to nitrogen, oxygen and carbon dioxide respectively, Also unburned hydrocarbons (HC) are converted to carbon dioxide and water by the reactions given below.

$$2NOx \rightarrow xO_2 + N_2$$

$$2CO + O_2 \rightarrow 2CO_2$$

$$C_xH_{2x+2} + [(3x+1)/2]O_2 \rightarrow xCO_2 + (x+1)H_2O$$

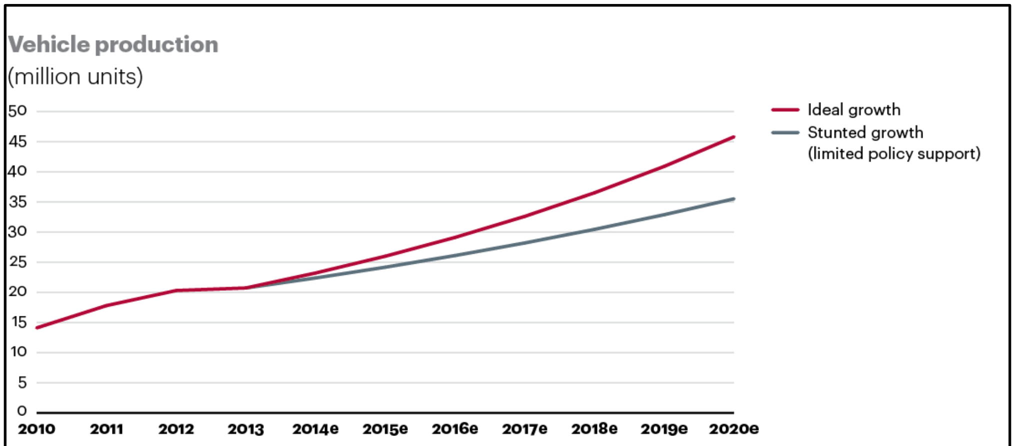
Selective catalytic reduction (SCR) is a unique technology to control the emissions of NOx particularly by injecting a liquid reductant agent through a catalyst system in the exhaust streams of engine. The liquid reductant used is generally ammonia produced from urea source. It converts NOx to nitrogen, water and traces of CO_2.

Diesel particulate Filters (DPF) in modern engines helps in capturing the particulate matter or soot in the exhaust stream of the engine.

Homogeneous charge compression ignition system (HCCI) technology is being used in recent engines where the well mixed fuel and air mixture is compressed to auto-ignition temperature of fuel to get combusted without any spark. This technology is able to achieve ultra low NOx emissions without the need of catalytic converters. The combustion technology is being controlled by microprocessors.

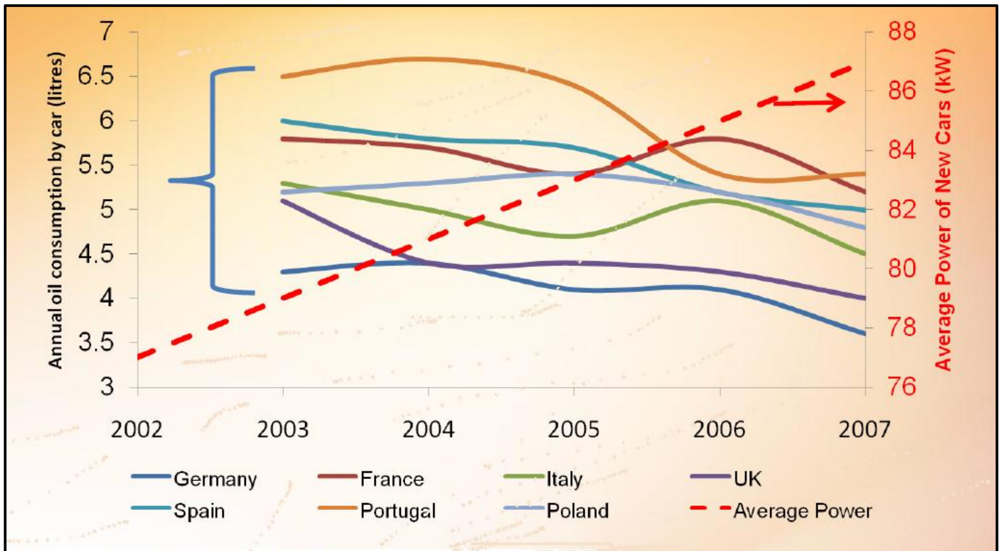
Fig. 1.4 shows the outcome of a survey on Indian Automotive Industry by SIAM (Society of Indian Automotive Manufacturers) and International Energy Agency which reveals that the total vehicular population in India is regularly increasing, and is expected to touch 50 million by 2020 and 300 million units by 2040. This means that major thrust would be visible on newer energy efficient engines in coming years. The graph from ACEA surveys at Fig. 1.5 shows that the global scenario is focused towards conserving energy and reducing emissions.

It is observed that while the annual oil consumption rates of lubricants is decreasing significantly, the average power output of the newer vehicles is increasing accompanied by engine downsizing and modifications in power trains to reduce emissions. Newer engines have become more compact and short in size. Vehicle and engine technologies to cope up with higher performance, lower emissions are getting more complex and sophisticated and is making engine more sensitive towards the fuel and lubricants qualities and properties.



Source : Society of Indian Automobile Manufacturers, Internation Energy Agency; Kearney analysis
https://www.atkearney.com/automotive/featured-article/-/asset_publisher/S5UkO0zy0vnu/content/the-contribution-of-the-automobile-industry-to-technology-and-value-creation/10192?_101_INSTANCE_S5UkO0zy0vnu_redirect=%2Fautomotive

Figure 1.4 Growth projections for India’s Auto Industry.



Source : ACEA, Surveys; ICIS World Base Oils Conference, London, 2010

Figure 1.5 Increase in Average power of cars around the globe.

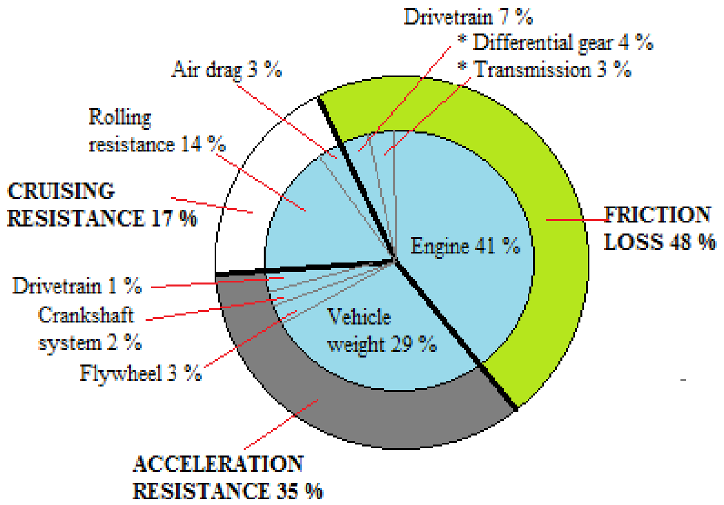
The quality of fuels is regularly changing with changes in environmental regulations for emissions. In case of gasoline, major improvements were seen in the phasing out of lead (from 0.56 g/l to 0.013 g/l), reduction in sulphur content (0.2% to 0.005%), enhancement in octane number (from 85 to 91) and reduction in benzene content (from 3% to 1% max.). In case of diesel fuel also reduction of sulphur (from 1% to 0.005%), enhancement in cetane number (from 45 to 52) and reduction in polyaromatic content were the major changes to reduce emissions. Higher octane gasoline and higher cetane diesel permits the use of engine with higher compression ratios resulting in better fuel economy, cold start ability, lesser noise and lower emissions.

Fuel Quality improvements for decreasing CO_2 emissions have made many fuel producers to bring increased usage of renewable fuels around the world. Some countries like Europe, Korea, Thailand, Indonesia, Taiwan and Australia have made necessary mandate for use of a fuel from renewable sources.

Increased fuel complexity is only one side of the equation. It is also essential that fuels do not compromise the performance of the advanced hardware systems (to meet tough fuel economy and emissions legislation requirements OEMs are making significant changes in hardware – particularly fuel injection systems). GHG restrictions impacting feedstock choice, alternative technologies near commercial reality and tightening legislation around fuel quality necessitate forming strong industry alliances between all stakeholders.

Segregated energy consumption in the engine is shown in Fig. 1.6. Frictional loss is the major portion (48%) of the energy wasted (Nakasa, 1995) [8]. The other portions are the acceleration resistance (35%) and the cruising resistance (17%). Out of the frictional losses, engine friction loss accounts for

41% and the transmission & gears friction accounts for 7%. With respect to the engine friction, sliding of the piston rings & piston skirt against the cylinder wall is definitely the highest contributor to friction. Frictional losses can be controlled by use of better energy efficient lubricants/engine oils.



Source : M. Nasaka (Toyota Motors) Proc. of Int. Tribo. Conf. Yokohama, 1995

Figure 1.6 Energy Losses developed in the engine.

1.1 Crankcase Lubricants

Engine technology developments towards downsizing and improvements in power trains have almost reaching to a stagnant level. Fuel quality improvement is also witnessing the same scenario. Use of alternate fuels is likely to see a greater demand in the future. This will obviously create new challenges for the engine oil formulations to be used in newer engines.

Hence understanding of engine environment arising as a result of engine modifications, fuel quality up-gradation, use of alternate fuels and its impact on engine oil performance is of paramount importance in design and development of engine oil.

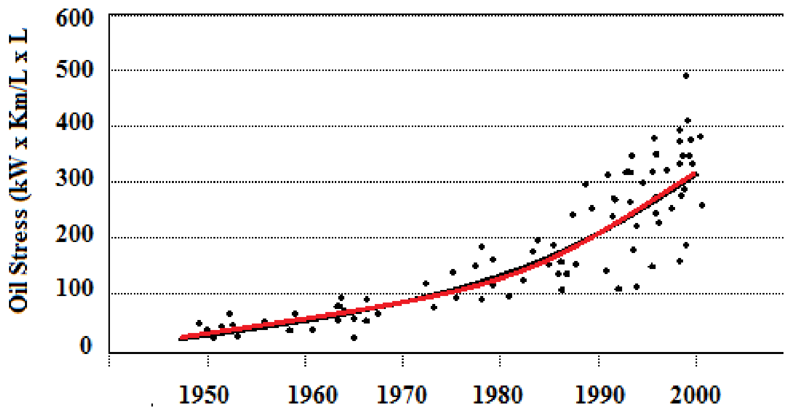
1.1.1 Engines downsizing effects on the engine oil

Engine oil has reduced residential time for the circulation and lubrication due to sump capacities of engine getting reduced. Engines will run hotter to generate more power; there will be reduced airflow for the cooling of engine parts. Hence the engine oil used in such engines needs to be thermally stable at such higher temperatures to withstand oxidation and degradation. Greater shearing of oil will take place as a result of higher torque generation & higher loads on small bearings. To increase fuel economy the introduction of thinner fluids is necessary for better lubrication, which can increase the wear in engine parts and therefore it would be a challenge for the lubricant to control such wear while maintaining good film strengths on the operating parts.

This means that stress on engine oil will be increasing manifold in newer engines. Fig. 1.7 shows the increase in oil stress factor in the engines from 1950-2000. The severity is likely to increase in new generation engines due to increasing power density. Oil Stress Factor for the engines is calculated by the equation given below [9].

$$Oil\ Stress\ Factor = \left(\frac{Engine\ Power}{Engine\ Displacement}\right)\left(\frac{Oil\ Drain\ Interval}{Sump\ Volume}\right)$$

We see from the equation that oil stress factor is directly proportional to the engine power and oil drain interval which are continuously increasing for the newer engines. Also the oil stress factor is inversely proportional to engine displacement and sump volume which are continuously decreasing. This means that Oil Stress Factor will increase advertently and exponentially in the future as illustrated in Fig. 1.7. The working temperatures of modern engines are touching ~ 350 °C. The engine oil, therefore, should be stable at such high operating temperature, which means that engine oil used should have less volatility and good inhibition towards oxidation and also have to maintain a good film strength on the engine parts so that lower wear takes place.



Source : R. I. Taylor, R. Mainwaring, R. M. Mortier, Engine Lubricant Trends Since 1990, Proc. I. Mech. E. Vol 219, Part J: J. Engg. Trib., p 335, 2005

Figure 1.7 Increase in Oil Stress of Engines.

Cost intensive technologies like diesel particulate filters (DPF), selective catalyst reduction (SCR) and lean NOx traps (LNT) should be compatible with the engine oil which is used in those engines. Sulphur and phosphorous ingredients, which are quite harmful to these after treatment solutions, should be low in the engine oil.

1.1.2 Fuel Quality Effects on Engine Oil

As the fuel quality is improving day by day the engine oil needs to be adjusted to cope up with such improvements. Also in some cases where gaseous fuels containing corrosive impurities such as H_2S from landfills are being used, the engine oil needs to be considerably stable and compatible to these fuels. As gaseous fuels have high calorific value and they burn cleanly the ash requirements of the engine oil should also be considered. The engine will get hotter and require additional thermo-oxidative properties to be met.

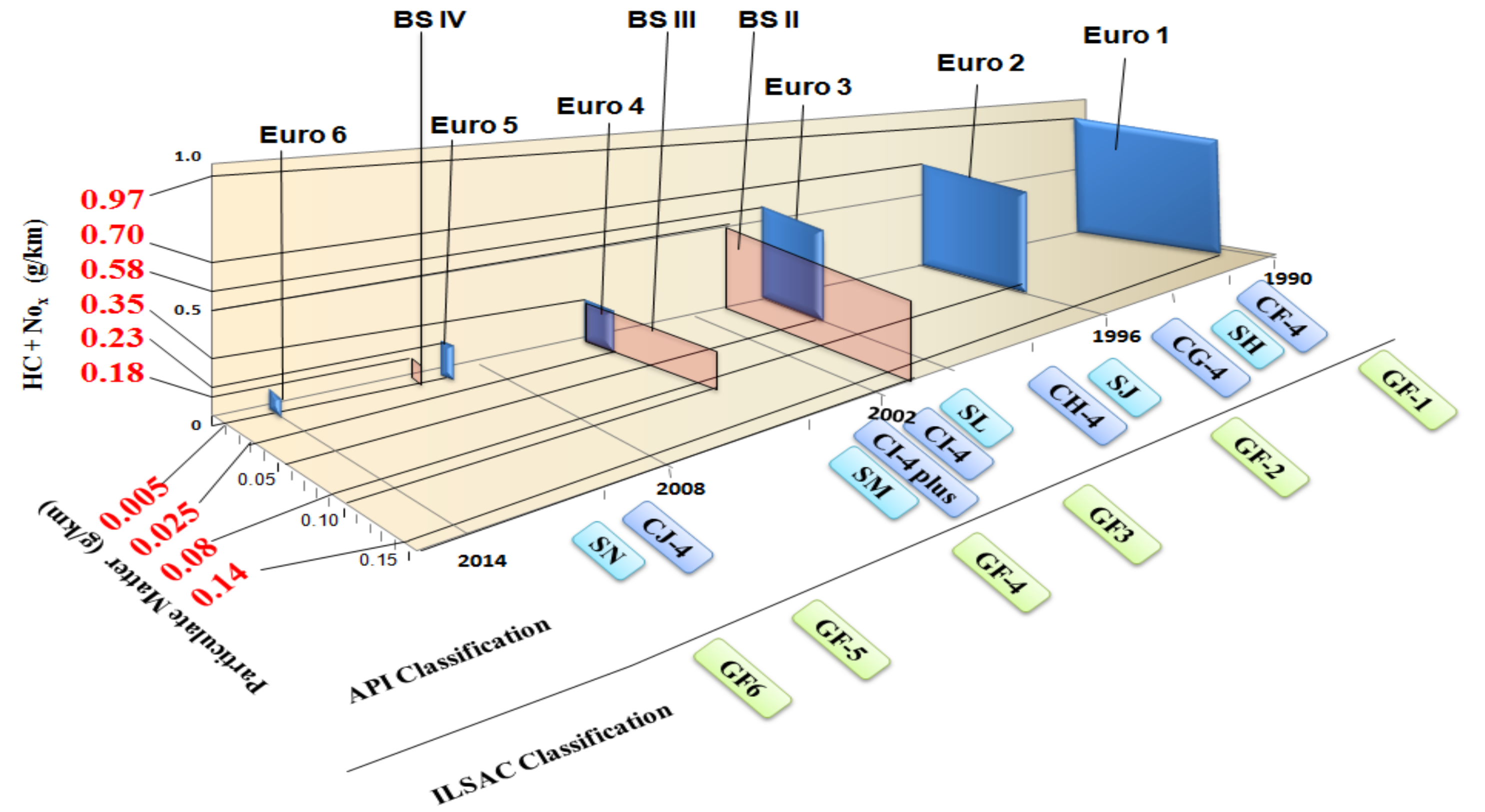
1.1.3 Lubricant Specifications & Degradation of Engine oil

Besides all these effects of engine technological advances and changes in the fuel quality on the engine oil, compliance with the changing lubricant specifications developed by the regulatory bodies around the world also become mandatory. The past two decades have, therefore, witnessed a rapid quality up-gradation in engine oil specifications.

Fig. 1.8 gives the information about the specification changes for Engine oils with respect to emissions reductions (NOx, HC & particulate matter) from 1990's to present. BS (Bharat Stage for India) emission norms vs Euro (European) emission norms are illustrated for comparison. As emissions limits are getting reduced continuously and nearing to zero, accordingly the specifications for engine oil are changing regularly. Engine oil design factor, therefore, assumes an important role in meeting the environmental emission requirements of newer engines and on the other hand is challenging too.

Coupled with performance enhancement, multi-viscosity grade features becomes a challenging option for improved fuel economy for lower emissions and higher drain intervals for sustainability, while maintaining engine oil durability for the entire range of operations. This area, therefore, draws a greater focus for pursuing research. As the present generation engines are running at higher thermal profiles the oil should have less volatility so as to cater the oil consumption loss and longer durability of engines.

Close examination of the image of a typical engine and its parts in the Fig. 1.9 provides a schematic understanding of the above factors for getting a feel of the above discussion. If the oil has high volatility the lighter volatile components gets vaporized, resulting in thickening of oil and lesser oil will be available for lubrication of engine parts leading to the wear of the engine parts and lastly failure of engine. Engine oil should have optimum viscosity along the temperature profile of engine which means the oil should have high viscosity index and also the oil should be stable towards oxidation. Oxidation is the most significant form of chemical degradation of engine oil and additives present in it. The additives present in engine oil continuously react with oxygen (air) inside an engine resulting in oxidation of oil and produces acidic oxidation products.



Graph drawn on data from :
https://en.wikipedia.org/wiki/European_emission_standards
https://en.wikipedia.org/wiki/Bharat_Stage_emission_standards
http://www.thehindubusinessline.com/todays-paper/tp-opinion/euro-versus-bharat-norms/article2167767.ece
http://www.api.org/~/media/Files/Oil-and-Natural-Gas/Engine%20Oil/MOTOR_OIL_GUIDE_2010_120210.pdf?la=en

Figure 1.8 Changes in lube oil & emission specifications from past to present.

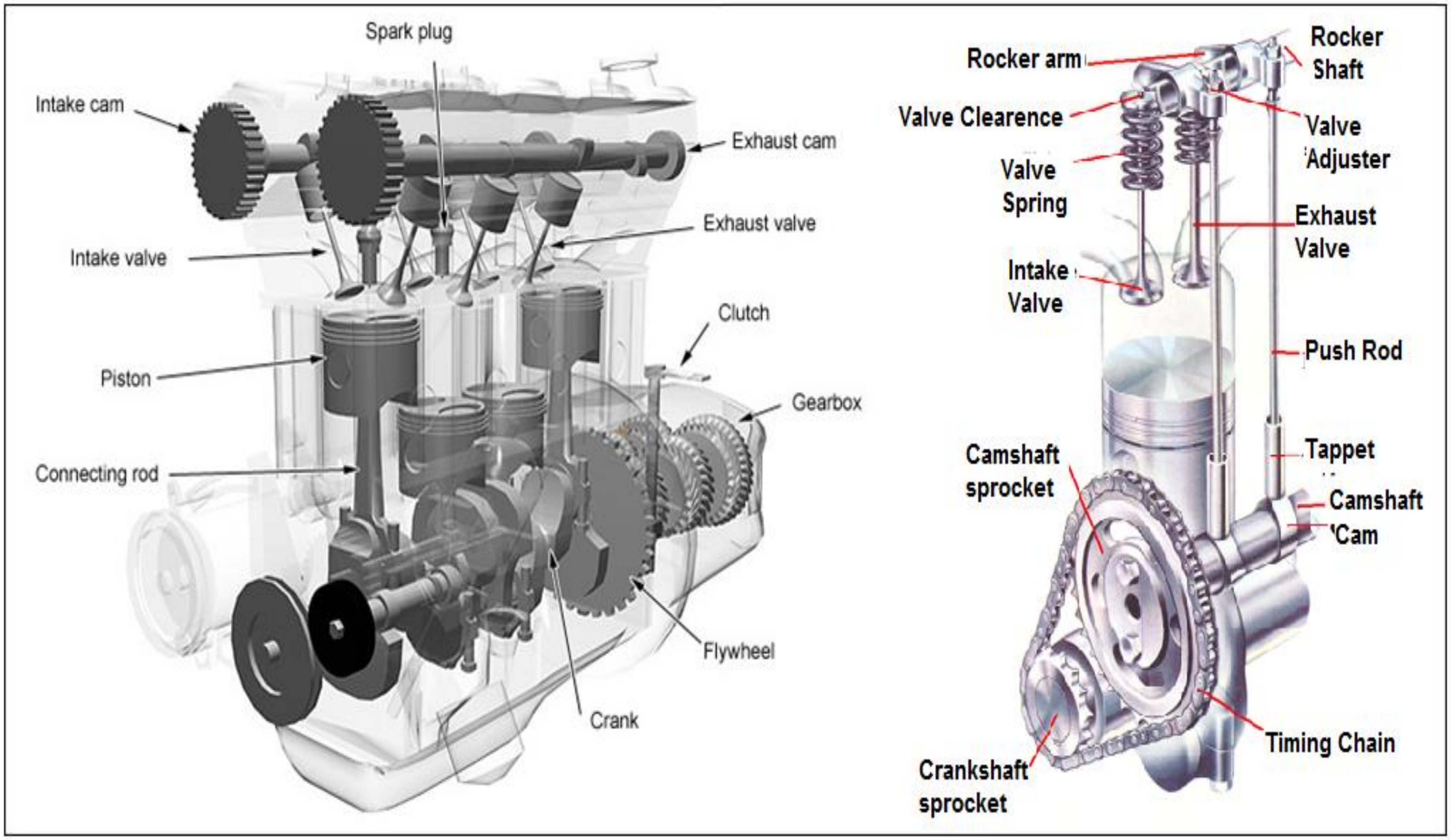


Figure 1.9 Typical 4-stroke engine and its parts.

Different acidic compounds thus formed, cause corrosion of internal engine parts, deposit formation, oil viscosity change, varnish and sludge formation and other insoluble oxidation products which severely affects the durability of engine. The oil oxidation products formed are less stable than their original basic hydrocarbon molecule structure. As an engine runs through multiple heating and cooling schedules, the sludge hardens which lead to various other problems such as blockage of passageways and decreased component durability. Varnish formation in the engine can result in piston ring and valve sticking. The deposits formed also affects heat dissipation from pistons to cylinder, and in serious cases, can result in seizure of the piston in cylinder. Pistons have oil return slots which can be plugged resulting in increased oil consumption and more deposit formation over the deposits that are already there, leading to oil breakdown.

Deposit formation also occurs on the top of pistons which, over a span of time, can cause other engine problems such as pre-ignition, increased fuel octane requirements, increase in hydrocarbon emissions due to incomplete combustion of fuel and an overall destructive effect on the engine internal components. Corrosion occurs when hot oil present in engine react with moisture formed, which finally damages the parts of the engine. In addition to it, moisture presence in oil for an extended period of time could also emulsify the oil resulting in formation of a mixture which is highly corrosive than the two components alone and finally form sludge which may block oil filters and small passages. Also the engine oil should have low SAP content so that it should not affect the environment. Majority of the performance properties of the engine oil/lubricant are related to its thermal stability, oxidative stability and its capability to form film strength and to reduce friction between the moving parts.

To mitigate these concerns oxidation inhibition and thermal stability of the engine oil along with good surface activity should be the primary focus for formulating an effective crankcase lubricant. Thus additives like antioxidants, friction modifier and viscosity modifier have high importance in developing crankcase lubricant. In any lubricant, base oil is the major constituent which constitutes about 80-90% of it and has a greater role to play in thermal stability of engine oil, i.e., base oil used for optimizing should be less volatile in nature. Energy-efficient engine oils with significant fuel-economy have become increasingly important on account of both the saving of natural resources and the environment [10-13]. As engines get downsized with more power, there will definitely, be more thermal stress on the lubricant. Hence thermo-oxidative stability of engine oil becomes an important factor, besides reduced friction and film thickening attributes.

1.2 Objectives of Research

This research endeavor aims to study the potential domains related to thermo-oxidative stability of engine oils for addressing the multifarious requirements of designs, operations and regulations of new generation automobile engines, along with studies on reducing friction and wear between engine parts. This will result in saving the energy or in other words will increase fuel economy. This project is driven by the primary requirement of newer engine designs and/or operational requirements for meeting the emission norms. Improvements in thermal stability & oxidation inhibition of engine oil[s] through effective design of engine oil attributes, leading to its increased extended drain, would be the primary focus to synergize with engine designs for lower emissions. The experimental approach would include bench screening tests to standard engine test programs. Laboratory bench tests utilizing various structural manifestations of the identified additives, experimental designs for optimization, and final validation in performance engine tests would be the areas of investigation.

1.3 Review of Literature

Research on enhancing thermal stability of engine oils and antioxidants performance has been reported. However, references on synergistic studies are limited. Recent engine designs and emissions regulations have made this an important area of study. Some current engine design features such as Low Heat Rejection Engine (LHRE) or the Insulated Engine which increases the combustion temperatures to reduce particulate matter, high fuel economy, and high power density call in for an effective thermo-oxidative stability of the engine oil. Component designs such as swirl chambers, articulated pistons, and use of higher fuel injection pressures put higher stress on the lubricant because of thinner oil films and higher top ring reversal (TRR) temperature [14]. Presence of carbon deposits on top land of pistons can result in loss of oil control. Loss of oil control can also result in increased engine emissions [15]. Higher operating temperature results in oxidation of oil molecules and affects oil properties [16].

The thermal and chemical interactions at the interface between the combustion zone and the lubricated top ring may lead to hard carbon deposit formation on piston lands and ring grooves. These deposits reported to be high molecular weight polyesters or oxygenated polymeric hydrocarbon result in a greater amount of oil being scraped on the cylinder wall. Although the importance of engine design in controlling oil consumption has been known for quite some time by the automotive industries, the other way to effectively reduce consumption of oil is by designing/optimizing the crankcase lubricants [17]. The base oil quality, inhibited additive systems, and oxidative breakdown of the polymeric VI improvers used, are some of the vital parameters that significantly influence the course of oxidative degradation of an engine lubricating oil [18].

The tendency of oil to form deposits, sludge and corrosive by-products depends on the degree of its inhibition to the oxidation [19]. Base oils features in relation to the engine temperatures have been studied by Hsu [14]. The aromatics, paraffins and naphthenic content of base oil decide the lubricant properties [20, 23-

24]. Base oil quality has a significant bearing on the performance of lubricant oil [16, 21]. The thermo-oxidative variations in the chemical structure can influence the properties of lubricating base oils [22]. Group III Base stocks have seen superior oxidation stability than Group II and IV Base stocks [25]. Action of different base oils during thermal/oxidative degradations are explained [26-27]. Kinetics during the degradation of base oil varying with the viscosities has been evaluated [28]. Viscosity index of base oil is dependent on the iso-paraffinic and aromatic content [29].

According to the research work reported varnish and lacquer deposits will build up with the oxidation of the lubricant and may cause complete breakdown of the engine being lubricated [30-31]. Antioxidants inhibit the start of radical chain reactions that are primarily responsible for increase in amount of degradation products. Antioxidants increase the time until sludge, lacquer, or deposits are formed due to secondary processes [31]. The property changes indicated that degradation of the oil was much more severe in the presence of metal catalysts. The presence of metal particles in oil during high temperature conditions accelerates the oxidative degradation of lubricants [32-33].

The anti-oxidation properties of oils are related to the phenomenon of thermal degradation of the additives used [34]. Volatility behavior of a formulated lubricant can be complex which mainly depends on volatility of base oil, thermal/oxidative stability of the base oil, volatility of the additive components and degree of inhibition to the oxidation by the additives present in it [15].

Diphenylamine's (DPA) are being used as antioxidants. Alkyl substituent in Para positions of DPA increases the stoichiometric factor when compared to the un-substituted DPA [34]. Organometallic complexes of different metals are used as antioxidants [35]. Kinetics of different antioxidants is correlated with induction periods of the same [36]. Antioxidant properties of Organo-molybdenum with dithiocarbamates complex are evaluated [37]. Improvement in oxidation stabilities by molybdate ester and phosphorated compounds in addition to alkylated DPA's have been studied [38-39].

Reduction in auto oxidation processes by use of radical scavengers and synergism showed by them were studied [18, 40]. Additives added to the lubricants are of different structure and will have different action mechanism. Additives used in the lubricant should have better solubility, good thermal/oxidative stability and compatibility within each other additives present in it. Additives with different molecular weights which are used to enhance performance in engine oil formulations could interact through their polar functional groups to form different complexes. The extent and direction of the changes depended on the chemical structure of the additives and their concentration in the blends [41]. Polar additives interact with each, exhibiting synergistic or antagonistic action on comparing with their individual performances [42].

Evaluation of antioxidants and thermo-oxidative stability uses various techniques such as RPVOT [30], TGA, PDSC and DSC [31, 33, 43-44]. Penn state micro oxidation test has been helpful in evaluating thermal and oxidative behavior of base oils [43]. The effect of engine oil on emission has been studied by measuring its volatile phosphorous content [44]. Thermo Oxidative Stability of oil has been evaluated by Panel Coker test [45], while oxidation deposit studies are reported with TEOST [46]. Evaluation of oxidation properties have been carried out by FTIR, Raman spectroscopic and NMR studies [46]. Excessive temperature profile in the engine may cause the oxidation of lubricant leading to the failure of the journal bearings in the Engines [47]. Oxidative inhibition characteristic of engine oil can influence the oils durability and also affects other performance attributes like basicity depletion, wear, deposit formation and thermal degradation [48]. The performance of Engine oils is analyzed effectively in Sequence IIIE Engine test under the oil specification API SH. In these tests, oil oxidation is evaluated by finding the variation of kinematic viscosity within new and used sump oils. The rise in viscosity can be calculated exactly as in bench tests and presence of insoluble matter indicates risk of piston deposits. Antioxidant properties are also been evaluated by this test [26, 49].

The next chapter will deal with constituents of engine oil i.e., different Base oils, Viscosity Index improvers, Friction Modifiers & Antioxidant, their selection and compatibility based on thermal stability and oxidation stability evaluation.

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Chapter 2

Key Elements of Matrix for Study

2.0 Base Oil

Developing engine oils to work effectively under severe conditions for long drain intervals is a challenging task [1]. An Engine oil contains about 80-90 % of Base Oil and 10-20 % of additives which are added to impart special properties. For meeting new generation oil specifications (ACEA, API, and ILSAC) engine oils need base oil[s] with less evaporation loss and high viscosity index to achieve higher fuel efficiency and lesser oil consumption. Base oils could either be derived from petroleum (mineral base oils) or synthetic. Around 2-3 % of base oils utilization in world is synthetic and is used for some unique and specialized applications like in aviation sector, industrial segments and in some high temperature applications [2].

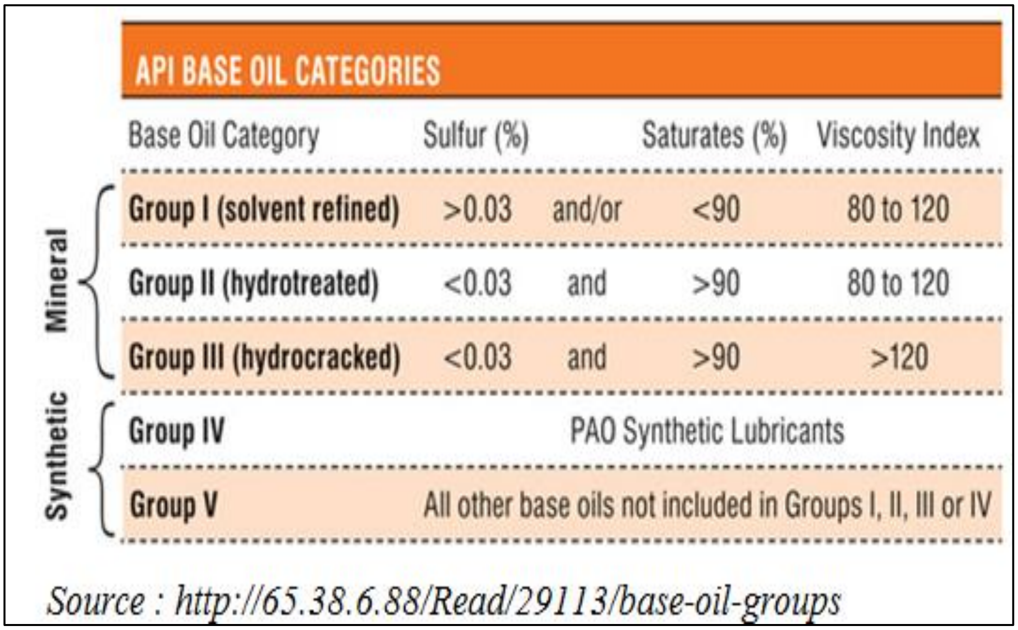
Mineral base oils are obtained from distilling the residue, obtained from atmospheric distillation of crude oils, under vacuum. These base oils as stand-alone cannot be utilized for formulating lubricants due to the presence of aromatic content, sulphur & nitrogen compounds, which make them unstable at higher temperatures. These undesirable aromatics, waxes, S/N compounds are removed by processes like solvent extraction, hydro-finishing & dewaxing. 1-2 % of base oils out of the residue are produced from the above said processes [3]. To improve further in yield and quality of base oils, to meet new generation engine oil specifications new hydroprocessing routes have been developed [4-10].

2.0.1 Classifications

Chemically base oils are very complex mixture of wide variety of molecules which includes paraffins, aromatics, naphthenes, polycyclic aromatics, sulphur and nitrogenous complexes [11-12]. The aromatics, paraffins and naphthenic content of base oil decides the lubricant properties [13]. Base oils are generally classified based on the paraffinic, naphthenic and aromatic content. Paraffinic base oils have high pour point, low viscosity and have adequate resistance to oxidation. Naphthenic base oils are characterized by low pour point, low viscosity index (VI), lower aniline point and are preferred in low temperature applications. Aromatic base oils have low VI, high volatility, poor oxidation resistance and therefore cannot be used in modern lubricants. Very high VI oils are paraffinic in nature and are produced by processes like hydro cracking, wax isomerization, hydro treating process.

To formulate improved lubricants, good quality base oils are pre-requisite. API responded to this need and came out with its base oil classification, where all the base oils were categorized by their sulphur content, saturate content and viscosity index in five groups (I to V). The API classification of base oils [14] is presented in Table 2.1.

Table 2.1 API classification of base oils.



API BASE OIL CATEGORIES

	Base Oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Mineral	**Group I (solvent refined)**	>0.03	and/or	<90	80 to 120
	Group II (hydrotreated)	<0.03	and	>90	80 to 120
	Group III (hydrocracked)	<0.03	and	>90	>120
Synthetic	**Group IV**	PAO Synthetic Lubricants			
	Group V	All other base oils not included in Groups I, II, III or IV			

Source : http://65.38.6.88/Read/29113/base-oil-groups

Group I

Among all the other groups Group I base oils are the least refined. These base oils usually contain a mixture of various hydrocarbons with no uniformity. Some of the automotive oils present in the market are blended with Group I stocks, which are normally used in less demanding applications. Saturates content present in the Group I base stocks doesn't exceed 90 % and the sulfur content in it is minimum 0.03 %. The Viscosity index of these base oils lies between 80 and 120.

Group II

The most common mineral base oils used currently in the market is Group II base oils. This is due to their adequate performance in lubricating properties such as volatility, oxidative stability and flash/fire points. Also good performance is seen in areas of pour point, cold cranking viscosity and extreme pressure wear. Group II base oils contain more than 90 % saturate content and with sulfur content less than 0.03 %. The viscosity index ranges in between 80 and 120 as in the case of Group I.

Group III

These base oils are the highest refined of mineral base oils used. Group III base oils give excellent performance in various performance attributes. These base oils have good molecular uniformity and stability. These base stocks also contains saturates content more than 90 % and sulfur content less than 0.03% as that of Group II. These base oils have viscosity index more than 120.

Group IV

Group IV base stocks are known as chemically modified synthetic base stocks containing polyalphaolefins (PAO). These base stocks exhibit very good performance when mixed with additives for various lubricating properties. These base stocks contain highly uniform molecular chains with highly stable chemical compositions, and are used in specialized applications such as very high/low temperature applications where mineral oils fail.

Group V

The base oils that are not included in Groups I, II, III and IV are categorized as Group V base stocks. Generally polyesters and esters find a place in Group V category. These base oils can add additional properties to other base oils, when mixed with them in small quantities.

While observing API base oils classification it is observed that the sulfur content in the higher group base oils is very less when compared to lower group base oils. Refineries are currently producing ultra low sulfur base oils due to hazardous impact of sulfur on the environment.

According to the literature the oxidation stability of the base oils is due to its sulphur content, so if sulphur is getting reduced in the present world scenario for higher group base oils due to environmental concerns, the same has to be adjusted by the additives for extra stability which will be also discussed in this thesis. The increased consistency of lower sulphur and higher saturate concentration together with higher viscosity index for these base oil Groups is advantageous for formulating high performance lubricant products [15]. Thus the study of base oil features would also be included in the matrix of experimentation.

2.0.2 Properties of Base oils

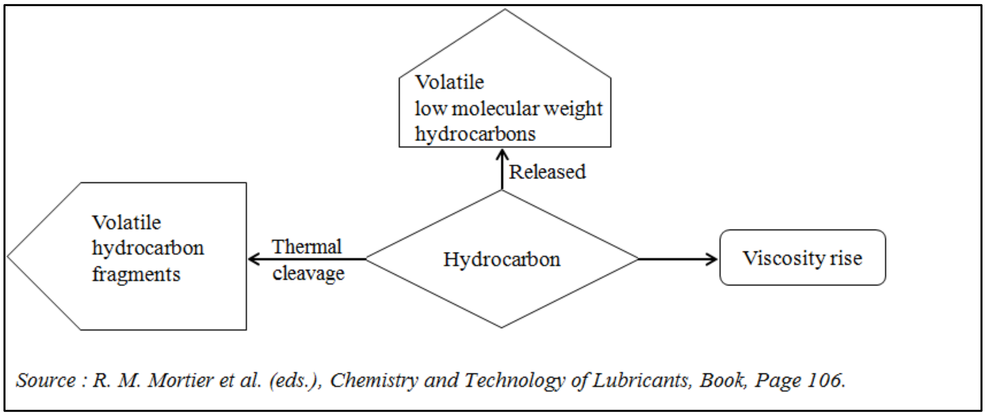
The primary function of Base oil fluid is to lubricate the engine parts and act as a carrier of additives besides reducing friction & wear, cooling the engine parts and keep it clean by controlling the contaminants. The lube base stock is the building block in which optimum additives are selected and properly blended to achieve good performance characteristics of the finished lubricant. Base Oils exhibit two types of properties:

- First which are inherent of the individual base oils
- Second which can be enhanced by adding performance additives.

The inherent properties of base oil cannot be changed. These properties of the base oil are listed below:-

- Carbon Residue
- Aniline Point
- Thermal Stability
- Flash Point
- Air Release Value
- Volatility
- Cloud Point
- Biodegradability

These properties are dependent on the molecular structures of the various entities present in the base oil itself. Due to the increasing thermal profile of the engines recently as a result of engine downsizing, the thermal degradation of the engine oil needs to be controlled. Engine oil consists of hydrocarbons with different molecular weights. As shown in the Fig. 2.1, when engine oil is exposed to the higher thermal profile of the engines "thermal cleavage" takes place and loss of volatile low molecular weight hydrocarbons happens. This results in the viscosity rise of the engine oil resulting in further implications of reduced efficiency in modern engines. This made "thermal stability" and "volatility" very important in controlling the deposits and oil consumption in engine oil. The selection of the base oil for the development of engine oils for modern engines therefore should depend on these two properties as said above. There are other properties like pour point, dispersancy, corrosion, rusting, oxidation stability, detergency, friction properties, foaming, load carrying ability, and antiwear which can be improved by the use of additives.



Source : R. M. Mortier et al. (eds.), Chemistry and Technology of Lubricants, Book, Page 106.

Figure 2.1 Thermal degradation process of the engine oil.

2.0.3 Experimentation, Observation and Inference

Base oil combinations used in the present set of studies utilized either a specific group or a combination thereof of different groups for a target viscosity range and studied for basic physico-chemical attributes. FTIR, Mass spectrometry and ^{13}C NMR technique are used to determine the paraffinic (Cp), aromatic (Ca) and naphthenic (Cn) content in base oils [16-19]. The paraffinic content is further divided to normal paraffin (Cp-n) and iso-paraffin (Cp-i). Physico-chemical data has been evaluated on these combinations like kinematic viscosity (KV), volatility loss, oxidation onset temperature (OOT) etc., are illustrated in the Table 2.2.

Table 2.2 Physico-chemical properties of different base oil mixtures.

Parameters	**Gp I based**	**Gp II based**	**Gp III based**	**Gp IV based**
KV @ 100 °C, cst	5.529	5.61	5.93	5.97
KV @ 40 °C, cst	31.94	30.68	30.31	29.92
VI	110	123	145	150
Volatility loss %	13.8	10.8	7	7.2
Cp-Normal %	38.9	36.1	38.5	67.1
Cp-Iso %	56.3	59.2	61.1	32
Ca %	3.6	0.3	0.3	0.3
Cp %	59	57.2	59.4	65.4
Cn %	37.4	42.4	40.3	34.2
OOT in °C	229	197	199	198
Density	0.8703	0.8517	0.8541	0.8194
Pour Point in °C	-9	-18	-27	-45

From the table it is observed that on moving from Group I to IV based base oil the aromatic carbon content is decreased while naphthenic & paraffinic carbon content is increased. According to literature, paraffinic carbon content is responsible for high viscosity index (VI), Low volatility and good low temperature properties. The OOT (oxidation onset temperature) value, evaluated on DSC (Differential Scanning Calorimeter), gives information about the oxidation stability of the base oil. The higher the OOT the oxidation stability is more for that particular oil.

Table 2.3 Mass Spectrometry elucidation of Group I-III base oil mixtures

Hydrocarbon classes(% w/w)	**Gp I based**	**Gp II based**	**Gp III based**
Paraffins	8.7	16.7	21.6
Monocycloparaffins	21.7	30.1	32.5
Dicycloparaffins	15.7	23.2	18.1
Tricycloparaffins	10.2	14.2	11.1
Tetracycloparaffins	3.0	8.6	8.4
Pentacycloparaffins	0.0	1.7	4.5
Hexacycloparaffins	0.0	0.0	0.0
Heptacycloparaffins	0.0	0.0	0.0
Saturates	**59.3**	**94.5**	**96.2**
Alkylbenzenes	9.1	1.9	0.9
Benzocycloparaffins	5.3	0.6	0.7
Benzodicycloparaffins	3.0	0.3	0.2
Naphthalenes	3.3	0.9	0.5
Acenaphenes, biphenyls	2.3	0.3	0.3
Acenaphthylenes, fluorenes	2.7	0.8	0.6
Phenanthrenes	2.2	0.4	0.4
Pyrenes	0.4	0.0	0.0
Chrysenes	0.0	0.0	0.0
Benzopyrenes	0.0	0.0	0.0
Aromatics	**28.3**	**5.2**	**3.6**
Thiophenes	0.0	0.0	0.0
Benzothiophenes	2.3	0.2	0.1
Dibenzothiophenes	0.0	0.0	0.0
Naphthobenzothiophenes	0.0	0.0	0.0
Sulfur Compounds	**2.3**	**0.2**	**0.1**

Mass Spectrometric elucidation of mineral based Gp I - III base oil mixtures have been done for further understanding of the behavior of the mixtures and illustrated in Table 2.3. Group IV, being synthetic type has not been included into this group of mineral oils. According to the literature mononaphthenes (monocycloparaffins) are responsible for good low temperature properties [20]. In case of volatility loss the Group III & IV base oil mixtures reported very less when compared to Group I & II indicating good thermal stability of such mixtures. Further the same has been proved in the TGA experiment.

Thermal stability of base oils is evaluated by thermo-gravimetric analyzer (TGA). 10-15 mg of base oil mixture in platinum TGA pan is subjected to 20 °C/min temperature ramp up to 500 °C under nitrogen atmosphere to know the base oil ability to withstand higher temperatures (ASTM E1131) [21]. The thermograms of different base oils are given in the Fig. 2.2, and temperatures corresponding to identified weight % losses are calculated and tabulated in Table 2.4.

Table 2.4 Temperature data of base oil mixture at different % Wt. loss.

% Weight Loss	**Gp I based**	**Gp II based**	**Gp III based**	**Gp IV based**
5	216	219	242	246
10	237	240	261	264
20	260	263	281	285
30	275	279	294	299
40	286	291	305	311
50	296	303	315	321
60	305	313	323	330
70	315	324	331	339
80	324	336	339	349
90	336	350	348	359
95	346	359	353	365

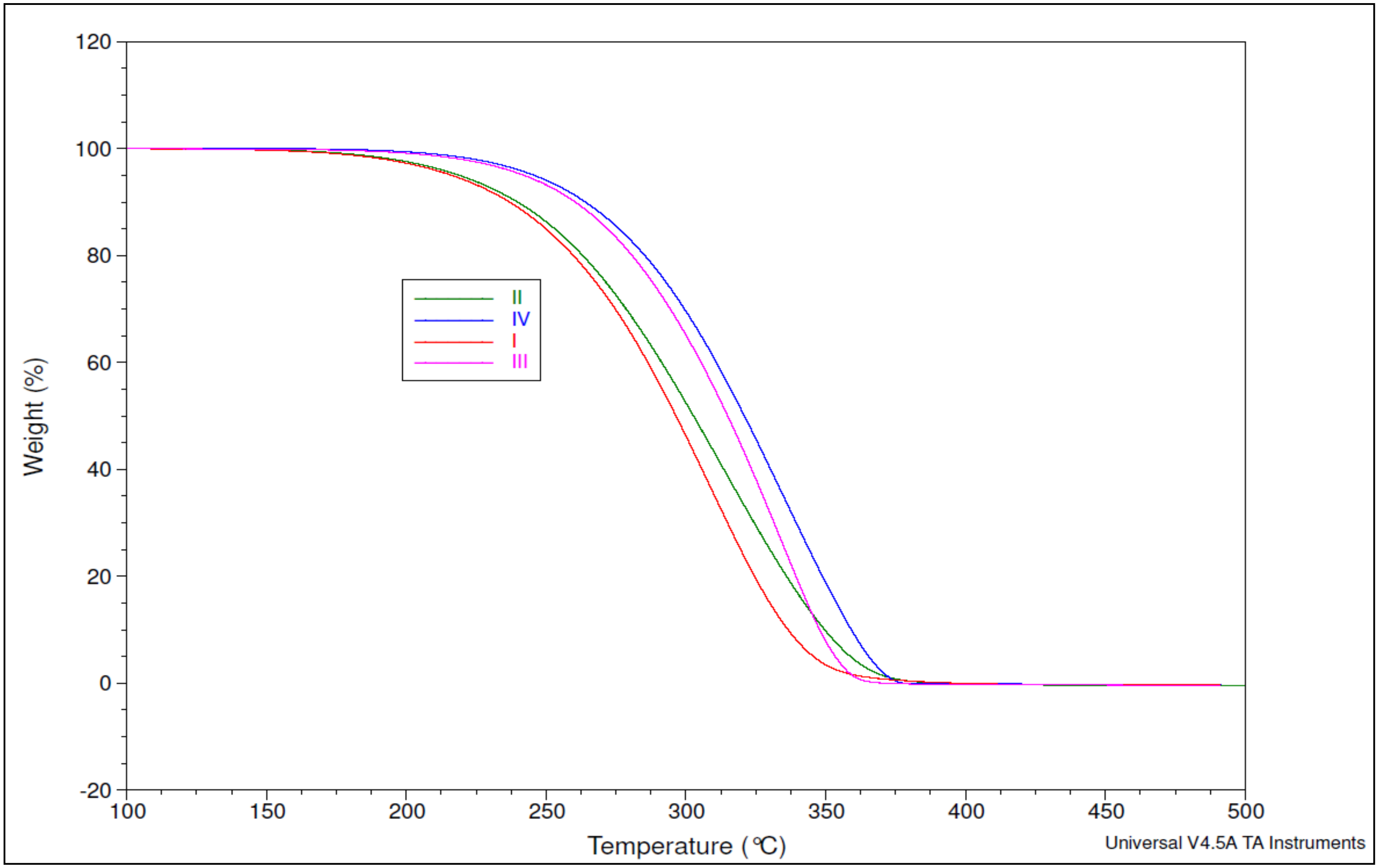


Figure 2.2 Weight loss curves of different base oil mixtures by TGA.

From the values tabulated and from the curve it is clear that the stability of base oil to withstand higher temperatures is in the order of IV > III > II > I. The tabulated data and TGA thermograms show that group IV and group III base oils combinations are more stable at higher temperatures (only 40 % loss over 300 °C when compared to loss of ~ 60 % with I and II).

Beside thermal stability of base oils, frictional properties & oxidation stability are the main focus in coming days due to the increasing stress on the engine oil. Additives are chemical compounds which are supplemented to the base oils to impart specific properties of the finished oils. As fuel economy is a prime subject of interest for the reduction of environmental emissions frictional properties of the oil are equally important while maintaining good film strength between the engine parts under higher operating temperatures.

2.1 Viscosity Modifiers & Friction modifiers

Engine oil should have a good surface activity on the engine parts. Frictional properties can be controlled by the effective combination of viscosity modifiers (VMs) & friction modifiers (FMs) in engine oils. It should form good stable film strength on the moving parts so as to prevent the moving parts from wear and also reduce the friction. The viscosity modifier used in the engine oil should be shear stable along the temperature profile and mechanical shear stress of the engine to maintain the film strength.

Next generation engine designs are developed for low viscosity fluids. This is all probability, is likely to result in lower viscous drag without impacting durability. Also new specifications will require engine oils with low viscosity to work at higher operating temperatures, thereby leading to formation of thinner films and hence higher wear of engine parts. Both friction modifiers and reduction in viscosity of engine oils can improve the fuel economy of automobiles.

Hence the use of VMs & FMs to maintain film thickness and reduce friction will continue to be a challenge. An automotive engine is a very complex system in which it can have multiple frictional regimes occurring simultaneously at a time [22]. Correlation of different frictional/lubrication regimes with engine parts is given in Fig. 2.3 [23]. Reducing engine oil viscosity to decrease friction in the hydrodynamic region will have a negative impact at the boundary/mixed region and can lead to frictional losses and wear. At a sufficiently low viscosity, the boundary losses in the form of friction and wear can diminish any benefits which are obtained from the reduced hydrodynamic losses.

Decreasing the oil viscosity too low will have a negative effect on fuel economy. Very low viscosity results in possibly not having an adequate film to withstand the increased load and friction. Increased wear with very low viscosity oil can be seen at highly stressed contacts like the valve train. Since the Fuel economy benefit is likely to be realized through a shift in viscosity grade, a corresponding challenge is also likely to manifest in durability (wear). One additive which can give a better viscosity-temperature profile in such cases is viscosity modifier.

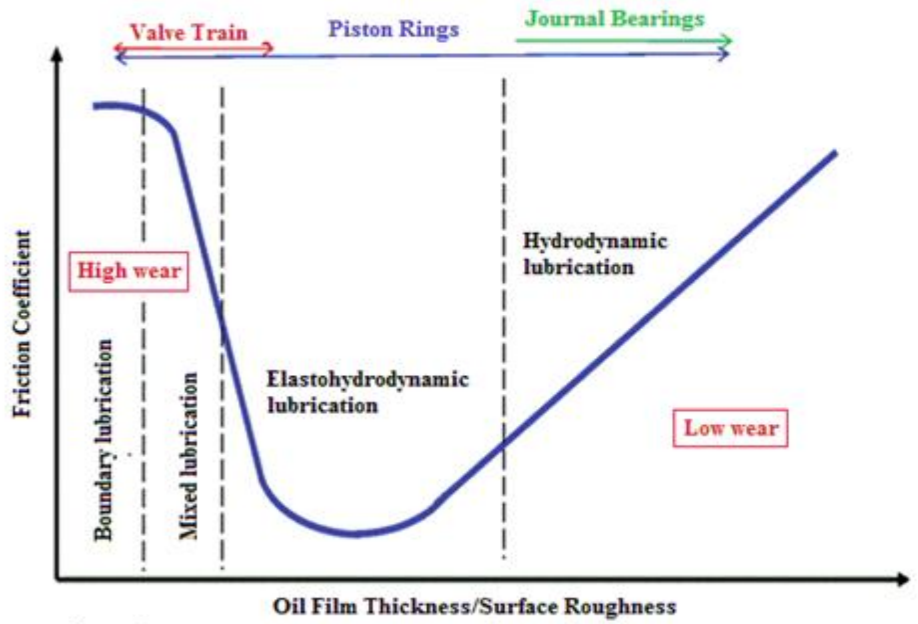


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Figure 2.3 Lubrication regimes in various Engine parts.

Viscosity modifiers (VMs) should have optimum balance on viscosity which is of prime importance for low wear, while having decreased viscosity contributions at lower temperatures important for fuel economy. VMs should also help to reduce wear by forming a protective film on metal surfaces. VMs have the ability to form thicker lubricating films under engine operating conditions. Adequate lubricant films will save metal surfaces resulting in minimizing wear under the shear conditions occurring in the engine. VMs use will result in lowering bulk oil viscosity under the actual running conditions of the vehicle resulting in lower viscous pumping losses for any given viscosity grade. All VMs are affected by some amount of shear thinning (A temporary loss in viscosity with the shear field formed during the engine operation) [22].

This reduction in viscosity can translate to fuel economy benefits, especially in hydrodynamic and mixed lubrication operations. The use of FM helps the effort to reduce the viscosity to a greater extent by protecting boundary lubricant friction. FM will come into action on their own as (and when) oil viscosity is reduced to improve fuel efficiency. FM reduces light surface contacts (sliding and rolling) that occurs in engine operation. FM also provides a reduction in friction under boundary or mixed lubrication conditions where there is surface-to-surface contact.

The engine oil used must protect the engine parts that it lubricates. In some cases this protection is in the form of a fluid film that keeps opposing surfaces separated [24]. This can be taken care of by using effective combination of FM & VMs [25]. VMs used should be stable at higher temperatures and should be helpful in maintaining film strength around the temperature profile of the new generation engines. FM used should be able to reduce friction between the moving parts in different regions of the engine.

2.1.1 Experimentation, Observation and Inference

Three VMs are used in this study. 2 VMs are non-dispersant olefin copolymers with different SSIs (Shear Stability Index) {35, 25} and other is dispersant olefin copolymer {SSI-24}. Shear Stability index is defined as the resistance of particular VI improver to mechanical degradation. All 3 VMs are analyzed for active content by dialysis and ^{13}C NMR technique. The samples were subjected to dialysis by hexane to separate out active content and base oil. The weight percentage of active content and base oils are reported in Table 2.5. All the three VMs are also evaluated for molecular weight determination by Gel Permeation Chromatography technique. The samples are dissolved in THF (Tetra Hydro Furan) and are evaluated by GPC for molecular weight profiles (Mp, Mn & Mw) in daltons against polystyrene as standard. The results obtained are tabulated in Table 2.6. The active content and base oil for each of the 3 VMs are analyzed by ^{13}C NMR technique and results were tabulated in Table 2.7.

Table 2.5 Active Content of VMs by Dialysis.

Sample	**Components**	**Dialysis (Wt. %)**
VM 1 (25 SSI)	Active content	11.50
	Base Oil	88.50
VM 2 (35 SSI)	Active content	11.00
	Base Oil	89.00
VM 3 (24 SSI)	Active content	11.40
	Base Oil	88.60

Table 2.6 Molecular weight Distribution of VMs by GPC.

Components		**(Mp)**	**(Mn)**	**(Mw)**
VM 1	Active Content	184254	103227	176758
	Diluents	622	617	635
VM 2	Active Content	261935	136175	229722
	Diluents	635	623	645
VM 3	Active Content	154923	83051	153092
	Diluents	626	605	615

Table 2.7 ^{13}C NMR analysis of VMs (Active Content & Base oil).

Sample	Active Content	Base Oil
VM 1	Ethylene-propylene copolymer Ethylene content [46.2 (wt %), 56.3 (mole %)] Propylene content [53.8(wt %), 45.7 (mole %)]	Ca - 5.7% Cp - 71.3% Cn - 23.0%
VM 2	Ethylene-propylene copolymer Ethylene content [47.3 (wt %), 57.4 (mole %)] Propylene [52.7 (wt %), 42.6 (mole %)]	Ca - 6.0% Cp - 73.3% Cn - 20.7%
VM 3	Aromatic polyamine derivative Ethylene-propylene copolymer Ethylene content [52.7 (wt %), 62.0 (mole %)] Propylene [47.3 (wt %), 38.0 (mole %)]	Ca - 5.7% Cp - 71.3% Cn - 23.0%

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Friction Modifiers selected for the study comprise of two organo-molybdenum compounds, one with sulphur and other without sulphur content. The basic data for friction modifiers analyzed on density meter, ICAP and XRF for the two FMs were reported in Table 2.8.

Table 2.8 Basic Data for selected friction modifiers.

Parameters	**FM 1**	**FM 2**
Density @ 15 ^{o}C	1.08 g/cm3	1.06 g/cm3
Molybdenum Content	8 %	10 %
Nitrogen Content	3 %	4 %
Sulphur Content	-	11 %

2.2 Antioxidants

To improve fuel economy, many OEMs strategized to increasing oil temperature to reduce oil viscosity. Though this may appear to be a simple change, increasing oil temperature accelerates oil oxidation [26]. Oxidation being the main cause of engine oil degradation, it is the most relevant that the oxidation stability be maximized [27]. Mechanism of oxidation is elucidated as a prelude to the work carried out and results obtained thereof. The operating temperatures in the running engine reaches up to 300-350 °C. At such high temperatures the engine oil containing mainly hydrocarbons undergoes oxidation which is a self-accelerating auto-oxidation process which proceeds by free radical mechanism [28-29].

There are different stages of Oxidation process.

- ■ Initiation
- ■ Propagation
- ■ Branching
- ■ Termination

2.2.1 Initiation

The first step is the free radical formation, which starts with the reaction of hydrocarbon molecule RH with oxygen at higher temperatures resulting in the removal of hydrogen and production of the alkyl free radical as given in the equation below.

$$RH + O_2 \rightarrow R_* + HO_*$$

Under the influence of heat, light or nuclear radiations more radicals can be formed as given below.

$$R\text{-}R \rightarrow R_* + R_*$$

2.2.2 Propagation

The above reaction continues to advance by forming peroxide radicals ROO_* due to reaction between alkyl radical and oxygen, which can further generate more and more free radicals and hydroperoxides ROOH.

$R_* + O_2 \rightarrow ROO_*$

$ROO_* + RH \rightarrow ROOH + R_*$

$HO_* + RH \rightarrow H_2O + R_*$

Thus the free radical R_* can react with large number of hydrocarbon molecules to create equal number of hydroperoxide molecule.

2.2.3 Branching

The hydroperoxide molecules are unstable which get spitted to produce two new free radicals and the chain reaction branches continue.

$ROOH \rightarrow RO_* + HO_*$

$RO_* + RH \rightarrow ROH + R_*$

$HO_* + RH \rightarrow H_2O + R_*$

The free radicals formed further react with other hydrocarbons or the hydrogen present within them and the cycle continues and branching occurs.

2.2.4 Termination

The concentration of hydroperoxides goes on increasing until the total hydrocarbon is consumed. This termination in the final phase makes the degradation process to stop which results in the formation of ketones and aldehydes as given. Once formed, the hydroxyl and alkoxy radicals abstract the hydrogen atoms in unselective reactions:

$R\text{-}CH_3 + OH_* \rightarrow R\text{-}CH_{2*} + H_2O$

$R\text{-}CH_2\text{-}R' + OH_* \rightarrow R(R')CH_* + H_2O$

$R\text{-}CH_2O_* + R\text{-}CH_3 \rightarrow R\text{-}CH_2OH + RH_2C_*$

While secondary and tertiary alkoxy radicals form aldehydes and ketones.

$R(R^1)CHO_* \rightarrow RCHO + R^1{}_*$

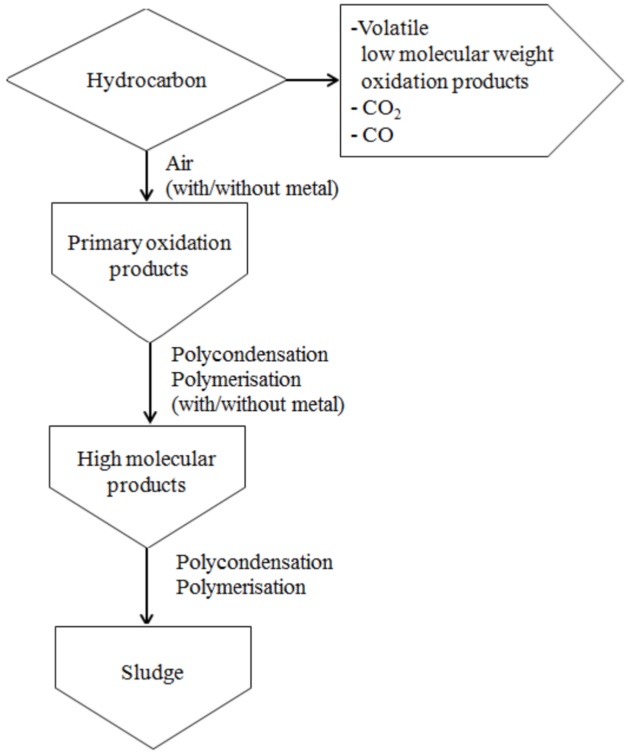
$$R(R^1)(R^2)\text{-}C\text{-}O_* \rightarrow R^1COR^2 + R^3_*$$

The free radicals formed also react by two additional ways to stop the oxidation process.

$$R^* + R^* \rightarrow R\text{-}R$$

$$R^* + ROO^* \rightarrow ROOR$$

At higher temperatures generally above 120 °C acids are generated which further increases the viscosity of the medium due to further transformation by polymerization and polycondensation, thereby resulting in high molecular weight products so called sludge. This type of reactions occur very fast or catalytically in the presence of metallic engine parts. Varnish formation occurs on metallic parts as thin shiny film. This results in deposit formation in engine parts leading to engine failure. A schematic representation of oxidative degradation process was given in Fig. 2.4.



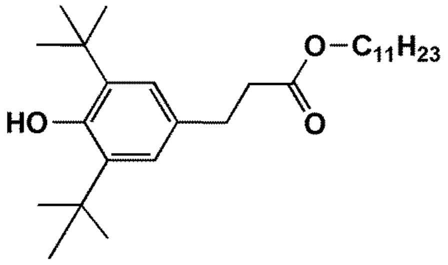
Source : R. M. Mortier et al. (eds.), Chemistry and Technology of Lubricants, Book, Page 106.

Figure 2.4 Oxidative Degradation process of the engine oil.

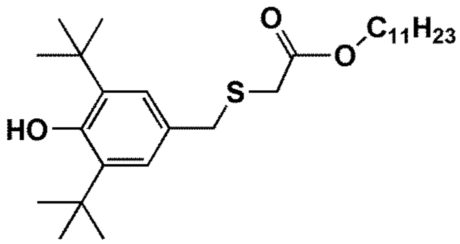
Hence there is a need to stop the oxidative degradation process of the lubricant. This process can be inhibited/delayed by the addition of antioxidants [30]. These should be capable to inhibit the formation of alkyl & alkylperoxy radicals, hydroperoxides, alkoxy and hydroxyl radicals to stop the oxidation process.

2.2.5 Experimentation, Observation and Inference

For the present study two types of antioxidants viz., aminic and phenolic were used out of which Aminic antioxidants (alkylated diphenyl amines) were four in number with varying combinations of Alkyl groups (butyl, octyl, nonyl, napthyl, undecyl). Phenolic antioxidants were two in number differentiated on sulphur content (P_1 doesn't contain Sulphur and P_2 contains 0.5 % Sulphur). The structural elucidations of the selected antioxidants as elucidated by ^{13}C NMR are illustrated in the Fig. 2.5 (a, b).

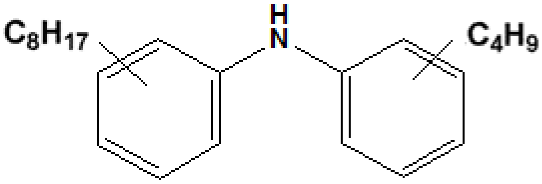


P_1 - Undecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate

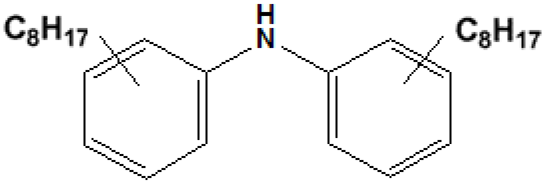


P_2 - Undecyl [(3,5-di-tert-butyl-4-hydroxybenzyl)sulfanyl]acetate

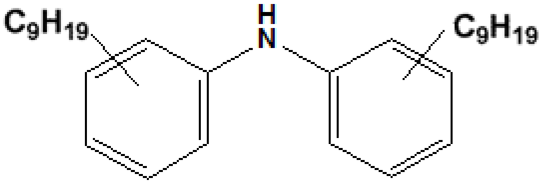
Figure 2.5 (a) Structures of selected Phenolic antioxidants by ^{13}C NMR.



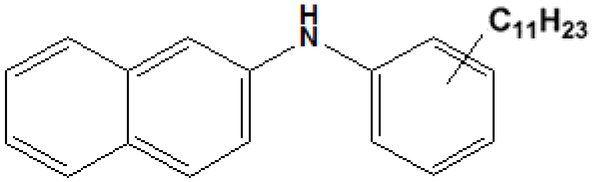
A_1 - Butyl Octyl Diphenylamine
N-(4-butylphenyl)-4-octylbenzenamine



A_2 - Di Octyl Diphenylamine
[bis(4-octylphenyl)amine]



A_3 - Di Nonyl Diphenylamine
[bis(4-nonylphenyl)amine]



A_4 - Undecylated Phenyl Alpha Naphthylamine
[N-(4-undecylphenyl)naphthalen-2-amine]

Figure 2.5 (b) Structures of selected Aminic Antioxidants by ^{13}C NMR.

The thermal stability profile by TGA for the antioxidants is shown in Fig. 2.6. The procedure for experiment remains same as for base oils. To understand better the temperatures at different weight % losses are calculated and tabulated in Table 2.9.

For determining oxidation stability, 3-5 mg of sample in pan is subjected to a temperature ramp of 10 °C/min from 40-300 °C under continuous flow of oxygen at 50 ml/min in DSC cell and OOT values are evaluated [31]. The OOTs of selected antioxidants were plotted in Fig. 2.7. Observing the curves (Fig. 2.6 & 2.7) and the tabulated values in Table 2.9, it is inferred that phenolic antioxidant (P_2) reported higher OOT and thermal stability than phenolic antioxidant (P_1). Also among the aminic antioxidants the thermal stability by TGA for antioxidants is in the order of $A_4 > A_3 > A_2 > A_1$ and the oxidation stability as reported by OOT (Fig. 2.7) is in the order of $A_3 \sim A_4 > A_2 > A_1$.

Table 2.9 Temperature Data of Antioxidants at different % Wt. loss.

% Weight Loss	**A_4**	**A_3**	**A_2**	**A_1**	**P_1**	**P_2**
5	261	243	242	198	196	245
10	285	269	261	217	214	266
20	311	296	282	232	234	283
30	327	312	295	252	245	292
40	338	324	304	263	254	298
50	347	334	311	273	261	304
60	355	341	317	281	267	310
70	362	348	323	288	212	317
80	368	355	328	296	277	327
90	375	361	332	303	281	346
95	377	365	335	307	284	365

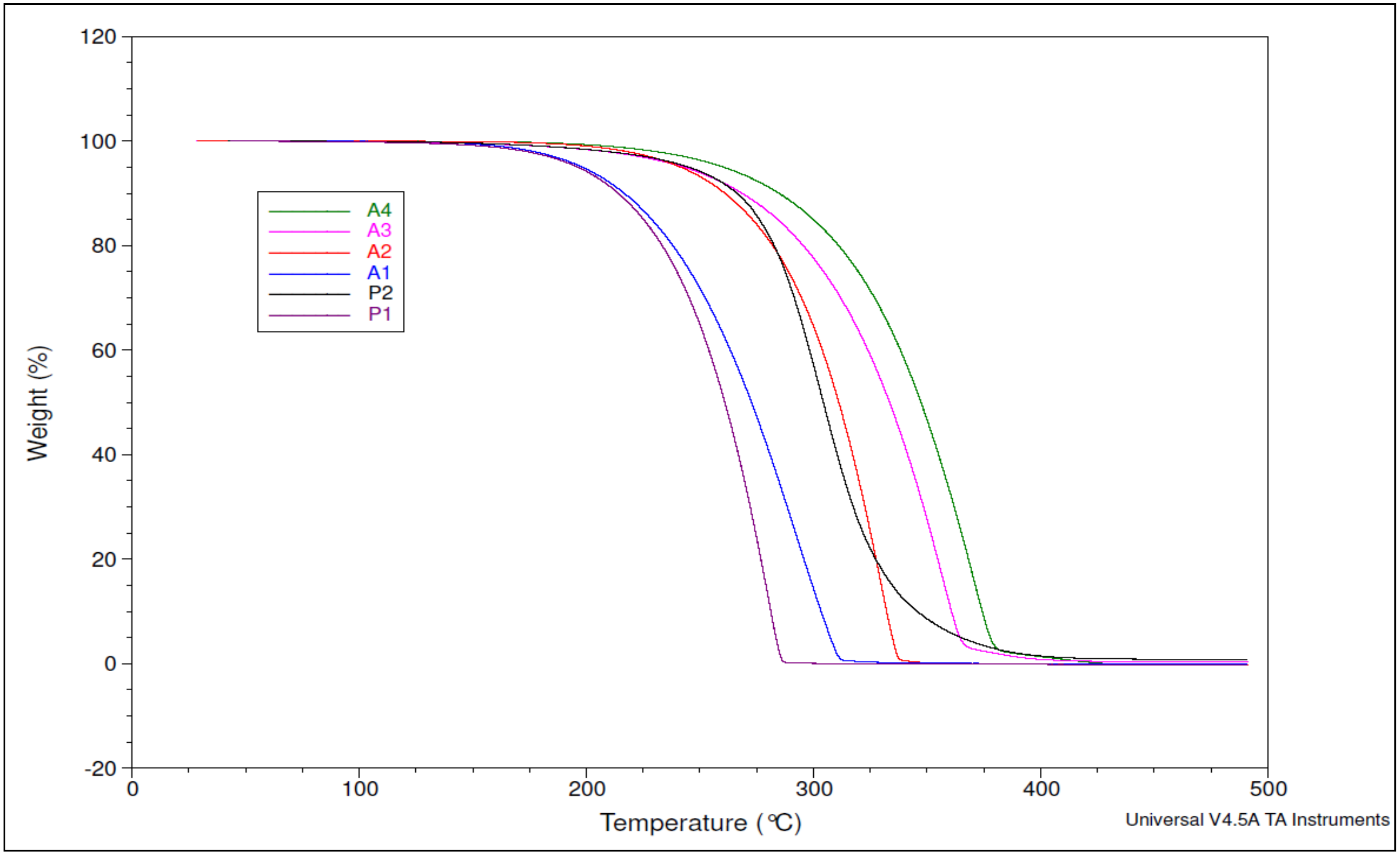


Figure 2.6 Weight loss curves for different antioxidants on TGA.

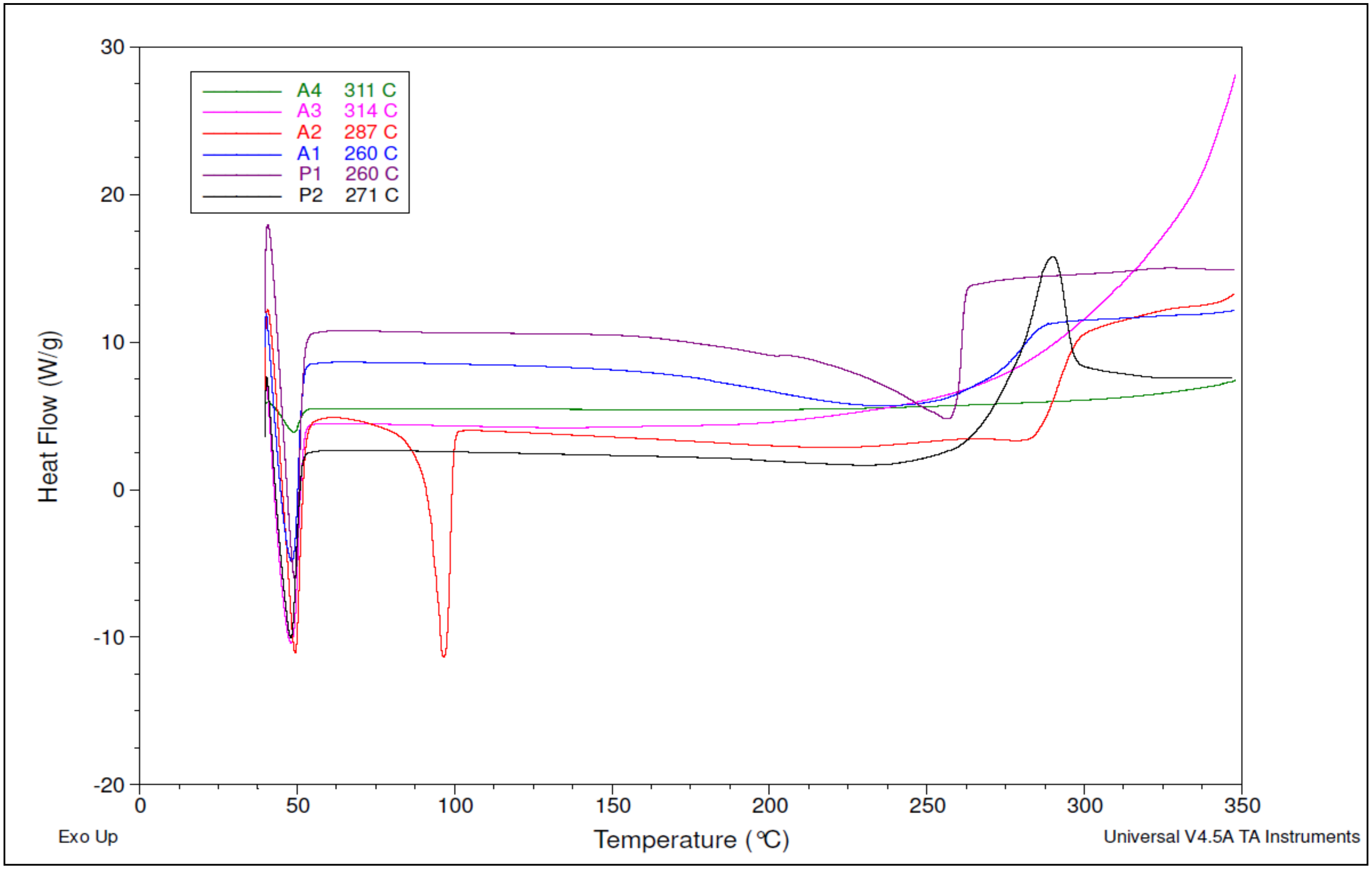


Figure 2.7 OOT curve of antioxidants used by DSC.

2.2.6 Compatibility of Base oil & Antioxidant

The designated base oil mixtures are doped with the selected aminic antioxidants at different treat levels for the determination of compatibility studies. All the samples containing antioxidant in 5 different treat levels (0.1 %, 0.2 %, 0.3 %, 0.4 %, 0.5 %) with each of the base oil mixtures were tested for oxidation stability by DSC. Near about 80-100 samples are optimized for screening of best base oil mixture with its compatibility of selected antioxidants. Oxidation stability is determined by determining OOT by the DSC instrument. The values of OOTs are tabulated in Table 2.10 & 2.11 for the aminic antioxidants with the base oils in different treat rates. While observing the Table 2.10 & 2.11, Group I Base oil mixture have reported higher OOTs values due to the presence of sulphur in it as earlier explained.

The response of all selected antioxidants w.r.t base oil mixtures is observed in the order of Gp IV ~ Gp III > Gp II > Gp I and the response of all the base oil mixtures w.r.t to antioxidants is in the order of $A_4 > A_3 > A_2 \sim A_1$. Therefore it is clear that the higher group base oils have given better response for the antioxidants (seen as more rise in OOT from base oil mixtures) and the antioxidant A_4 & A_3 giving better responses with base oil mixtures followed by A_2 & A_1. Aminic antioxidants with base oil mixtures were also evaluated for thermal stability to know about the collective (thermal & oxidative) stability response.

For this all 4 selected Aminic antioxidants at a treat rate of 0.5 % in all 4 base oils were tested for thermal stability on TGA and thermograms are depicted in the Fig. 2.8 (a-d). To understand better the temperatures at different weight % losses are calculated and tabulated in Table 2.12 (a-d). It is observed that all the selected aminic antioxidants have enhanced the thermal stability of the base oil mixtures (black curve) except for A_2 (red curve) in which a decrease in thermal stability was observed. Aminic antioxidants response in the base oil mixtures are in the order of $A_4 > A_3 > A_1 > A_2$ in all the base oil mixtures except for Group I base oil mixture, in which the response was in the order of $A_1 > A_3 \sim A_4 > A_{2.}$

Table 2.10 OOTs in °C for base oil mixture doped with Antioxidants A_1 and A_2.

Base Oil Mixture	A_1					A_2				
	0.1%	0.2%	0.3%	0.4%	0.5%	0.1%	0.2%	0.3%	0.4%	0.5%
I (237)	221	237	242	255	253	248	246	251	261	263
II (197)	213	219	222	222	224	217	218	224	222	226
III (199)	216	220	222	223	223	218	222	226	225	224
IV (198)	217	237	223	225	233	231	224	229	227	228

Table 2.11 OOTs in °C for base oil mixture doped with antioxidants A_3 and A_4.

Base Oil Mixture	A_3					A_4				
	0.1%	0.2%	0.3%	0.4%	0.5%	0.1%	0.2%	0.3%	0.4%	0.5%
I (237)	229	256	255	266	269	220	240	248	248	257
II (197)	216	219	223	223	225	221	229	232	238	244
III (199)	217	222	225	227	227	223	231	233	237	239
IV (198)	220	224	226	227	235	226	234	239	239	242

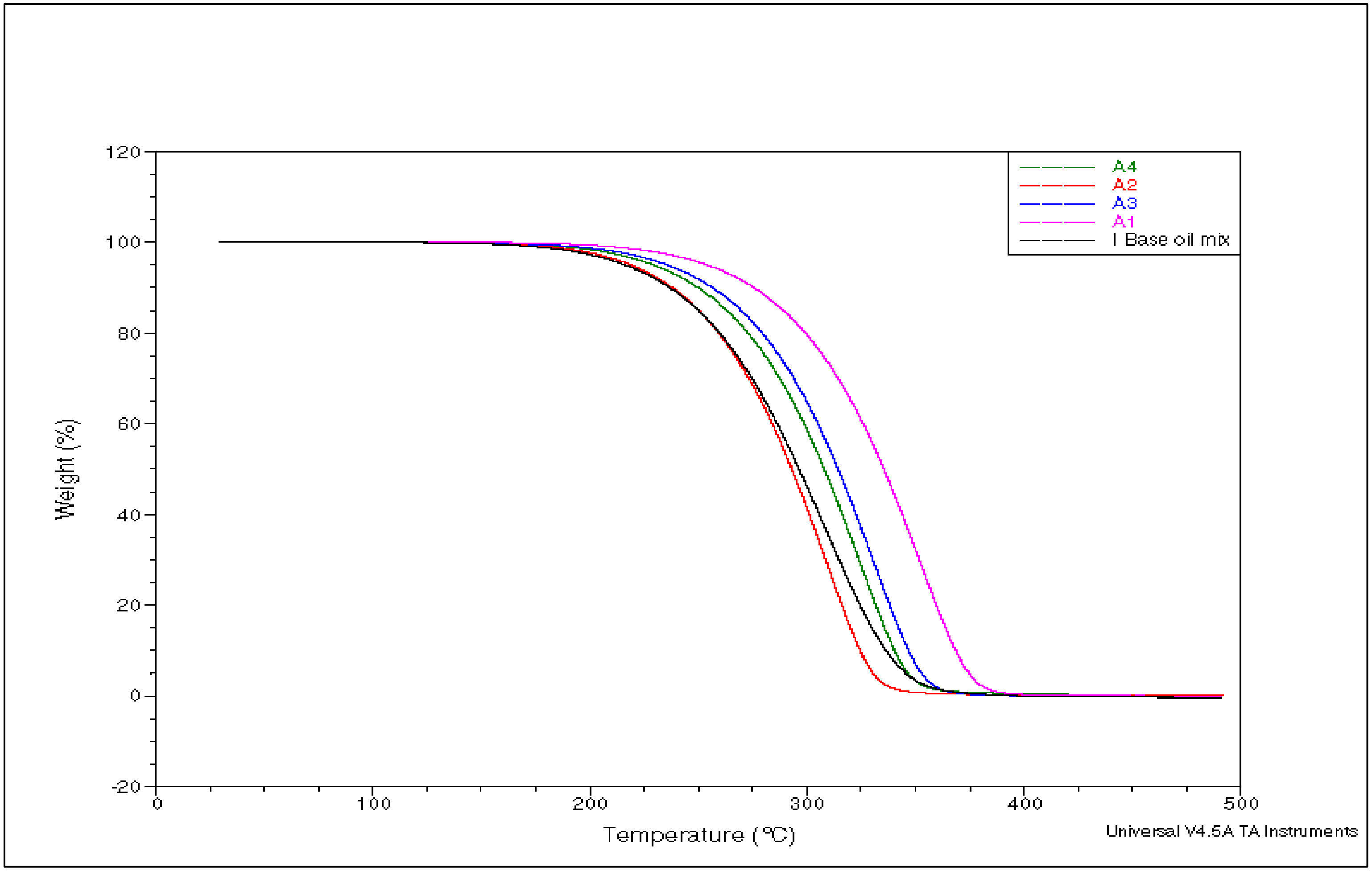


Figure 2.8 (a) Thermal stability curves for aminic antioxidants in Group I base oil mixture.

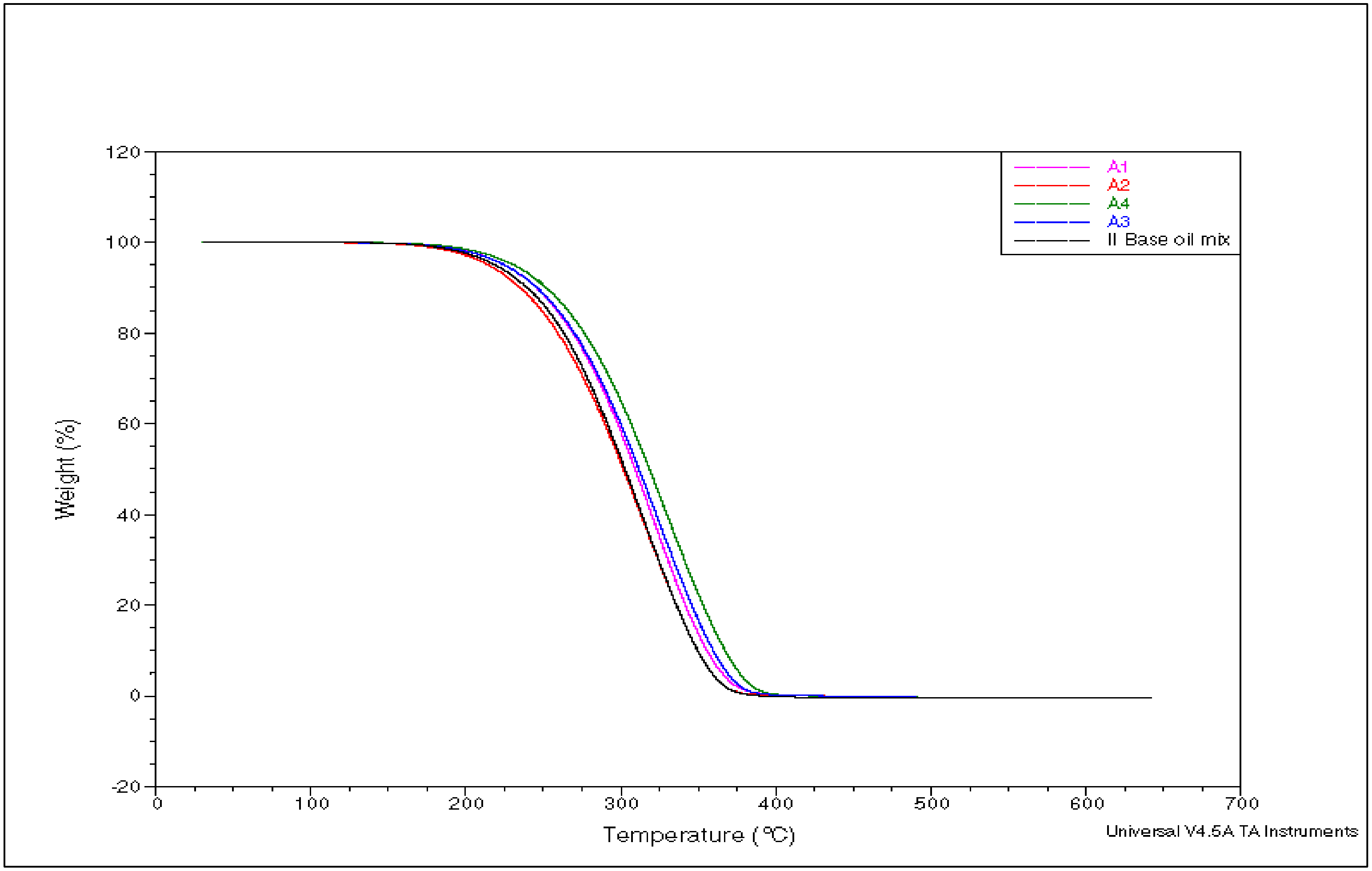


Figure 2.8 (b) Thermal stability curves for aminic antioxidants in Group II base oil mixture.

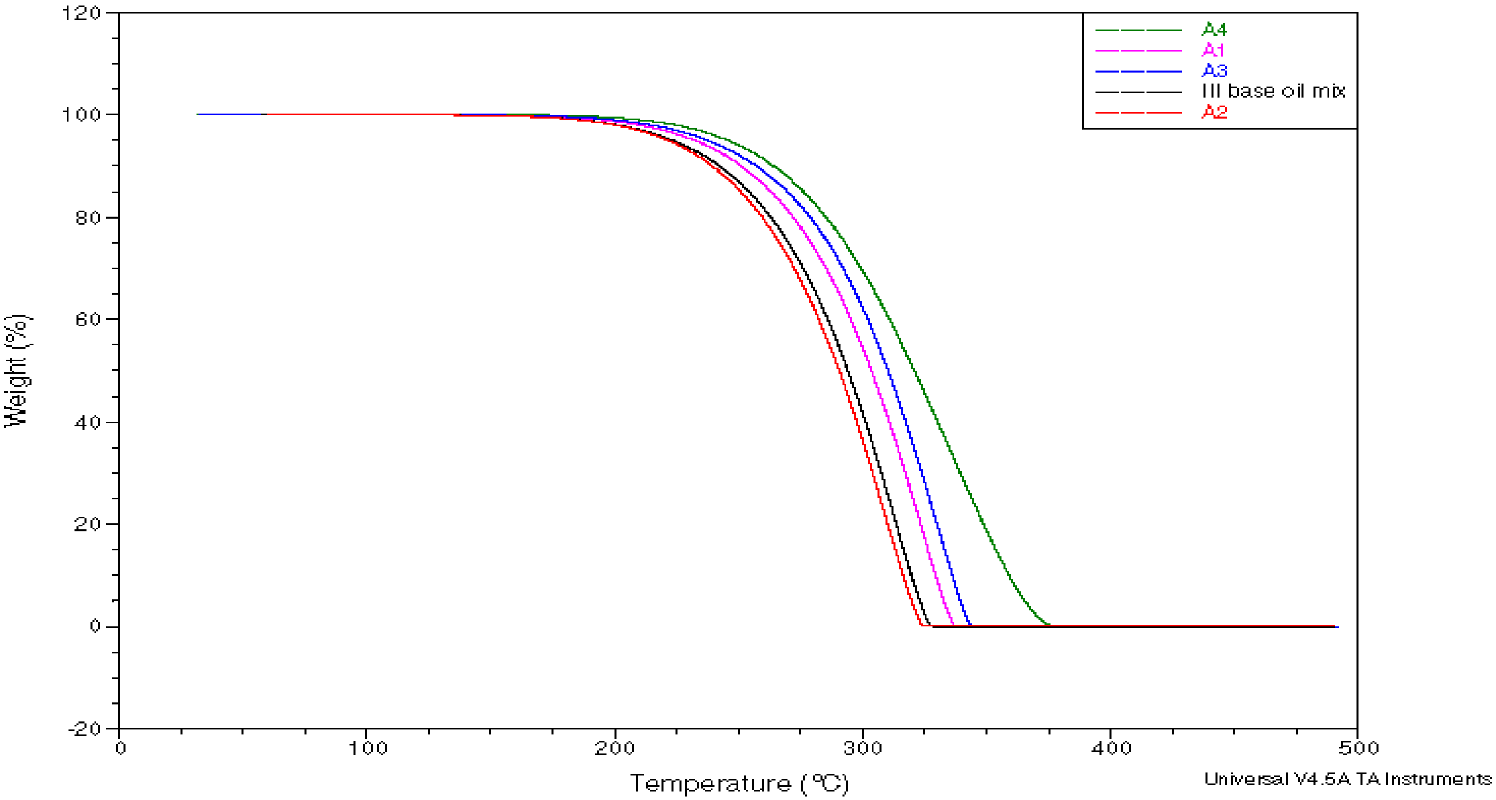


Figure 2.8 (c) Thermal stability curves for aminic antioxidants in Group III base oil mixture.

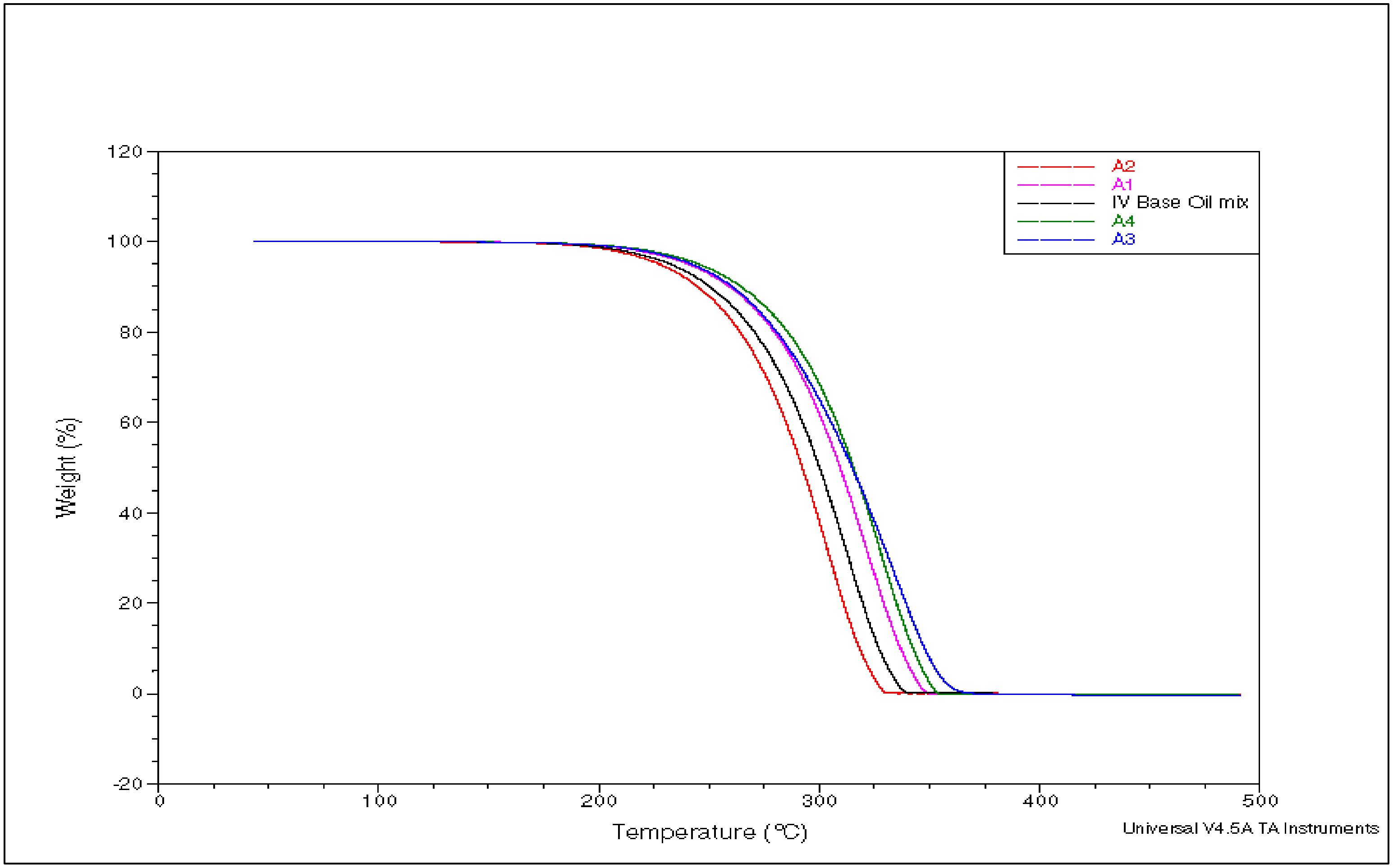


Figure 2.8 (d) Thermal stability curves for aminic antioxidants in Group IV base oil mixture.

Table 2.12 (a) Temperature data of aminic antioxidants in Group I base oil mixture at different % Wt. loss.

% Weight Loss	**A_1**	**A_2**	**A_3**	**A_4**
5	254	236	225	229
10	276	257	244	250
20	299	279	265	273
30	314	294	279	288
40	326	305	290	299
50	335	314	299	308
60	344	323	307	316
70	352	330	315	324
80	360	338	322	332
90	369	347	331	340
95	375	353	337	347

Table 2.12 (b) Temperature data of aminic antioxidants in Group II base oil mixture at different % Wt. loss.

% Weight Loss	**A_1**	**A_2**	**A_3**	**A_4**
5	225	215	225	231
10	246	235	246	252
20	269	259	270	276
30	285	276	287	293
40	298	290	300	307
50	309	302	312	319
60	320	313	323	330
70	330	324	334	341
80	342	336	346	353
90	356	350	360	367
95	365	358	369	377

Table 2.12 (c) Temperature data of aminic antioxidants in Group III Base oil mixture at different % Wt. loss.

% Weight Loss	**A_1**	**A_2**	**A_3**	**A_4**
5	224	222	232	238
10	242	239	251	257
20	263	260	272	279
30	276	272	285	292
40	286	282	295	302
50	294	291	304	310
60	301	298	311	317
70	308	304	317	324
80	314	310	323	330
90	320	316	329	336
95	323	320	333	339

Table 2.12 (d) Temperature data of aminic antioxidants in Group IV base oil mixture at different % Wt. loss.

% Weight Loss	**A_1**	**A_2**	**A_3**	**A_4**
5	232	227	241	245
10	251	245	259	265
20	271	264	280	286
30	283	276	292	298
40	292	285	302	308
50	300	292	309	316
60	307	300	322	316
70	313	305	329	323
80	320	311	335	329
90	327	318	343	337
95	332	323	347	342

The Gp I based oil is phasing out in many refineries due to its bad impact on the environmental emissions as a result of higher sulphur content. Group IV base oils are fully synthetic and are used only for some specialized applications where it is needed. Group III base oils are considered to be semi-synthetic and are also superior in properties than Group II base oils. Based on the above discussion and extensive work on the base oil mixtures thermal stability and oxidation stability and the literature, group III base oil system is selected due to its consistent thermo-oxidative stability over the other group base oils, the iso-paraffinic content is also more in group III than group IV which is also useful in giving better response to the additives [32-35].

The next chapter will deal with the design of engine oil or in other words formulating the energy efficient engine oil and experimentation details regarding the validation of the formulated oils in laboratory bench tests.

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Chapter 3

Designing Energy Efficient Engine Oil

3.0 Design Protocol

In view of the requirements of thermal and oxidative stabilities of engine oil explained in chapter 1 and chapter 2, design and workout of formulation of engine oil is carried out. Newer engine designs have added an additional stress on engine oil to function properly in reduced space under increased temperatures [1]. The prime factor in the development of new generation engine oil, therefore, is evaluation and validation of the crankcase lubricant in withstanding the rigors of high temperature and oxidation environment. This is in addition to the major requirement for reducing friction and maintaining film strength of the lubricant in operation.

Recent engine design changes put more stress on the lubricant that circulates in these engines which work under temperatures ~350 ˚C [2]. In such environment engine oil has to be designed keeping in mind of the following key factors such as thermal stability, oxidative stability, volatility and also its heat dissipating characteristics.. This engine oil should be capable of

- Longer drain intervals – low oil consumption – low volatility
- Better deposit control – high oxidative stability
- Lower emissions – low SAP technology
- Better lubricity and cooling capacities

The three main mitigation components (additives of importance) needed in the designing of engine oil are – Viscosity Modifier (VM), Friction Modifier (FM) & Antioxidants (AO). This chapter focuses on VM & FM study (film forming capacity & friction reduction) in Part I and Antioxidants study (oxidative inhibition) in Part II; all the other additives being combined and added as partial package.

3.1 Part I – Viscostiy Modifier & Friction Modifier Study

This segment of the chapter deals with the frictional studies data and film strength of engine oils with respect to thermo-oxidative stability of engine oils. Fuel economy is becoming a focal point for the lubrication industry. Synergism of VM and FM are explained in this part by evaluating their properties regarding the oxidative stability and tribological behavior. Effect of VM on film strength, Effect of FM on coefficient of friction and the added action of FM as oxidative inhibitor will be the main areas covered in this part. Good engine oil should have a low coefficient of friction along with a good thermo-oxidative stability while maintaining good film strength.

Engine oil samples formulated under this study comprise of an additive package (consisting of detergents, pour point depressant, antifoam agents, corrosion inhibitors, etc.,) apart from FMs and VMs mixed in a Group III base oil system. As discussed in earlier chapter, VM selected in this study comprise of a non-dispersant olefin copolymer with 2 different SSIs (Shear Stability Index) and a dispersant olefin copolymer. FMs selected in this study comprises of 2 different Organo-molybdenum compounds, one with sulphur and other without sulphur content.

The viscometrics of all the optimized blends have been kept same for better comparison. The engine oil samples are optimized with different FMs and VMs combination as illustrated in Table 3.1. Blends optimized as given are tested for different performance properties. The performance property validated in this part is related to engine oils tribological behavior. This includes film strength/thickness, coefficient of friction mainly in addition to their effect on thermo-oxidative stability. Elasto-hydrodynamic (EHD) film thickness [3] and coefficient of friction (SRV Tribometer) [4] are evaluated under tribological behavior of the samples. Thermo-oxidative properties are evaluated using PDSC and DSC method and are correlated with the tribological behavior.

Table 3.1 Blend compositions with different VM & FM.

Blend	**Compositions**
A	Base Oil + Additive Package + VM 1
B	Base Oil + Additive Package + VM 1 + FM 1
C	Base Oil + Additive Package + VM 1 + FM 2
D	Base Oil + Additive Package + VM 2
E	Base Oil + Additive Package + VM 2 + FM 1
F	Base Oil + Additive Package + VM 2 + FM 2
G	Base Oil + Additive Package + VM 3
H	Base Oil + Additive Package + VM 3 + FM 1
I	Base Oil + Additive Package + VM 3 + FM 2
VM 1&2	Non – Dispersant Copolymer with different SSI (25 & 35)
VM 3	Dispersant Copolymer with 24 SSI
FM 1	Organo Molybdenum compound without sulphur
FM 2	Organo Molybdenum compound with sulphur

3.1.1 Measurement of film thickness

EHD Machine Details

The EHD instrument is a fully automated computer controlled instrument for evaluating the film thickness of engine oils in the Elastohydrodynamic (EHD) lubricating regime. This instrument is capable of measuring lubricant film thickness as low as 1 nm with a precision of +/- 1 nm. Actual simulation of contact pressures and shear rates which are supposed to found in, gears, rolling element bearings and cams of engine can be simulated in this equipment.

An initial film of oil is placed on a glass disk and is rotated against a steel ball. The parameters of the test profile are temperature, load and rotation speed which are controlled by computer. The instrument measures the lubricant film thickness in the contact formed in between a ¾” (19.05 mm) diameter steel ball and a rotating glass disc by optical interferometery. The image of the instrument has been illustrated in Fig. 3.1. The lubricant film thickness at any point in the image can be accurately calculated by measuring the wavelength of the light at that contact. Normally the system measures the wavelength of the light returned from the central plateau of the contact and hence calculates the central film thickness.

The control software runs on a standard computer and allows the user to easily define a test profile containing a sequence of temperatures, loads and speeds. After setting the initial film thickness, the selected profile steps the instrument through the test sequence, recording data as required, without any intervention by the user. The test is conducted at two temperatures 60 °C and 100 °C. Since the engine oil circulates in the running engine from hot areas to cold areas regularly, two temperature profiles have been selected for the test.

Source : http://pcs-instruments.com/product/ehd-elasto-hydrodynamic-lubriction-2/

Figure 3.1 Image of EHD instrument.

Experimentation, Observation and Inference

All the 9 optimized blends were evaluated on EHD instrument for film thickness. EHD film strength data is illustrated in graphical form in Fig. 3.2. Also a typical graph of EHD film thickness measurement can be seen in Fig. 3.3. From the data in graph, it is observed that the film thickness is directly related to the VM and FM combination. All the three VM used have shown significant improvement in the film thickness strength with FM 2 as compared to FM 1 and blends without FM. The synergism of individual VM with FM in the film thickness is in the order of VM 3 > VM 2 > VM 1. It was observed that VM with high SSI has the ability to form good film strength than the VM having lower SSI among the non-dispersant VM. The dispersant VM has given even better strength in film thickness than non-dispersant VM though having a lower SSI.

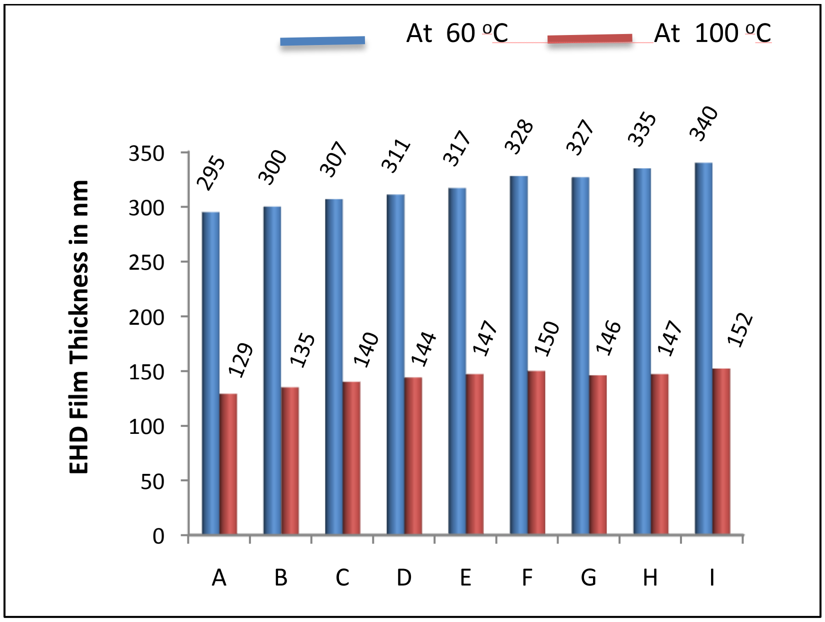


Figure 3.2 EHD film thickness data.

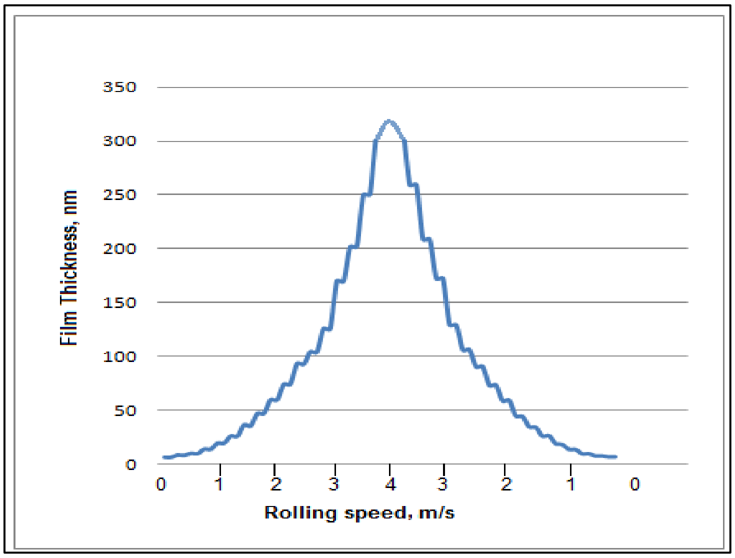


Figure 3.3 Typical graph of EHD film thickness.

3.1.2 Coefficient of friction

SRV Machine Details

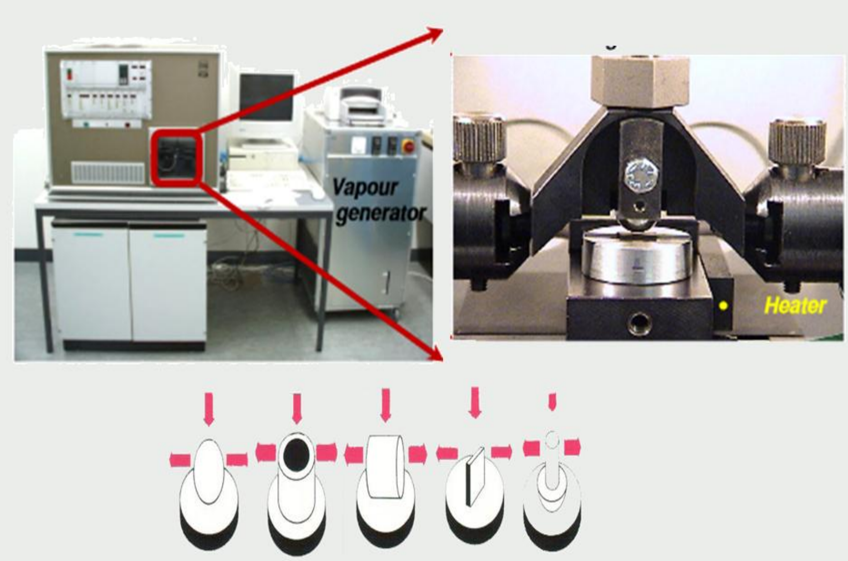
For evaluating frictional characteristics the coefficient of friction is calculated by evaluating the sample in the Linear Oscillating SRV Tribometer. DIN 51834 is the standard test method for measuring coefficient of friction. The linear oscillating tribometer can provide information on friction and wear behavior of materials and coatings which are lubricated with engine oils, greases. Coefficient of friction being the measurable index in this instrument, it should be as low as possible for a better performance of engine oil. In other words, the role of the lubricant in friction reducing characteristic can be explained with the help of this tribometer.

This instrument is capable of simulating short linear sliding (fretting) and a variety of field conditions, in particular reference to relative humidity and varying temperature that are actually run in running automotive engine. The SRV linear oscillating tribometer measures the friction phenomenon between a steel ball and plate after placing a sample of oil on plate. The steel ball is vibrated / oscillated at a given frequency and a force is applied according to the test method. The test profile includes load, frequency and temperature which are controlled by computer. The SRV test can determine friction between materials actually used in an engine (for example, by taking a slice of the cylinder liner and the piston rings). The equipment setup with cross sections of sample test area and different points of contact have been illustrated in Fig. 3.4.

Experimentation, Observation and Inference

Coefficient of friction data for the optimized blends are shown in a graphical form in Fig. 3.5. This data is generated at two temperatures 60 °C and 100 °C. The load of the test was maintained at 300 N with 1 mm amplitude and was run for 1 hour at the test temperature. It is observed that the coefficient of friction in general, is decreased by the addition of FM to the blends A, D & G.

The blends B, E & H are optimized with FM 1 and the blends C, F & I are optimized with FM 2. FM 2 has been observed to provide better performance in reducing friction than FM 1.



Source : http://www.novaswiss.ch/webautor-data/56/1--High-frequency-oscillating-SRV-tribometer_Dez12.pdf

Figure 3.4 Equipment setup – Linear oscillating tribometer.

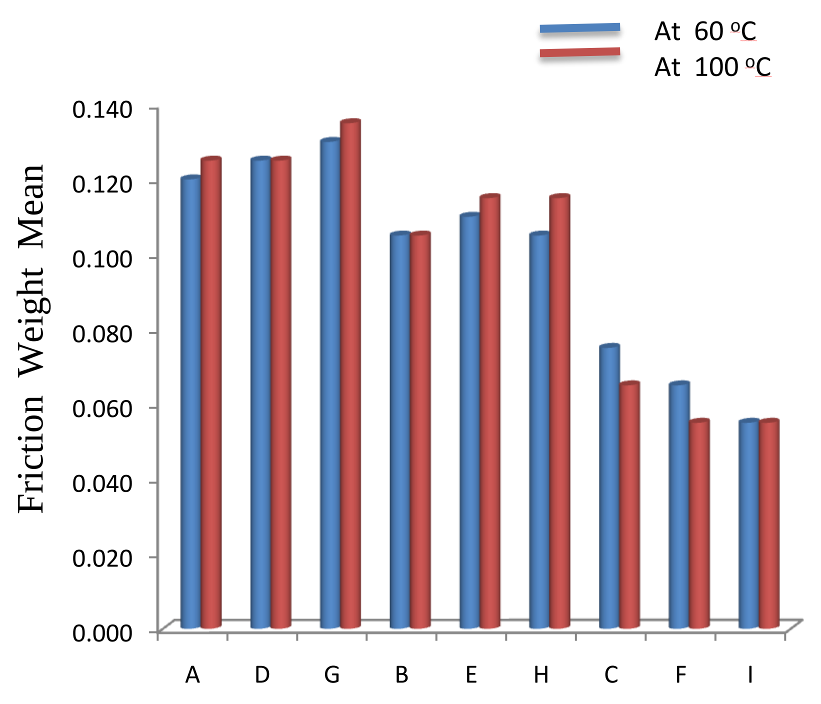


Figure 3.5 Coefficient of friction for the blends.

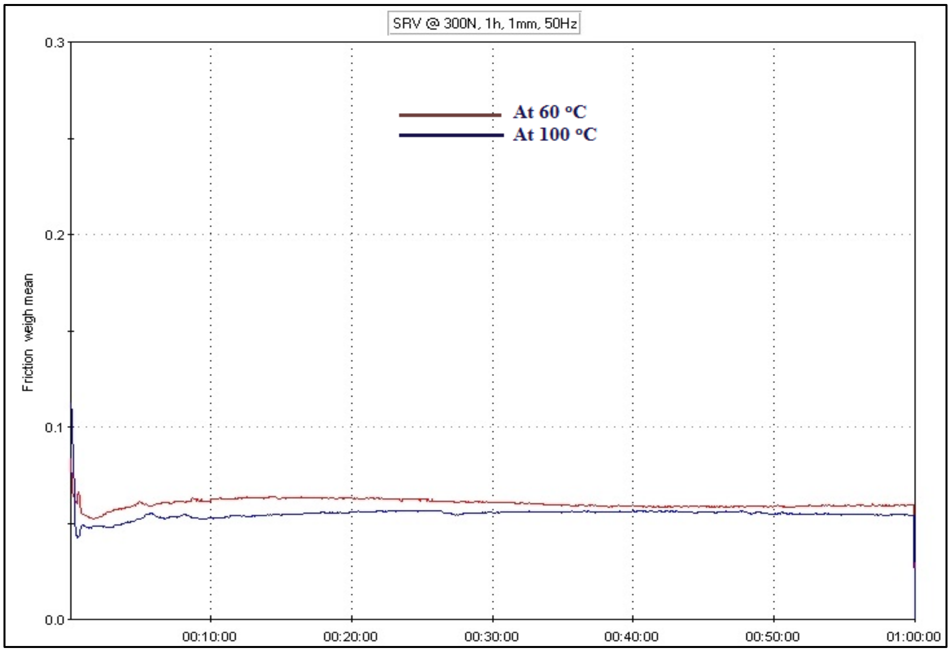


Figure 3.6 Coefficient of friction graph from the instrument.

The best synergism for VM and FM combination was seen in Blend I (VM 3, FM 2) combination. The typical coefficient of friction graph obtained from the instrument can be seen in Fig. 3.6.

3.1.3 Oxidation Induction Time OIT)

PDSC equipment details - Experimentation, Observation and Inference

Thermo-oxidative stability is very important attribute for engine oil used for new generation engines. Pressure Differential Scanning Calorimeter (PDSC) is an excellent test to determine the thermo-oxidative behavior of the samples. It determines the ability of the sample to inhibit oxidation under pressurized oxygen at high temperatures. 3-5 mg of sample in a pan in pressurized DSC cell is subjected to 500 psi oxygen pressure at a constant temperature of 210 °C. The above blends are thus evaluated for Oxidation Induction Time (OIT) by PDSC [5]. OIT is the time in minutes reported up to which the blend can withstand oxidation under pressure at high temperatures. Higher the OIT, better is the thermo-oxidative stability. The typical traces obtained from PDSC for these blends are given in Fig. 3.7.

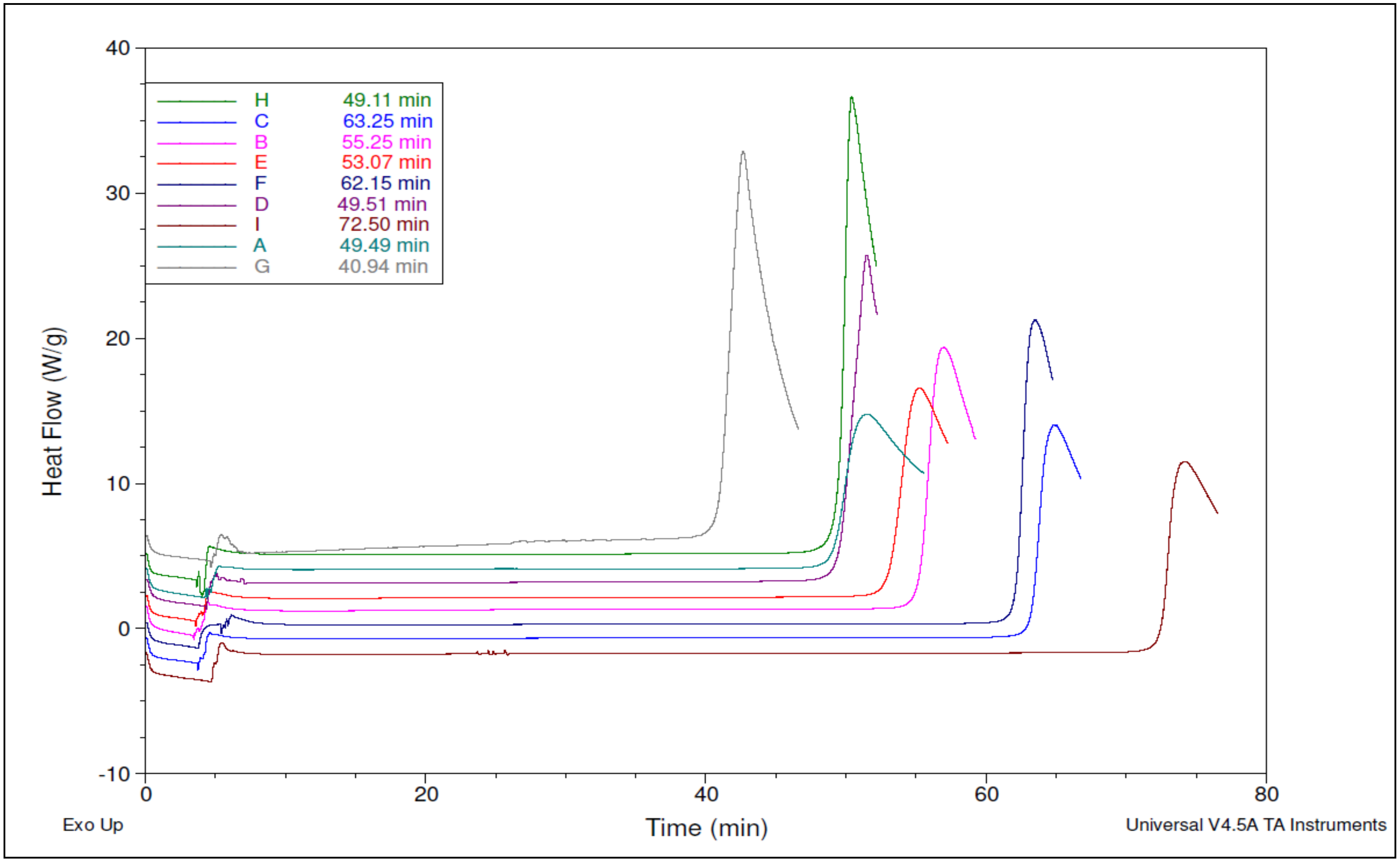


Figure 3.7 OIT graphs of blends by PDSC.

From the comparison of the traces it is very clear that the oxidation stability of blends is greatly enhanced by the addition of FM 2 when compared to FM 1 followed by the blends without any FM. These results are in line with the results obtained previously for film thickness and coefficient of friction. Therefore a friction modifier enhances the oxidation stability of the engine oils in which it is added. PDSC may be used as an advanced tool for identifying the best optimized blends which can reduce friction and form a good stable film thickness between the engines moving parts.

3.1.4 Oxidation Onset Temperature (OOT)

Experimentation, Observation and Inference

OOT is determined by DSC instrument according to ASTM E2009 method. 3-5 mg of sample in a pan in a DSC cell is subjected to continuous flow of oxygen at 50 ml/min with a temperature ramp of 10 °C/min from 40-300 °C. OOT test is an excellent test to determine the exact temperature where the oxidation of the sample starts. DSC determines the thermo-oxidative behavior of the samples.

In order to find the possible reason for superior performance of the FM 2, both the FMs viz., FM 1 and FM 2 were added in varying concentrations in the base oil. FM 1 separated beyond 0.6 % dosage. The oxidative stability OOT was determined by DSC. Oxidation onset temperature traces are given in Fig. 3.8 & Fig. 3.9 for FM 1 & FM 2 respectively.

Comparison indicates FM 1 to exhibit poor performance in oxidation stability with the reported values of OOT for the base oil with the FM at different concentrations below that of base oil itself. On the other hand FM 2 exhibited excellent lifts in OOT with all different concentrations of the FM well above the base oil alone. However FM 2 in base oils was found to exhibit a lowering of OOT beyond 0.7 % concentration. This experiment is, therefore, helpful in judging the optimum concentration of the said FM in the formulated Engine oil.

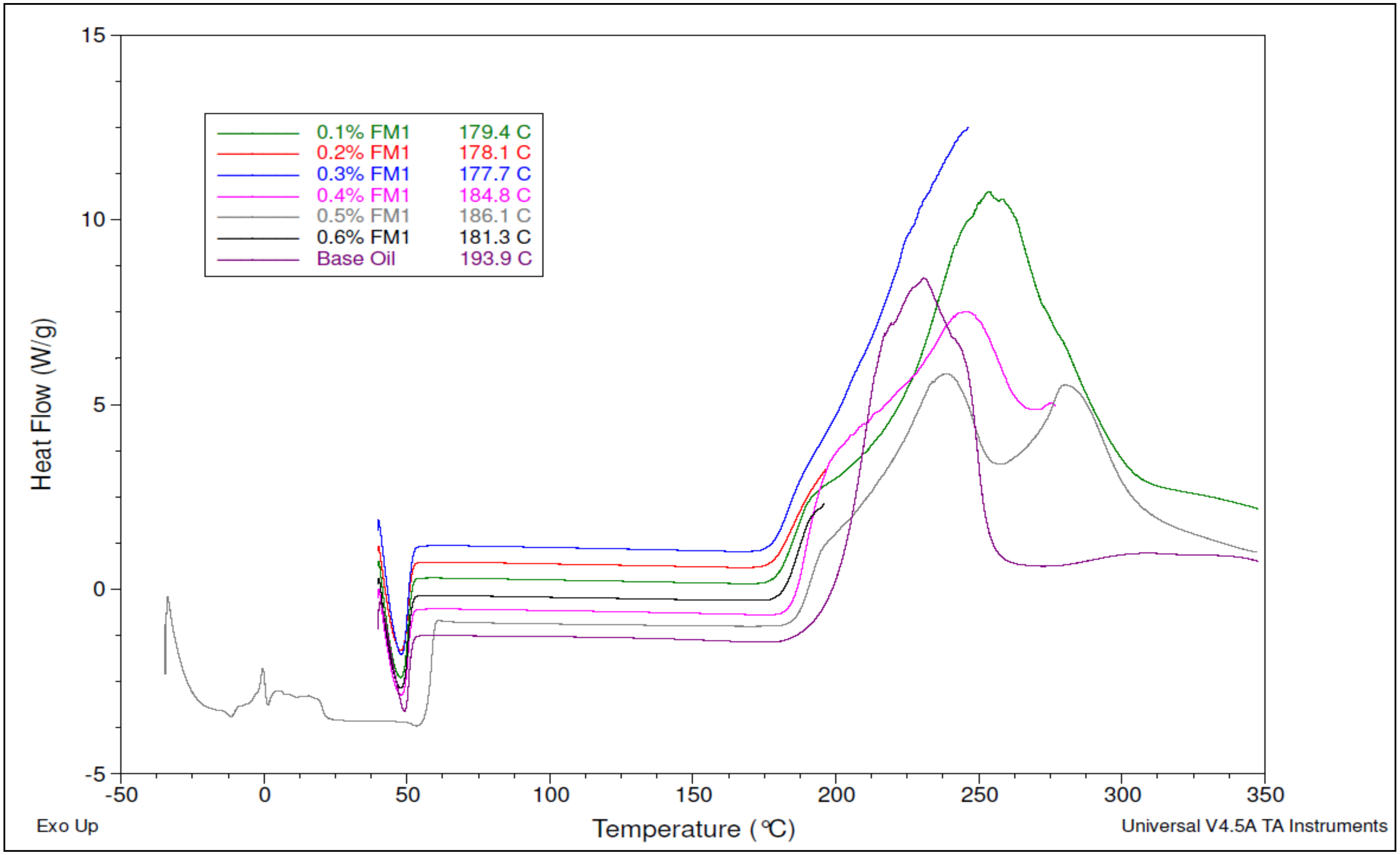


Figure 3.8 OOTs of base oil doped with FM 1.

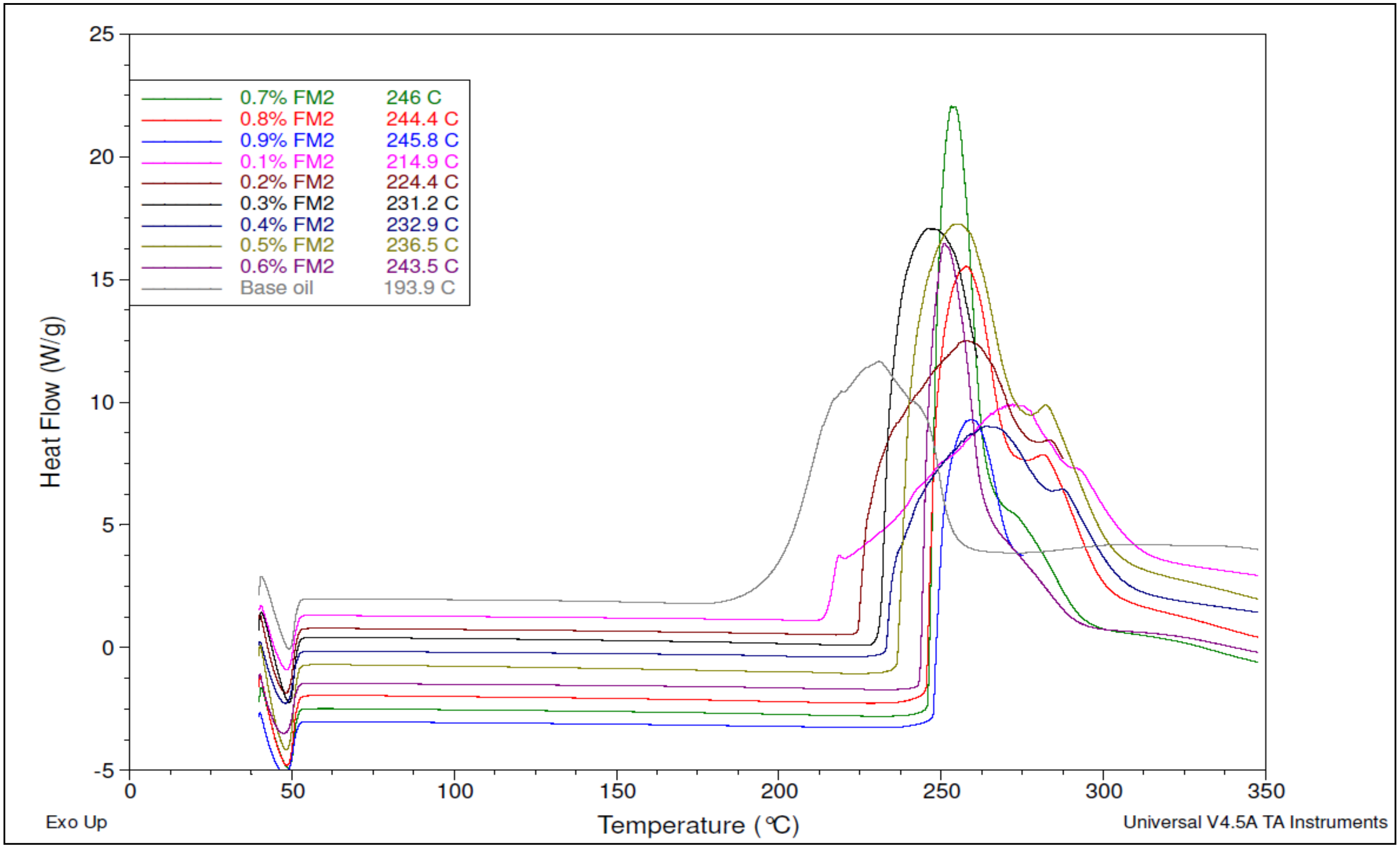


Figure 3.9 OOTs of Base oil doped with FM 2.

Synergism of FM & VM combination was best seen in the Blend I (FM 2, VM 3) combination. This particular blend had reported lowest coefficient of friction while maintaining highest film strength (thickness) among all the blends, also has good thermo-oxidative stability. Therefore this particular FM/VM combination was finalized for our further study with the antioxidants elucidated in the next part of research study in this chapter.

3.2 Part II – Antioxidant Study

Antioxidant[s] or combinations can destroy the precursors formed and control the formation of deposits and viscosity increase. Synergism of different antioxidants with base oil based on performance attributes like compatibility, thermo-oxidative stability, are discussed in this part of study. Relation of specific heat capacity to internal energy of lubricants is explained [6]. The oil internal energy varies with temperature. Heat capacity of engine oil at different temperatures has been determined and its possible role in selecting optimized blends has also been explained.

Experimentation Observation & Inference

In this study, various combinations of Gr III base oil mixture and antioxidants [4 Aminic (A_1, A_2, A_3 & A_4) and 2 Phenolic (P_1 & P_2)] detailed in previous chapter have been used. Engine oil samples thus formulated comprise of an additive package (doped with the selected VM & FM combination) and the antioxidants as discussed above. Different combinations of blends have been prepared according to the composition illustrated in the Table 3.2. The optimized blends of engine oil have been evaluated for thermal and oxidation stability using different laboratory tests. A comparative study was conducted on these 8 samples. 4 test samples contain P_1 (phenolic antioxidant without sulphur) and other 4 contained P_2 (phenolic antioxidant with sulphur). Finally 2-3 best combinations have been evaluated in performance test for deposit forming tendency and tribological characteristics. Engine test has been carried out for selected blend.

Table 3.2 Blend compositions with different antioxidants

Blend	Compositions
I	Base Oil mixture + Additive Package + P_1 + A_1
II	Base Oil mixture + Additive Package + P_1 + A_2
III	Base Oil mixture + Additive Package + P_1 + A_3
IV	Base Oil mixture + Additive Package + P_1 + A_4
V	Base Oil mixture + Additive Package + P_2 + A_1
VI	Base Oil mixture + Additive Package + P_2 + A_2
VII	Base Oil mixture + Additive Package + P_2 + A_3
VIII	Base Oil mixture + Additive Package + P_2 + A_4

Table 3.3 Temperature data of base oil mixture and blends at different % Wt. loss.

% Weight Loss	Base oil	I	II	III	IV	V	VI	VII	VIII
5	246	242	233	237	234	246	250	255	257
10	265	267	258	261	259	272	274	279	282
20	285	294	285	289	287	301	301	307	311
30	299	312	303	307	305	320	319	326	330
40	311	327	318	323	321	336	334	341	346
50	321	341	332	337	334	350	348	354	360
60	330	354	345	351	348	364	361	367	373
70	339	369	360	366	363	379	376	382	387
80	349	386	378	383	381	395	394	398	402
90	359	407	403	405	405	415	414	416	419
95	365	421	418	419	419	427	428	427	430

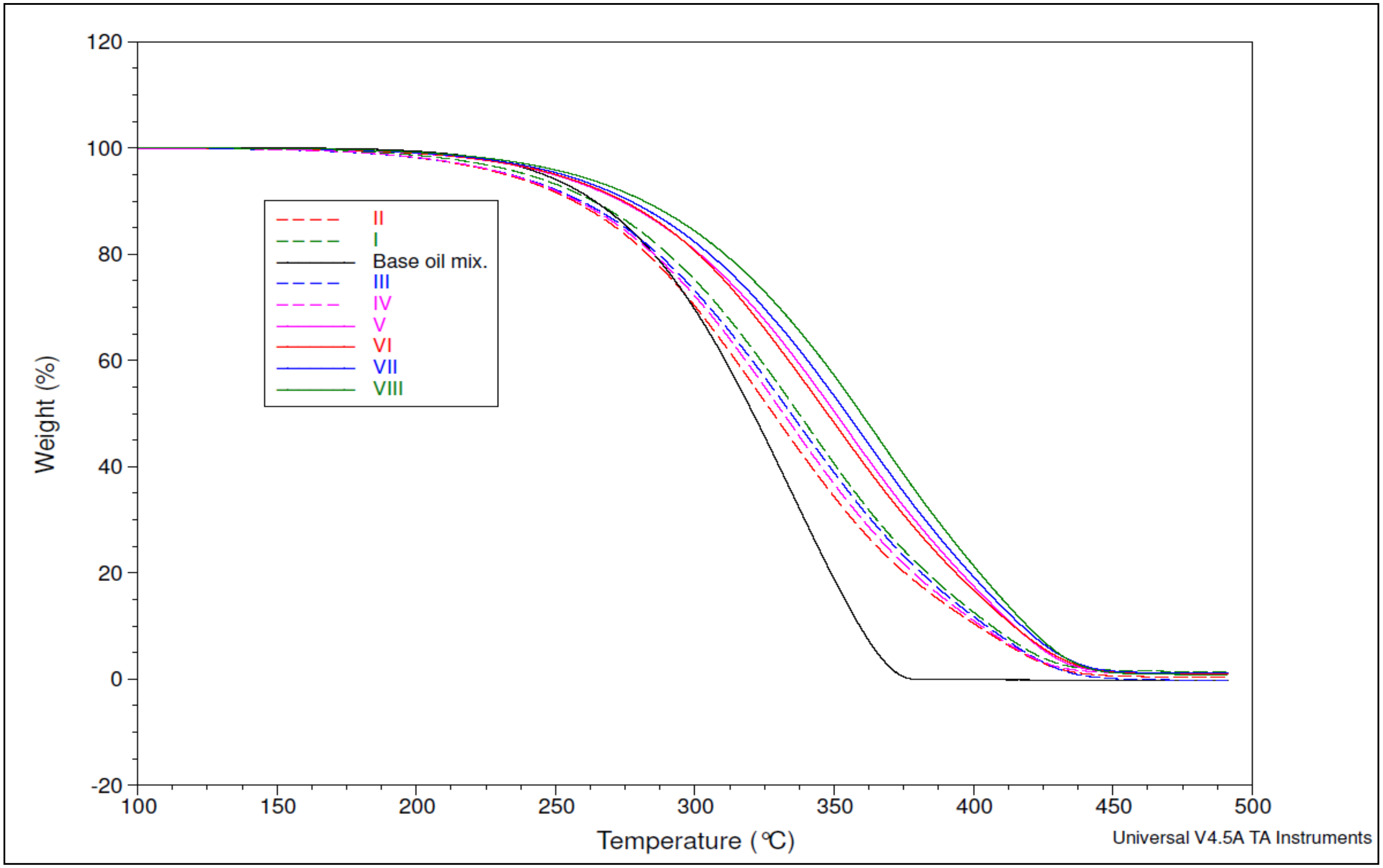


Figure 3.10 Thermal Stability curve for blends by TGA.

3.2.1 Thermal Stability

The blends are tested for thermal stability (weight loss w.r.t. temperature) in thermo-gravimetric analyzer (TGA) vis-a-vis the base oil mixture. About 10-15 mg of optimized blend taken in a platinum pan is subjected to a temperature ramp of 20 °C/min up to 500 °C under nitrogen atmosphere and continuously weight loss as a function of temperature is plotted. The comparative thermograms are presented in Fig. 3.10. For a better understanding temperatures at different weight % losses are calculated and tabulated in Table 3.3. It is observed that some of the blends retain their weight above 50% over 350 °C, an essential prerequisite for present generation engines.

3.2.2 Oxidation Stability

Above mentioned blends are also tested for oxidation stability in differential scanning calorimeter vis-a-vis the base oil mixture. About 2-3 mg of optimized blend taken in a aluminum pan and is subjected to a temperature ramp of 10 °C/min up to 350 °C under oxygen flow of 50 ml/min and continuous heat flow w.r.t. temperature graph is plotted. The oxidation onset temperature (OOT) value of the blends is reported in Table 3.4. The oxidation stability plots of the blends compared to base oil mixture is given in Fig. 3.11.

3.2.3 Thermo-Oxidation Stability

The above blends are tested for thermo-oxidation stability measured as oxidation induction time (OIT) in pressure differential scanning calorimeter vis-à-vis the base oil mixture. About 2-3 mg of optimized blend taken in an aluminum pan and is subjected to isothermal temperature of 210 ^{o}C under a pressure of 500 psi oxygen and heat flow w.r.t. time is continuously recorded. OIT of the blends is reported in Table 3.5. The PDSC thermo-oxidation stability curve of the blends against base oil mixture is given in Fig. 3.12.

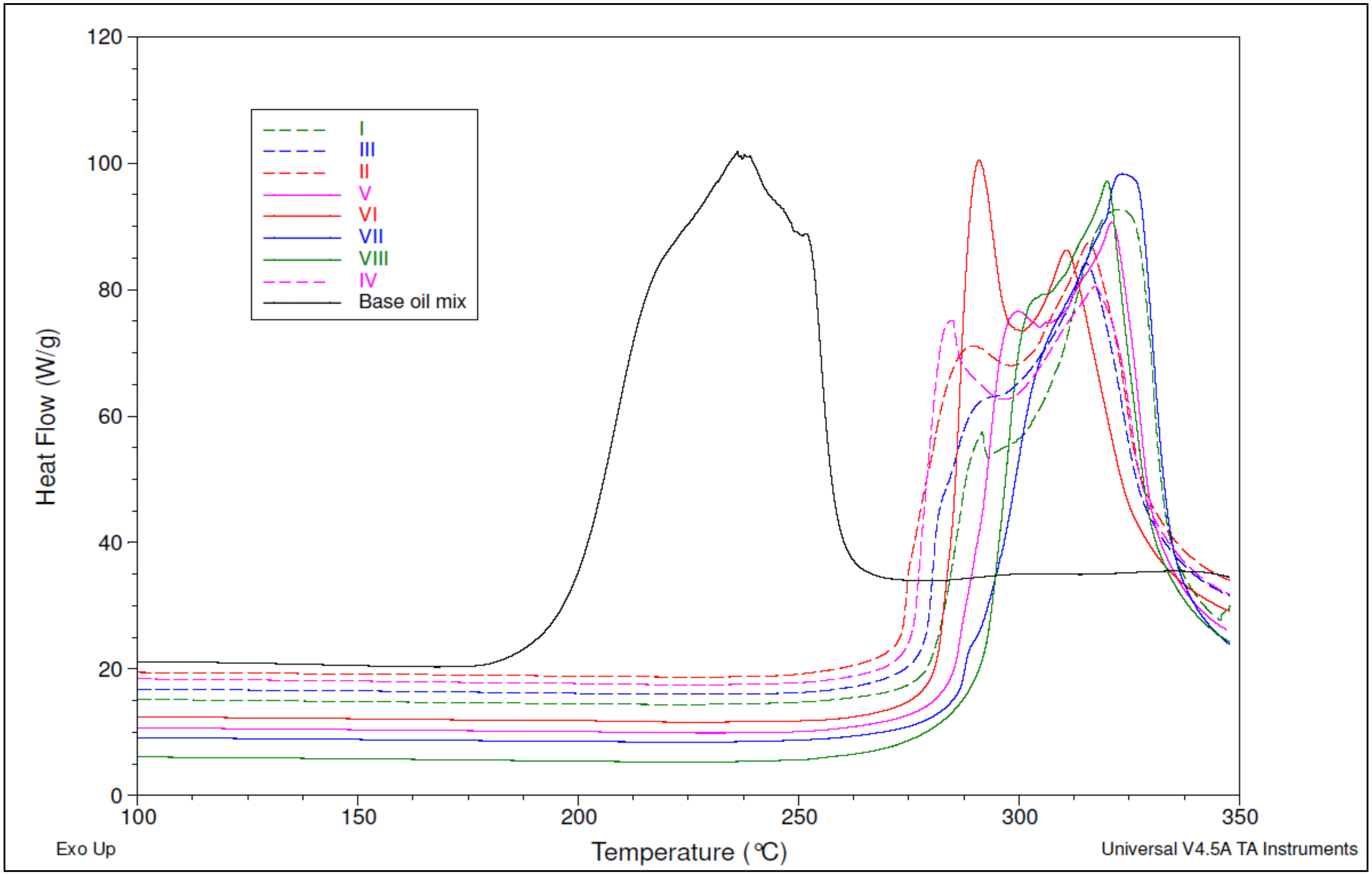


Figure 3.11 Oxidation Stability curve for blends by DSC.

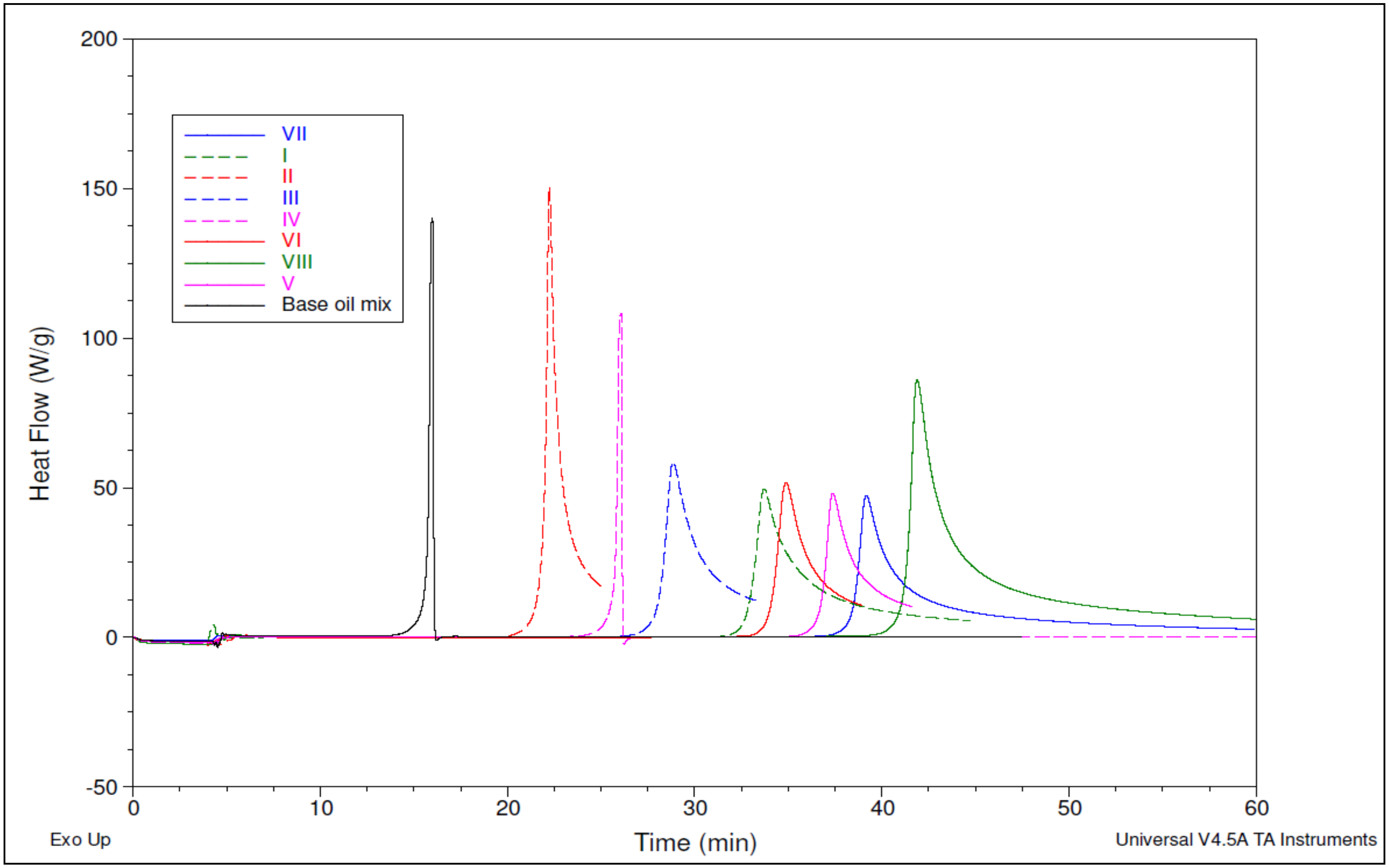


Figure 3.12 Thermo-oxidative stability curves for blends by PDSC.

Table 3.4 OOTs of Blend Compositions

Sample	OOT (°C)
Base Oil Blend	199
I	280.1
II	267
III	275.2
IV	272.1
V	286.7
VI	283.1
VII	289.2
VIII	291

Table 3.5 OITs of Blend Compositions

Sample	**OIT (min)**
Base Oil Blend	15.52
I	32.9
II	21.97
III	28.09
IV	25.75
V	36.73
VI	34.04
VII	38.46
VIII	41.26

From the plots (3.11 & 3.12) and Tables (3.4 & 3.5) it is observed that all the optimized blends exhibit higher OOTs and in OITs than the base oil mixture. This indicates that the antioxidant and package combination has resulted in significantly improved thermo-oxidation stability. Higher OOTs and OITs represent higher oxidation inhibition characteristics of the engine oils at high temperatures. The above combinations are, therefore, likely to result in such formulation that provide better durability and protection to the engine components under operation in severe environment.

3.2.4 TFOUT – Thin Film Oxygen Uptake Test

As engine oil form very thin films while the engine is operating, and hence thermo-oxidative stability requires to be excellent. The blends were tested in thin-film oxygen uptake test (TFOUT) for thermo-oxidative stability in which actual engine operating conditions are simulated by adding components of fuel, NOx catalyst and water to the oil films and is evaluated at 160 °C under pressurized oxygen at 90 psi according to ASTM D 7098 method [7]. The bar chart given in the Fig. 3.13 illustrates the oxygen induction times (OITs) determined by the TFOUT instrument. Fig. 3.14 schematically represents the basis for calculation of OIT from the TFOUT graph obtained in the instrument. For better performing oil the oxygen induction time should be higher. This represents the thermo-oxidative stability of the sample similar to PDSC but simulated in actual engine environment conditions.

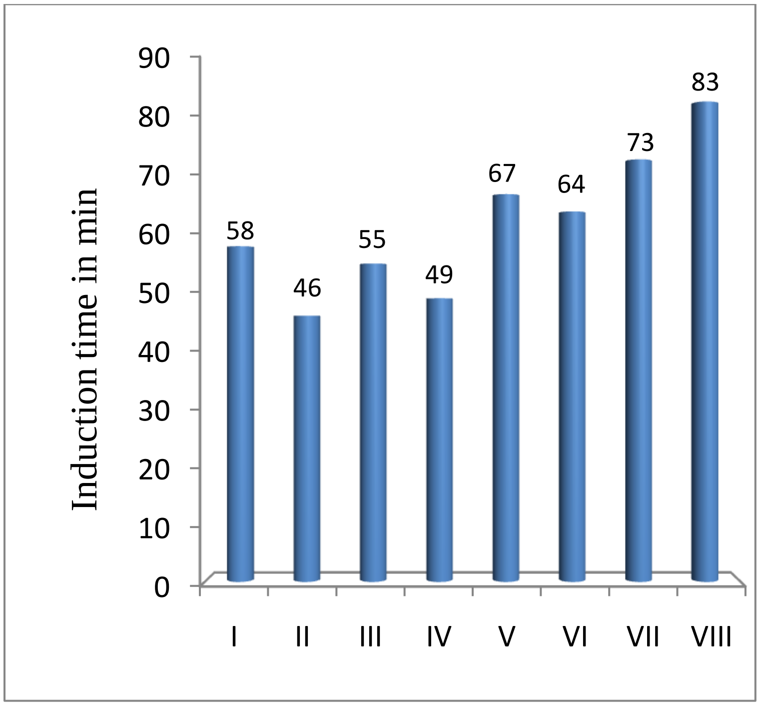


Figure 3.13 Oxygen induction time for blends as reported by TFOUT.

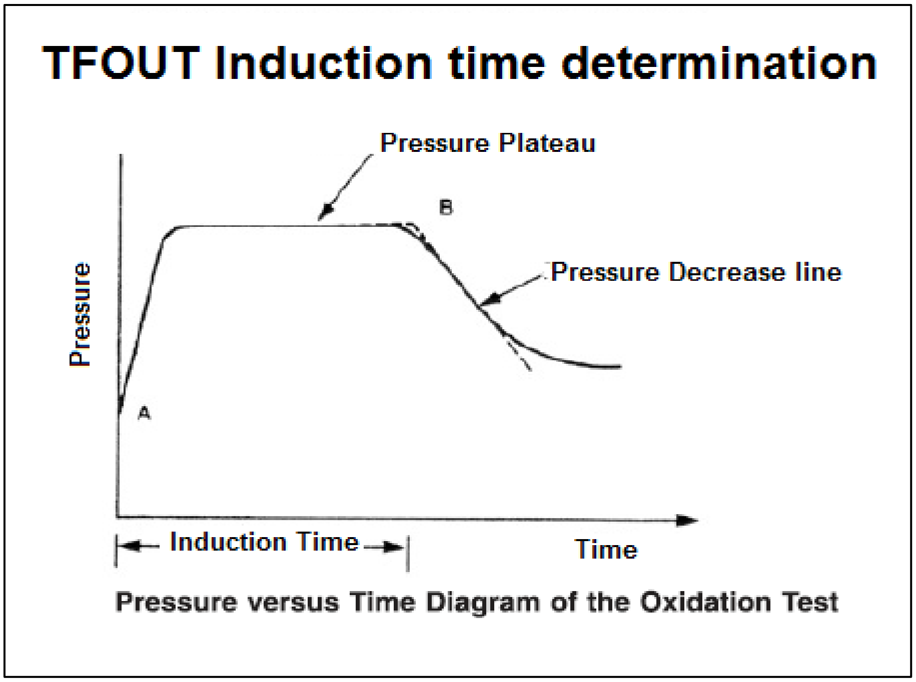


Figure 3.14 Calculation of oxygen induction time from TFOUT instrument graph.

3.2.5 Heat Capacity of Engine oil

Heat capacity gives valuable information about the internal energy stored in the sample at a particular temperature. Heat Capacity is evaluated in DSC instrument by Modulated DSC method [8] in which about 3-5 mg of sample in pan is taken in a DSC cell against reference pan & subjected to a ramp rate of 3 °C/min to 250 °C after modulating the cell +/- 1 °C every 60 seconds. Heat capacities at four different temperatures of 150 °C, 175 °C, 200 °C and 225 °C for all the blends are illustrated in Fig. 3.15. The heat capacity values at different temperatures are calculated and illustrated in Table 3.6. It is observed that the heat capacities of the blends at different temperatures followed totally opposite trend as per the results obtained by TGA, DSC, PDSC and TFOUT i.e., the blends which reported higher stability values have reported lower heat capacity values and vice versa. This is perfectly in order since the blends with faster cooling index will exhibit better thermo-molecular integrity at the engine operating temperature, thereby adding significant contribution to the cause of engine durability.

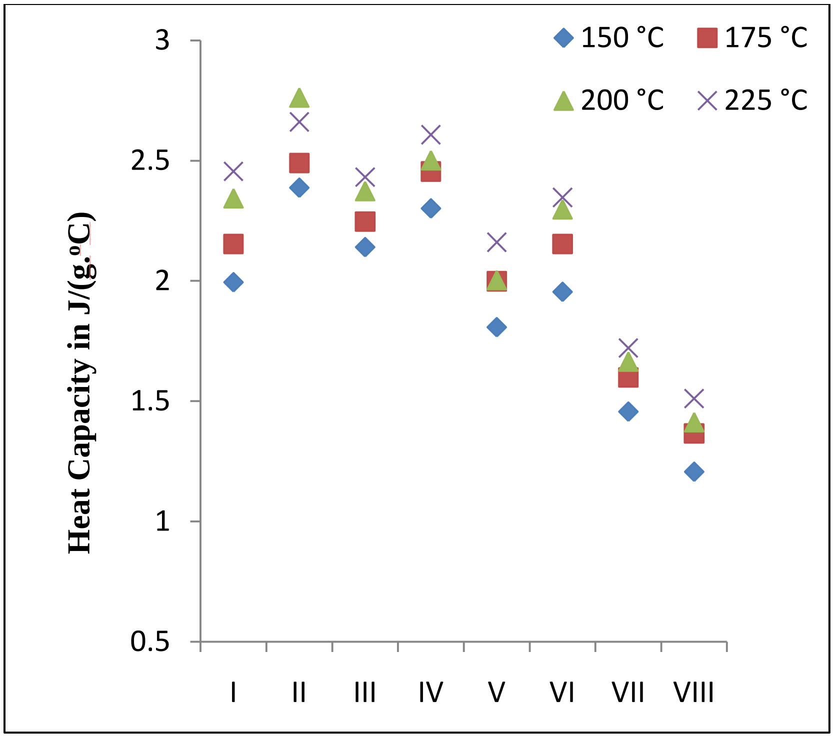


Figure 3.15 Heat capacity values for blends by modulated DSC.

Table 3.6 Heat Capacity in J/(g.°C) at different temperatures for blends

Blends	Temperatures of test			
	150	175	200	225
I	1.995	2.154	2.344	2.456
II	2.388	2.49	2.763	2.661
III	2.141	2.247	2.374	2.432
IV	2.302	2.455	2.502	2.608
V	1.808	1.9988	2.004	2.161
VI	1.955	2.154	2.298	2.347
VII	1.457	1.599	1.665	1.721
VIII	1.207	1.366	1.413	1.511

Three best combinations out of the 8 optimized blends showing excellent thermal stability, oxidation stability, film strength and lower coefficient of friction were selected. Two blends (VIII & VII) from the blends containing P_2 phenolic antioxidant and one blend (I) from the blends containing P_1 phenolic antioxidant which have given better results in all the laboratory bench tests and rigs were included. These selected blends were further validated, (against an industry standard sample), in performance tests such as deposit forming tendency, tribological performance and on Sequence III E engine test, and form a part of next chapter.

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Chapter 4

Validation of Engine Oil

4.0 Validation Process

The optimized engine oil formulation was validated against identified performance criteria. Engine oil formulation as described in chapter III had been evaluated for oxidation stability, thermal stability and thermo-oxidative stability. The P_2 phenolic antioxidant containing blends have been found to perform exceedingly better than the P_1 phenolic antioxidant containing blends.

The results that obtained in various laboratory bench tests have further been validated for performance criteria in three main areas of performance; viz.,

- Deposit forming tendency (thermo-oxidative stabilities).
- Tribology testing (frictional properties).
- Engine test (overall performance).

For this exercise, 3 selected best blends (from chapter III) along with industry standard (reference) are further evaluated for performance validation tests. Industry standard is selected based on the viscometrics of the sample blends which is available currently.

4.1 Deposit forming tendency of engine oils

Deposit formation in the engine components at higher or elevated temperatures mainly occur due to oxidation of engine oil. This superiority of engine oil is synonymous with least deposits. In the present scheme of work, two types of deposits have been evaluated for the selected engine oil.

4.1 (a) Type 1 deposit formation

This deposit formation is simulated for actual engine running conditions (i.e., in the presence of fuel, moisture, air and high temperature). This environment is created by mixing a special catalyst to the subject sample oil and evaluated in thermo-oxidation engine oil simulation test – moderately high temperature (TEOST-MHT) instrument according to ASTM D7097 [1].

TEOST – MHT: Experimentation, Observation and Inference

This test method is designed to predict the deposit forming tendencies of engine oil in the piston ring belt and upper piston crown area where temperatures reach up to 250-300 °C. These deposits formed in the engine pistons can create problems with engine operation and durability. Deposit formation with a given engine oil sample under actual conditions occurring in engine are simulated by circulating the oil-catalyst mixture on coiled hot rod maintained at high temperature in air.

In this test pre-calculated weight of catalyst mixture required for 8.5 gm of sample is taken through a micro-syringe in a sample flask. 8.5 gm of sample is added precisely to the sample flask and the mixture is well mixed with a magnetic stirrer for 10-15 minutes. The sample catalyst mixture is then guided / circulated on a pre-weighed coiled rod which is maintained at 285 °C under continuous flow of air (10ml/min) for 24 hours. The circulation speed of engine oil on hot coiled rod is maintained such a way that about 0.25 gm of sample is circulated on rod in a minute. After the completion of test the rod is removed from the equipment, washed with the solvent, dried and weighed. The washed solvent and the oil sample remaining after test is also filtered with a pre-weighed filter cartridge after which the cartridge is dried and weighed. Total deposits (deposits on rod and deposits in filter cartridge) are reported as the deposit of particular sample. The equipment setup is shown in the Fig. 4.1 and Fig. 4.2.

The selected blends & industry standard were tested for deposit forming tendency according to ASTM D7097, simulating the high temperature piston deposits in the engine. The total deposits obtained during the test on the coiled heated rod and in the filter cartridge are reported for the 3 selected blends and the images of after test rods are illustrated in Fig. 4.3. It is observed that the blend VIII showed lowest deposits followed by blend VII, I and then standard. All the selected 3 blends have reported significantly lesser deposits than the industry standard, thereby indicating that all the three blends have superior performance than the standard.

Figure 4.1 TEOST-MHT equipment.

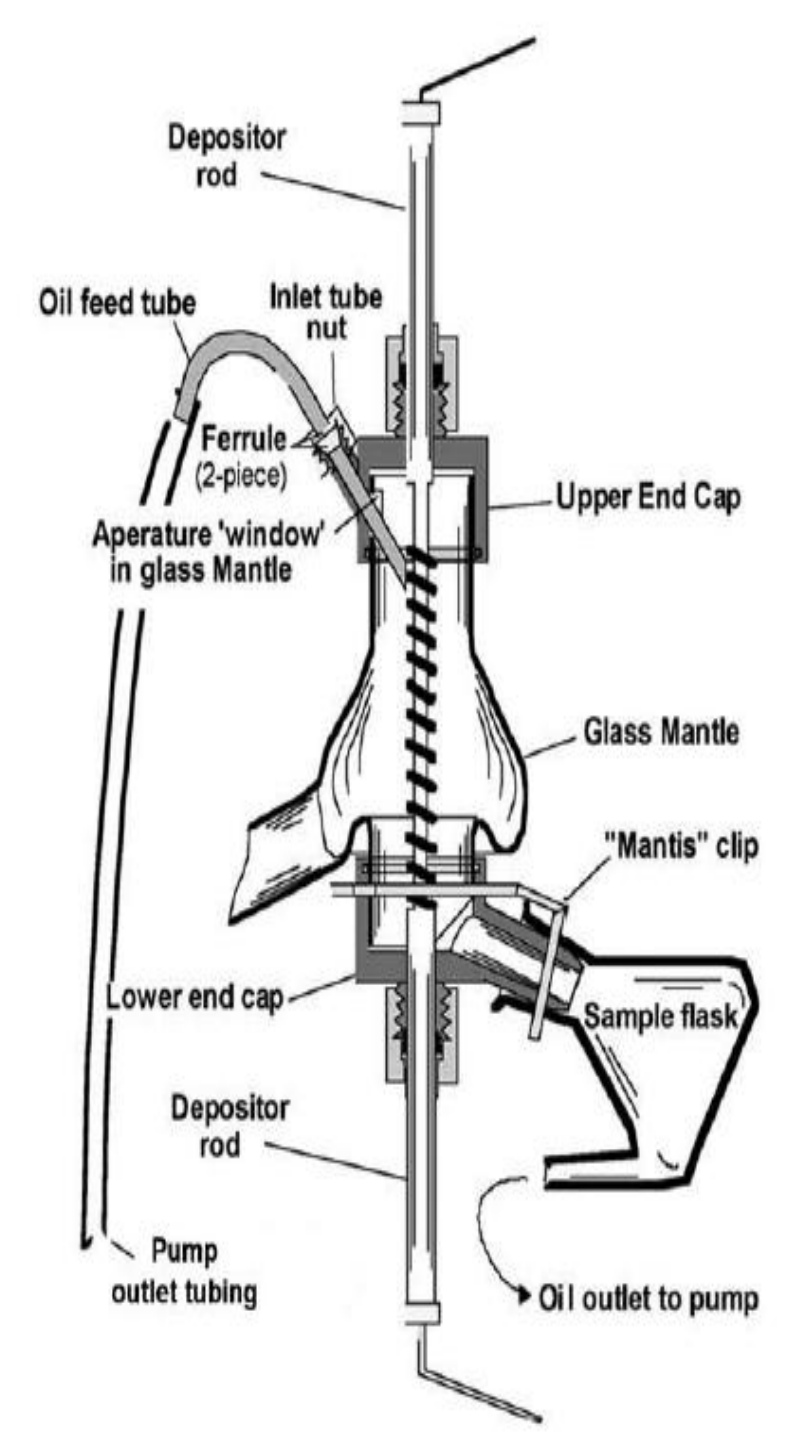

Figure 4.2 TEOST equipment setup.

Figure 4.3 TEOST rod deposit for blends.

4.1 (b) Type 2 deposit formation

This deposit formation is coking tendency of the engine oil which can happen when the engine oil comes in contact with elevated high temperatures in presence of air only. This coking tendency of engine oil is evaluated by uniform splashing of engine oil on a panel maintained at high temperature in panel coker test apparatus according to Federal Test Method 791B Method 3462 [2].

Panel Coker Test: Experimentation, Observation and Inference

This test method determines the tendency of finished oils to form coke when in contact with surfaces at elevated temperatures. A sample of oil is mechanically splashed against an aluminum test panel at elevated temperature. After test period, the weight of coke deposited on the panel is evaluated. Weight of deposit should be lesser for a given engine oil to give better performance. The typical equipment setup is shown in Fig. 4.4.

Aluminum test panel is cleaned and weighed. Adequate amount of sample oil is taken in oil sump of the apparatus which is maintained at 100 °C throughout the test. The sample oil is splashed uniformly, with the help of a splasher mechanically driven at 1000 rpm, on an aluminum test panel which is maintained at 300 °C for 6 hours. After the test, the panel is removed from the apparatus, cleaned dried and weighed. The weight of deposit formed is reported as coking tendency of oil.

The selected blends & industry standard were tested for coking tendency according to FTM-791B 3462 method. Cross section of panel coker setup is shown in Fig. 4.5 showing the oil sump, splasher and panel assembly. The deposit obtained during the test on aluminum panel is calculated for the 3 selected blends & industry standard and is illustrated in Fig. 4.6. It is observed that the blend VIII has reported the least formation of deposits on the panel and has a cleaner and shining image during the test followed by blend VII, I and then standard. All the selected 3 blends have reported far less deposits than the industry standard indicating that all the three optimized blends have superior performance than the standard.

Figure 4.4 Panel coker test apparatus.

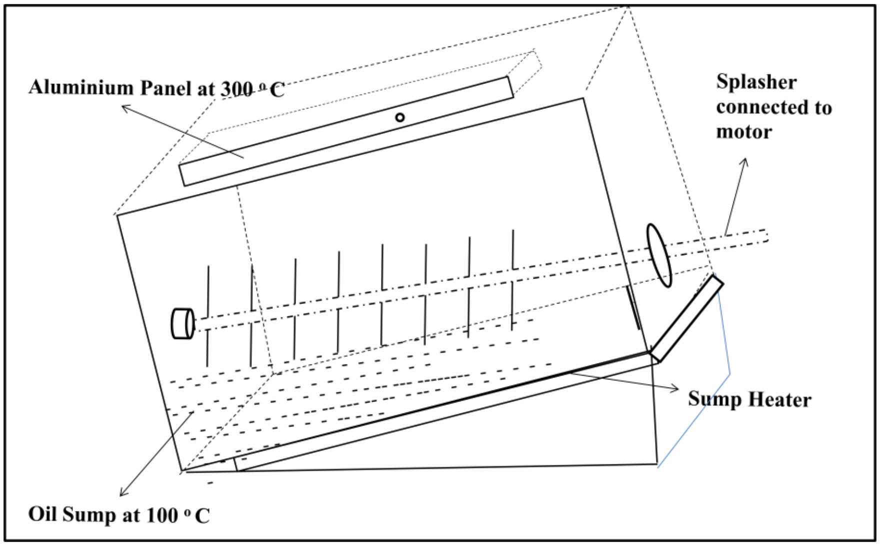

Figure 4.5 Cross section of panel coker assembly.

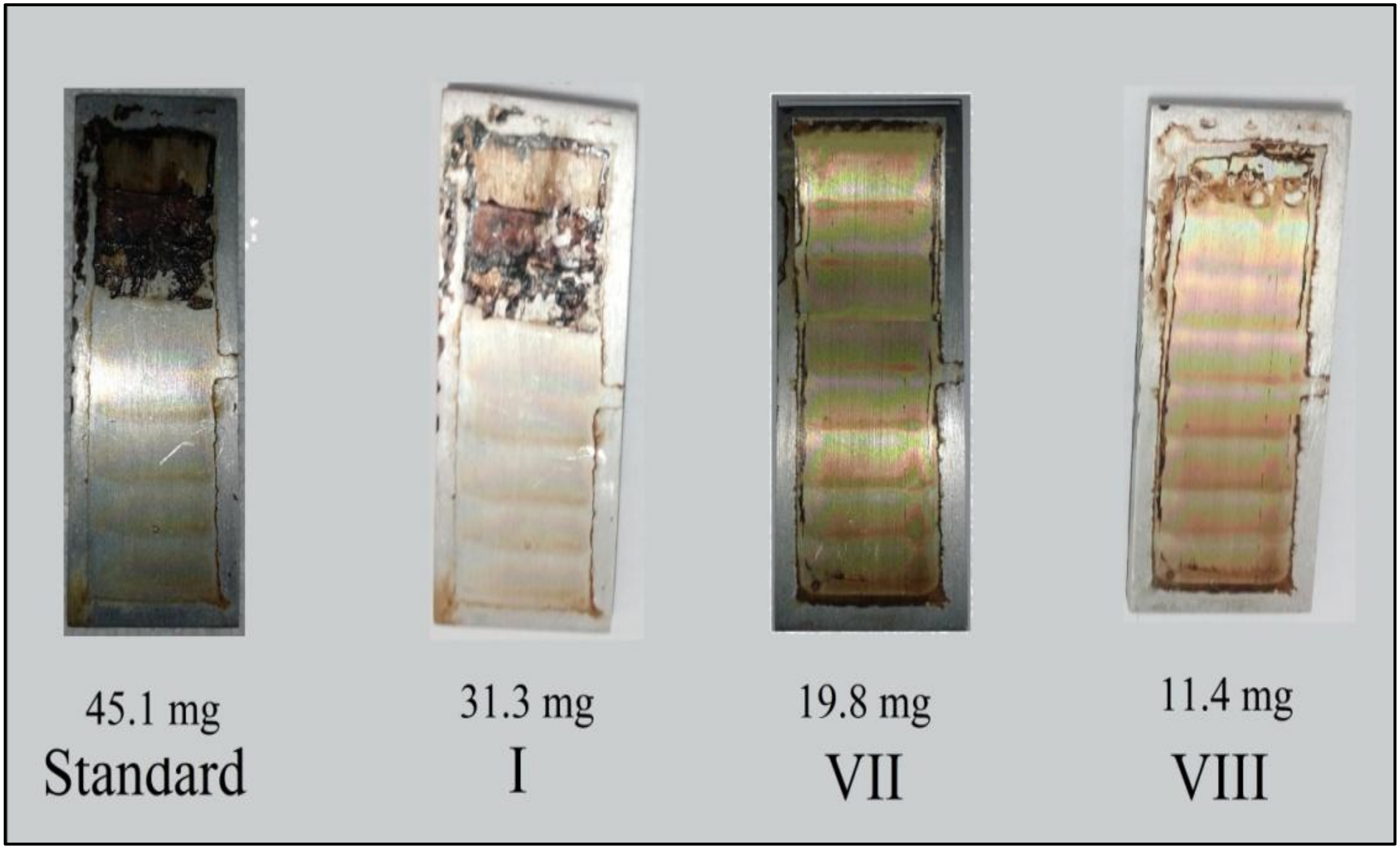

Figure 4.6 Deposits on panel for selected blends.

4.2 Tribological Properties: Experimentation, Observation and Inference

Friction reduction property is of prime importance along with good thermo-oxidative property, since it forms the basis for energy efficiency of engine oil. Friction reduction helps in saving the energy produced from the engine by reducing frictional losses.

The selected blends and standard were tested on SRV Tribometer at two different temperatures of 60 °C and 100 °C with conditions of test as 300 N load, 1mm amplitude, 50 Hz frequency and 1 hour duration. Coefficient of friction values obtained for the selected blends are illustrated in Fig. 4.7. The frictional traces are shown in the Fig.4.8 (a-d). Form the illustration it is clear that all the selected blends reported lesser coefficient of friction than the industry standard at both the temperatures. Blend VIII has reported the least coefficient of friction followed by blend VII, blend I and industry standard sample.

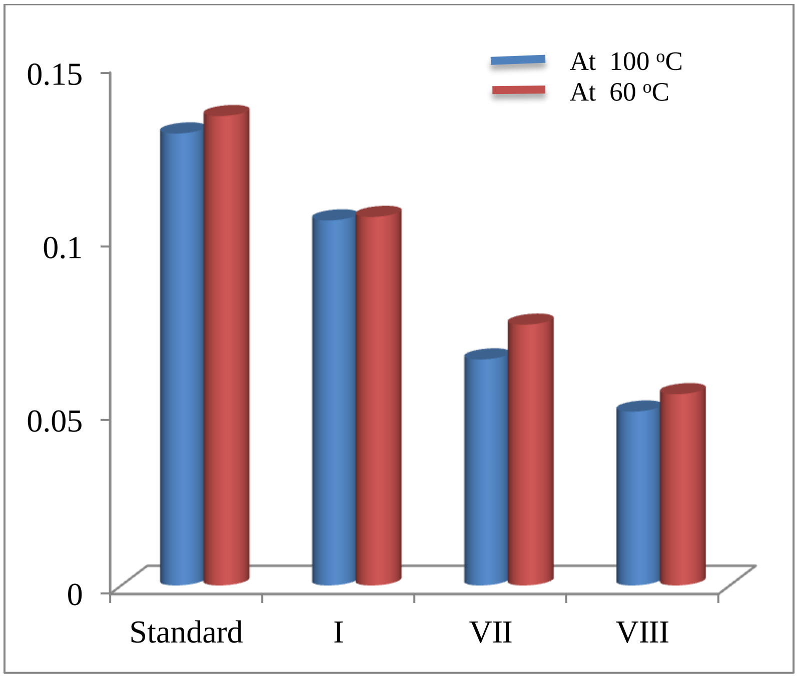

Figure 4.7 Coefficient of friction for selected blends.

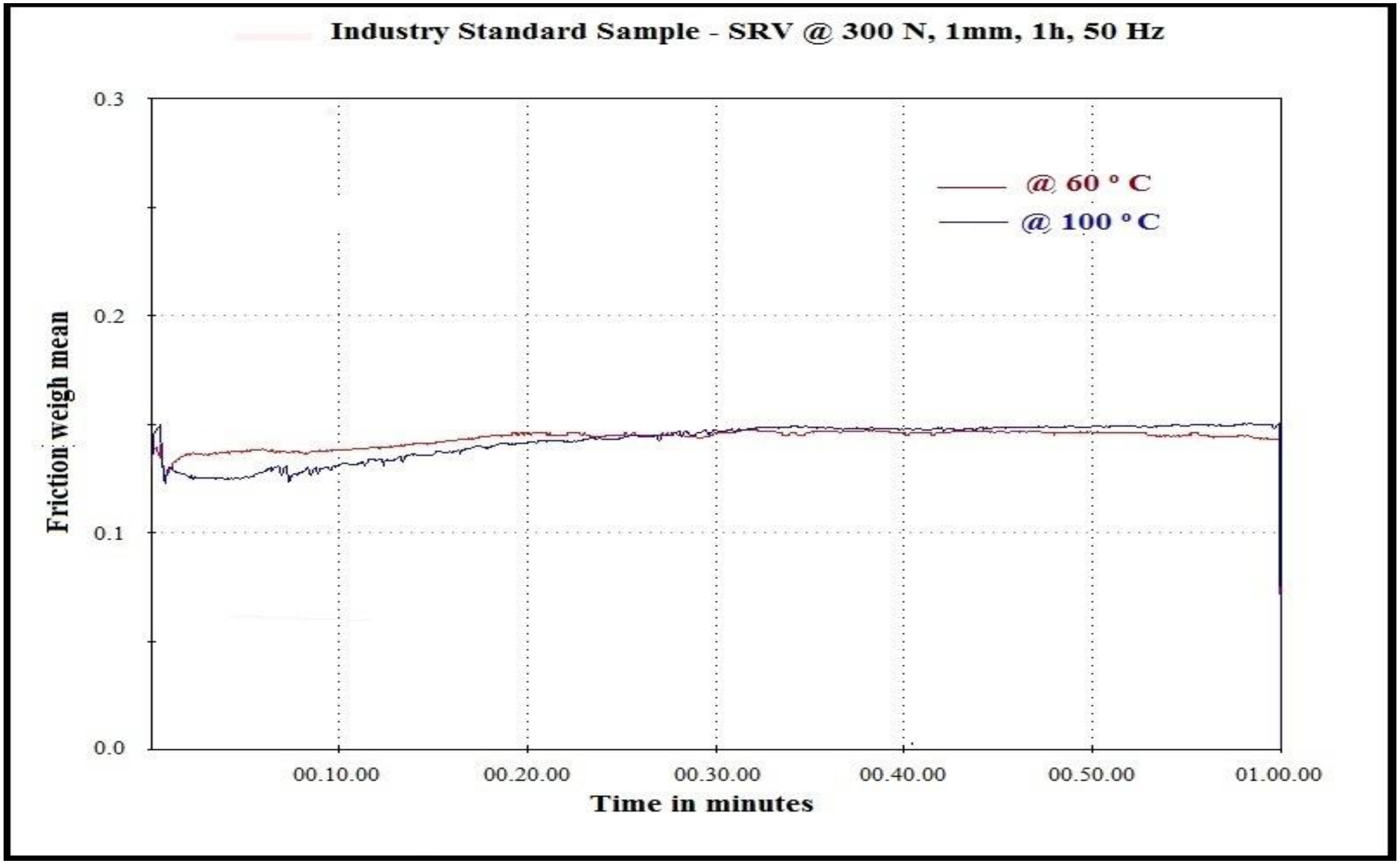

Figure 4.8 (a) SRV graph for industry standard sample.

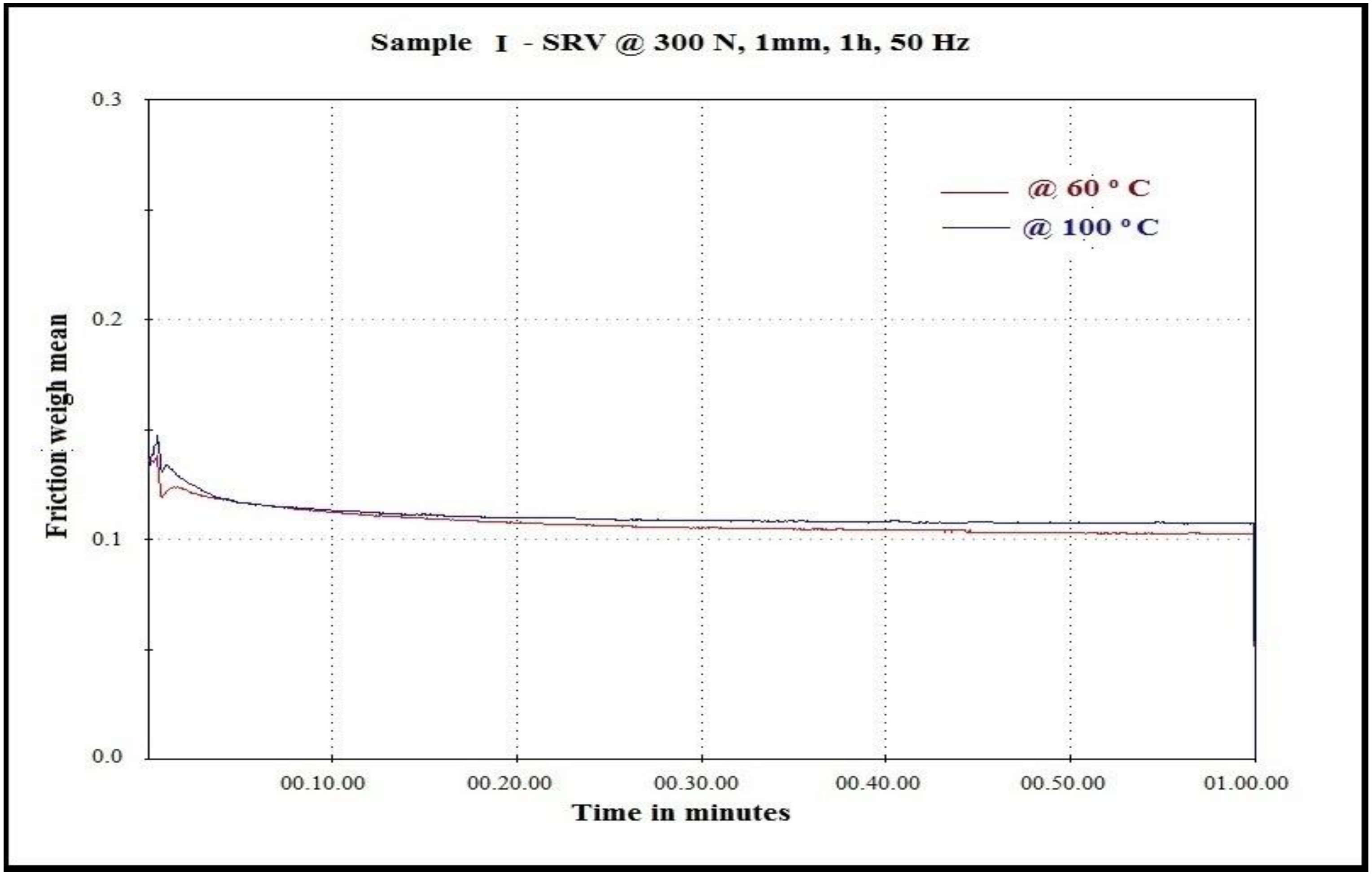

Figure 4.8 (b) SRV graph for sample blend I.

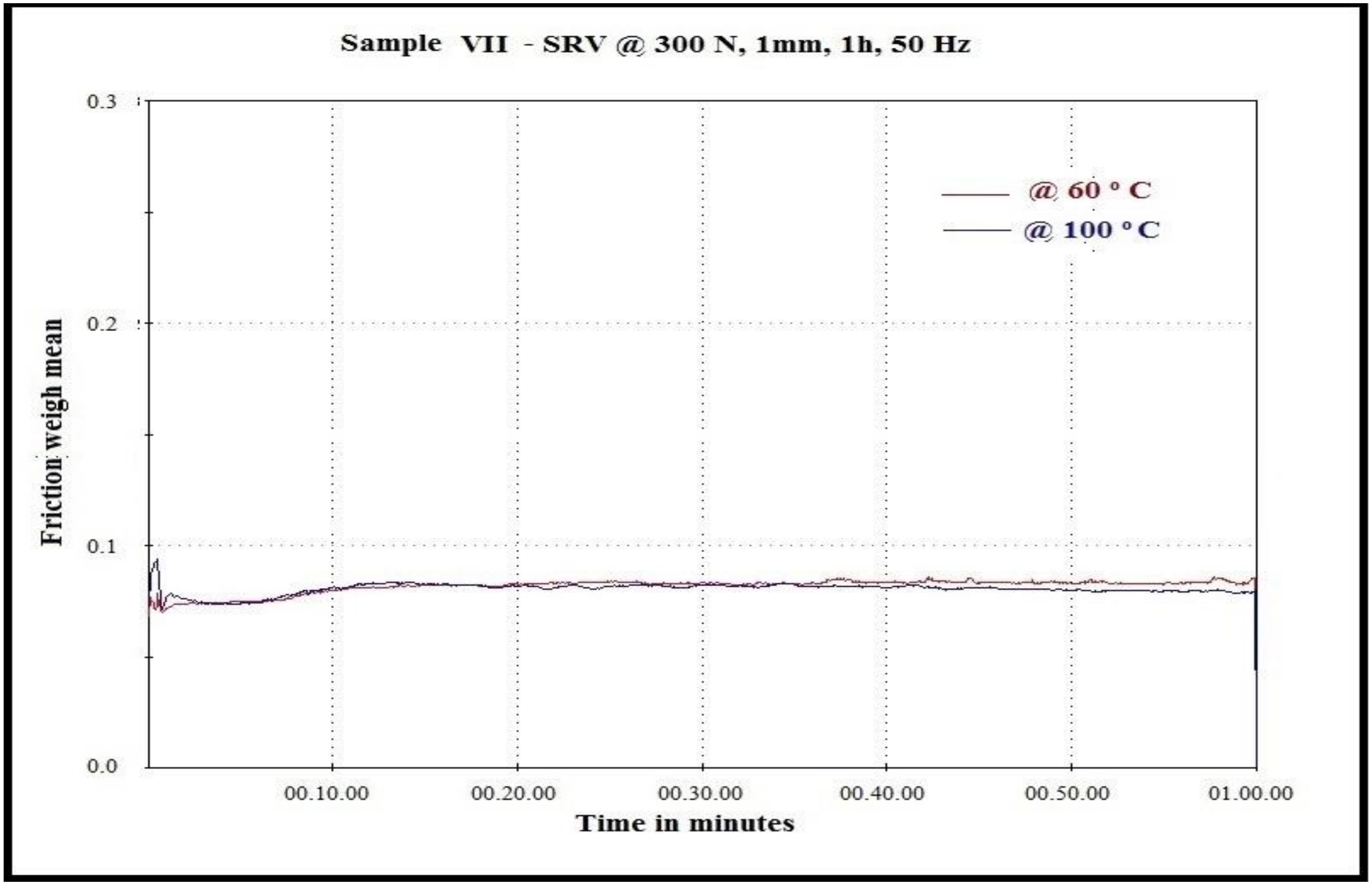

Figure 4.8 (c) SRV graph for sample blend VII.

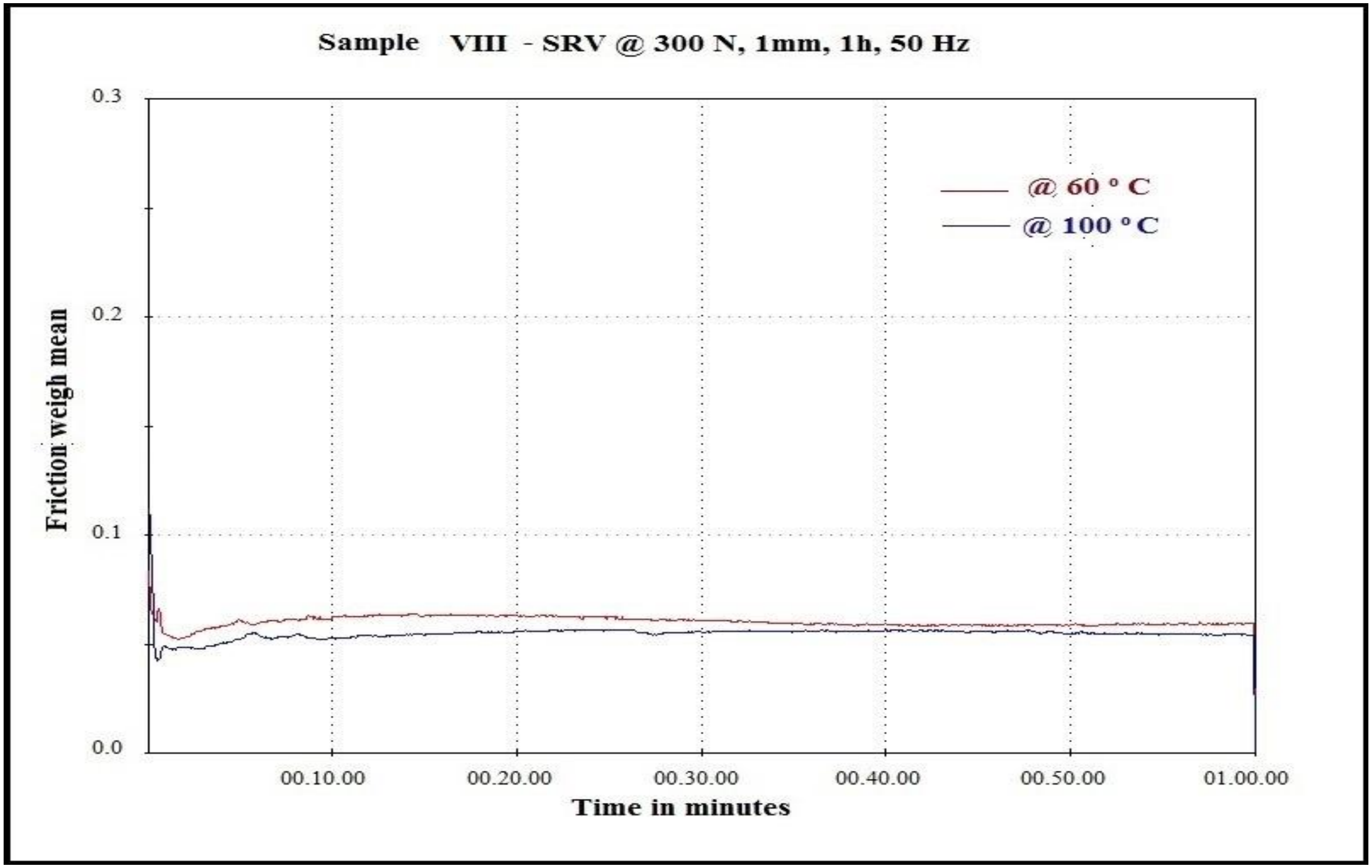

Figure 4.8 (d) SRV graph for sample blend VIII.

4.3 Performance Engine test: Experimentation, Observation and Inference

The final validation of the engine oil performance with respect to given parameter (in the present case oxidation inhibition characteristics) is required to be established in a performance engine test.

In the present work, Sequence III E engine test has been utilized for final validation of the selected engine oils. The objective of running this engine test program was to evaluate performance of the lubricants in minimizing high temperature oxidation and controlling cam lobe flat tapped lifter wear. This engine test simulates a drive at a constant speed of 110 kmph/70 mph on road [3]. The conditions of said engine test are given below.

- The test uses an 800 cc spark ignition 3 cylinder in line engine.
- The engine runs at a speed of 3000 +/- 10 rpm with 18.8 +/- 0.4 bhp load.
- The Air to Fuel ratio is maintained at 16 +/- 0.25: 1.
- The engine oil temperature is maintained at 149 ^{o}C with coolant temperature maintained at 116 +/- 1 ^{o}C.
- The engine test duration is for 64 hours which is interrupted every 8 hours for sampling of the oil.

End of Test percentage rise in kinematic viscosity at 40 °C from the fresh oil and cam lobe wear in microns are reported. The pass limits for the engine test are:

- ➢ Deviation of percentage viscosity rise at 40 ^{o}C from fresh oil should not exceed 375 % after the end of 64 hours.
- ➢ Average cam lobe wear should not exceed 30 microns.

The selected optimized blend samples and industry standard were subjected to this test program. All the samples exhibited pass results with average cam lobe wear less than 30 microns and % increase in viscosity significantly lower than the limit 375 %. The values of average cam lobe wear and percentage rise in viscosity at 40 °C is illustrated below in the Fig. 4.9 & Fig. 4.10 respectively.

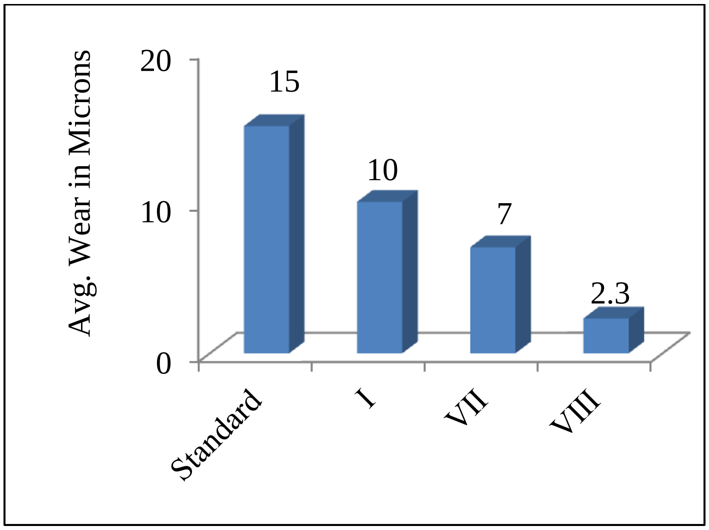

Figure 4.9. Cam lobe wear for blends.

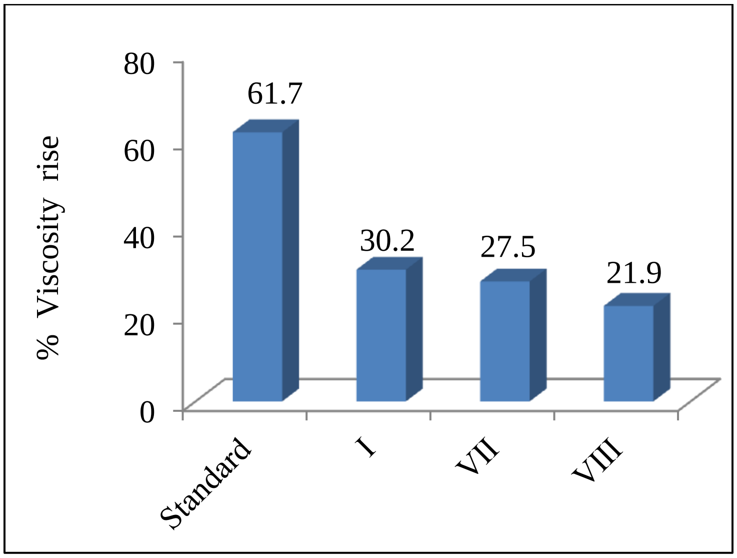

Figure 4.10 % Viscosity Rise at 40 °C for blends.

From Fig. 4.9 it is clear that all the three selected blends have shown lower cam lobe wear than the industry standard. The same trend in result is also observed in the % rise in viscosity values for these blends against the industry standard as shown in Fig. 4.10. The viscometrics data (before & after engine test) of these selected samples and industry standard sample have been tabulated in the Table 4.1 given below.

Table 4.1 Viscosity at 40 ^{o}C for the selected blends after engine test.

Sampling interval	Industry Standard	Sample Blend I	Sample Blend VII	Sample Blend VIII
Fresh Sample	84.57	90.35	87.56	89.18
After 8 hrs	86.74	94.11	90.26	91.54
After 16 hrs	92.02	97.2	93.84	94.08
After 24 hrs	99.56	101.9	96.37	96.72
After 32 hrs	106.9	104.3	100.8	99.82
After 40 hrs	113.4	108.2	103.7	102.4
After 48 hrs	120.7	111.3	106.2	104.3
After 56 hrs	128.5	114.8	109.5	106.5
After 64 hrs	136.8	117.6	111.6	108.7

4.3.1 Thermo-Oxidative stabilities of engine oil samples after engine test

The used oil samples obtained from the engine test were evaluated for thermal and oxidative stabilities to find the deterioration of the optimized blends. For this fresh engine oil and used engine oil from engine test after 64 Hrs for all the selected blends and industry standard were tested in DSC and TGA. The onset oxidation temperature (OOT) of the used oil by DSC is reported in Table 4.2. DSC oxidation stability curves and TGA thermal stability curves for engine oil after and before engine test, for the selected samples along with industry standard are illustrated in Fig. 4.11 (a-d) and Fig. 4.12 (a-d) respectively.

Table 4.2 Change in OOTs for the selected blends after Engine test

Test hours	Industry Standard	Sample Blend I	Sample Blend VII	Sample Blend VIII
Fresh Sample	276.7 °C	280.1 °C	289.2 °C	291 °C
After 64 Hrs	267.2 °C	274.1 °C	285.1 °C	288.7 °C
Variation in OOT	9.5 °C	6.0 °C	4.1 °C	2.3 °C

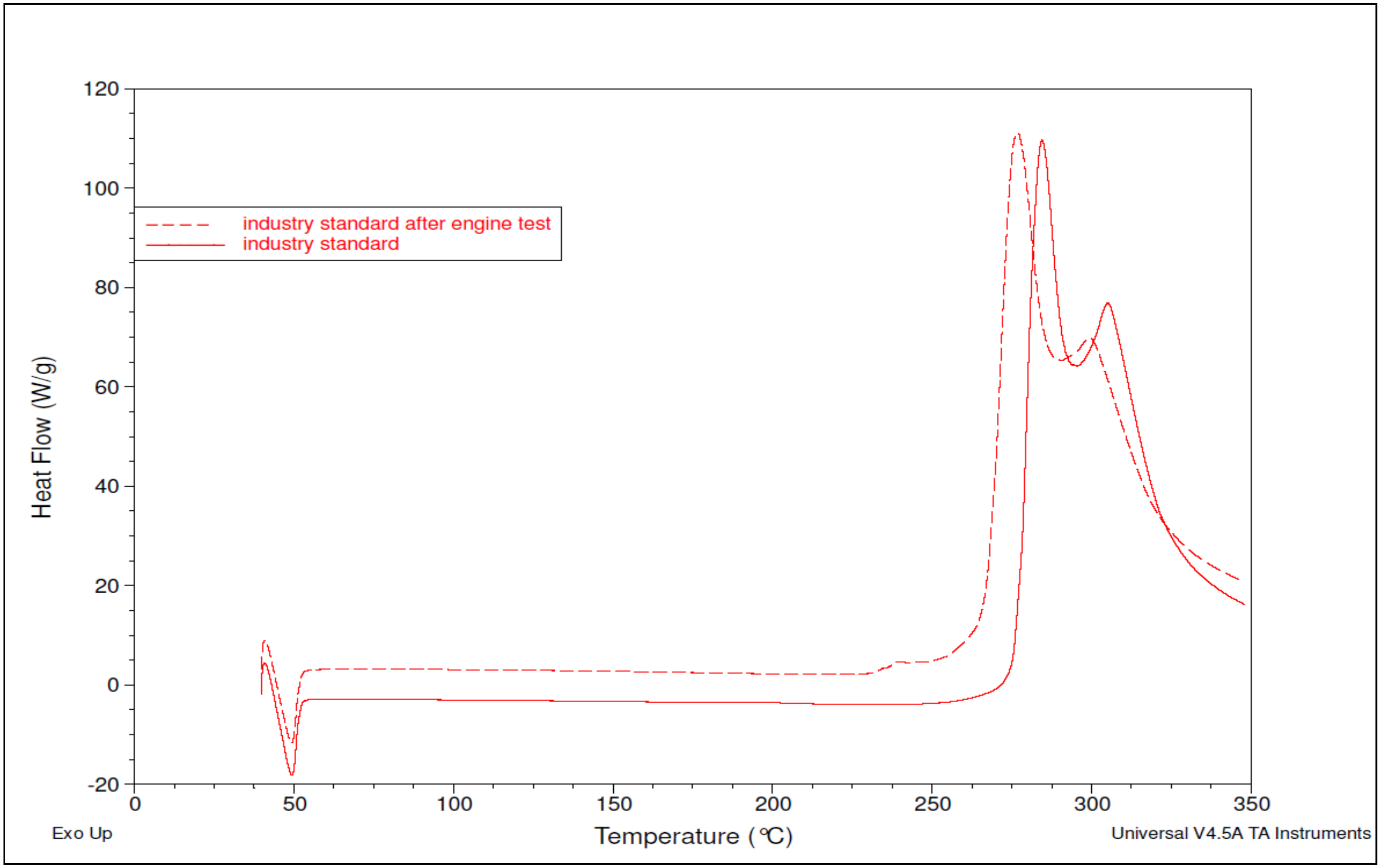

Figure 4.11 (a) OOT curve for Industry standard sample after engine test by DSC.

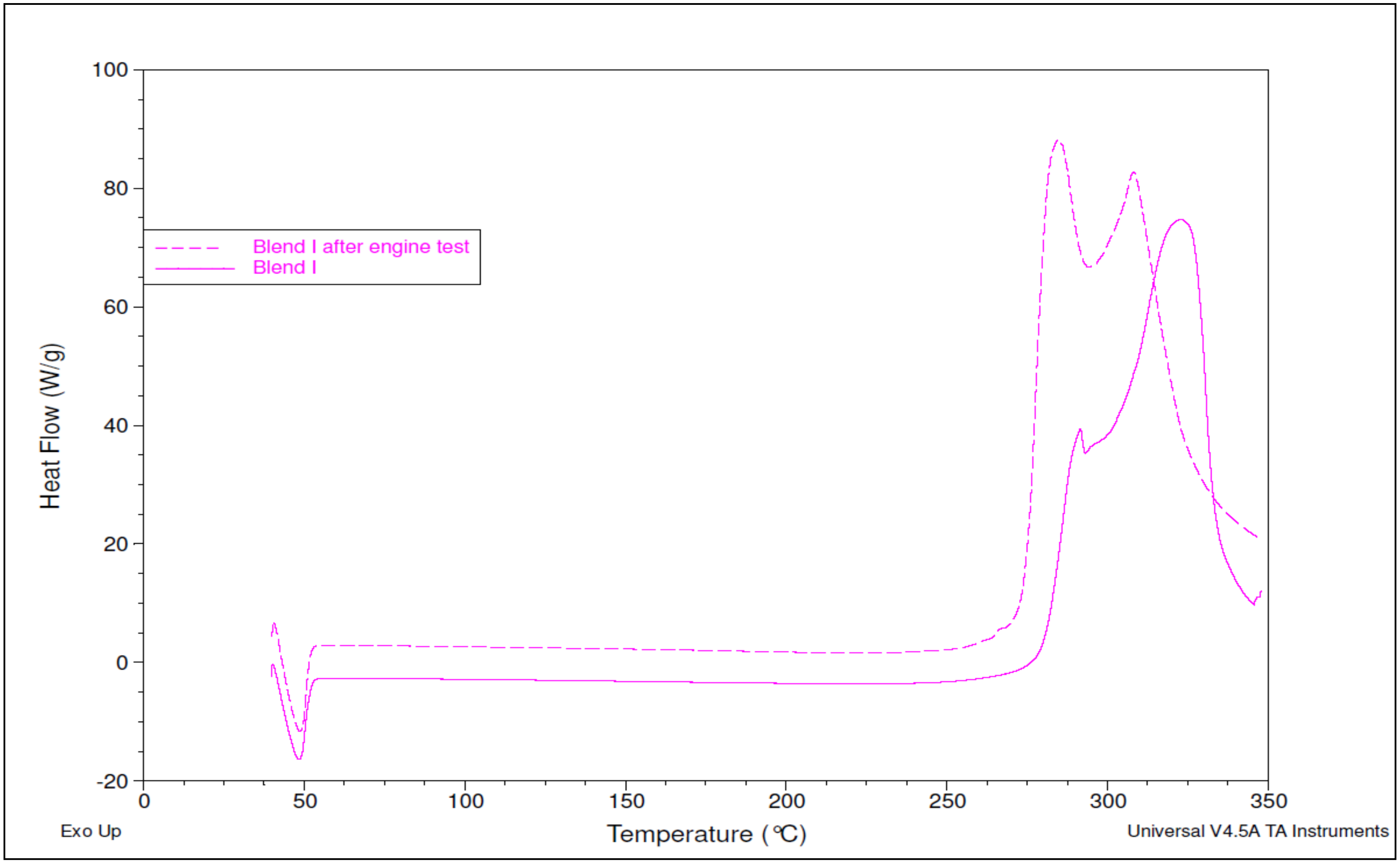

Figure 4.11 (b) OOT curve for sample blend I after engine test by DSC.

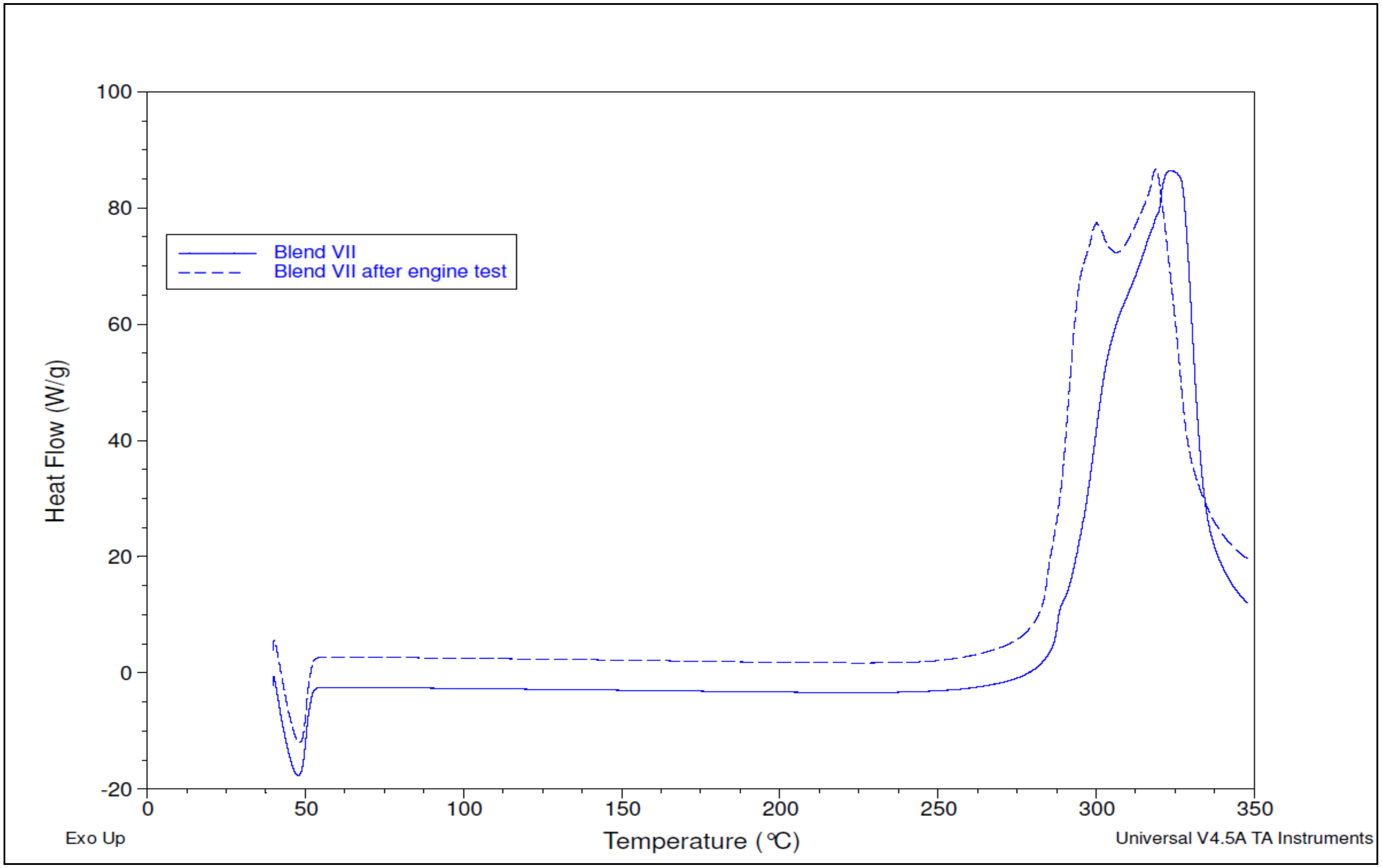

Figure 4.11 (c) OOT curve for sample blend VII after engine test by DSC.

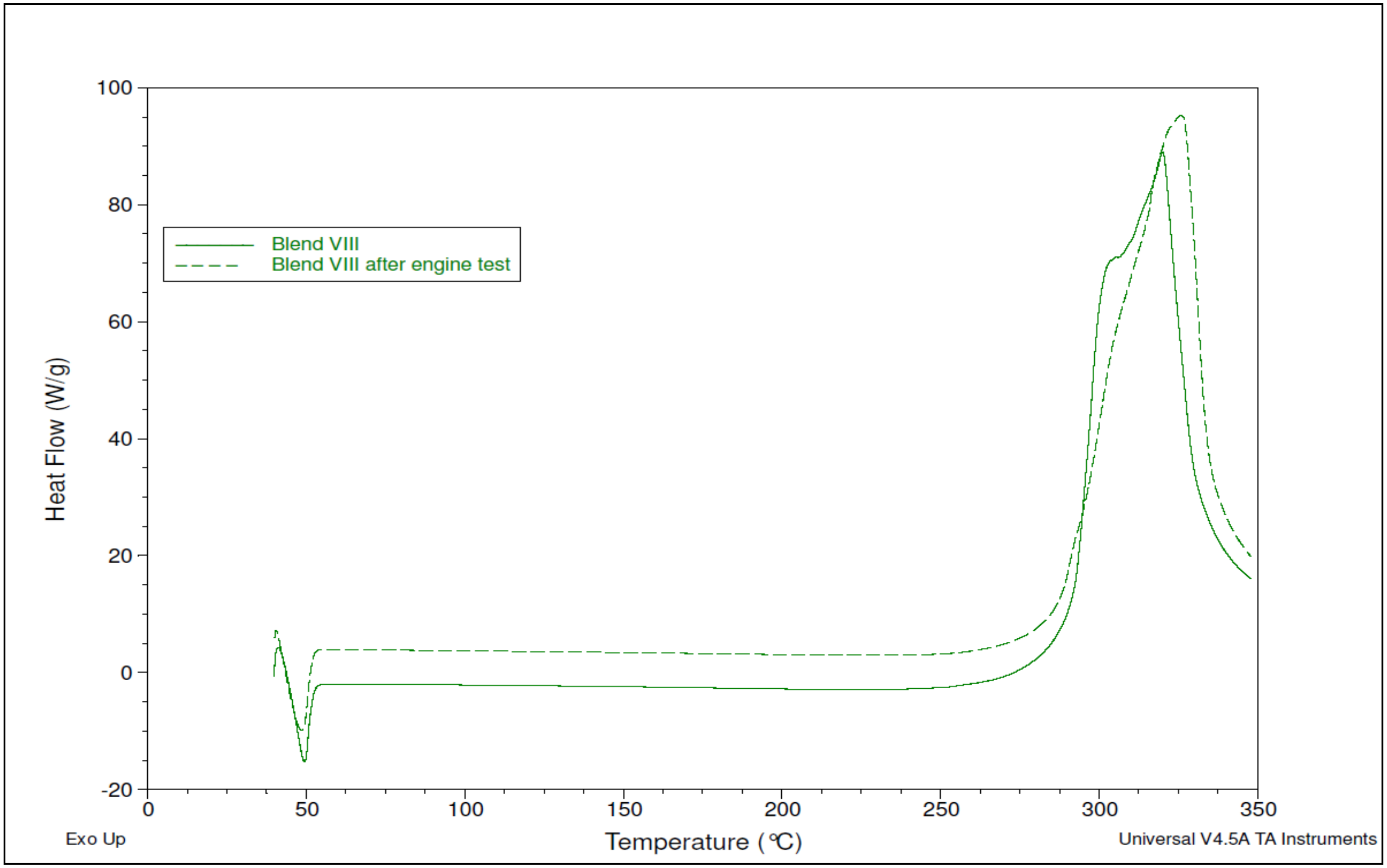

Figure 4.11 (d) OOT curve for sample blend VIII after engine test by DSC.

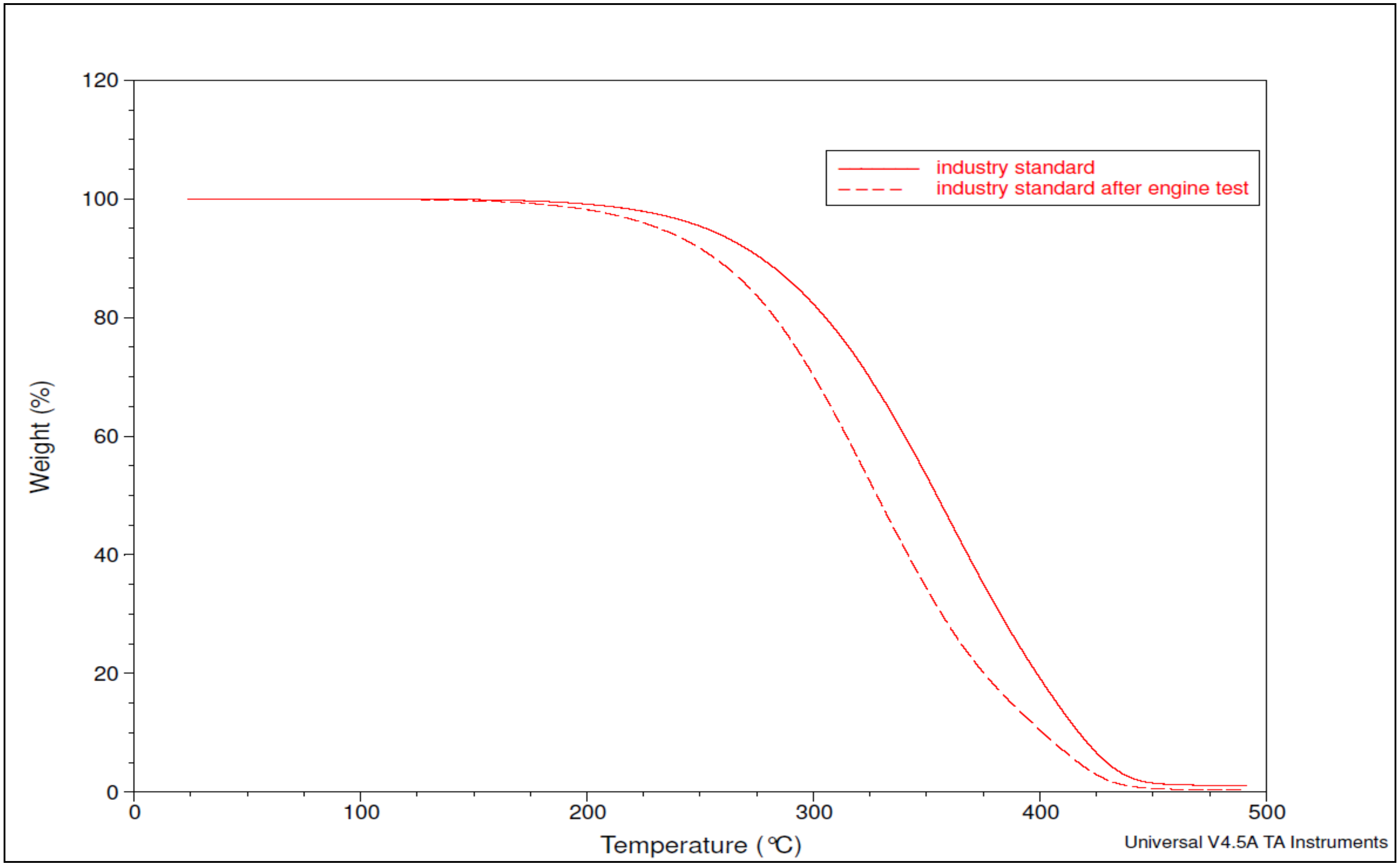

Figure 4.12 (a) Thermal stability curve for industry standard sample after engine test by TGA.

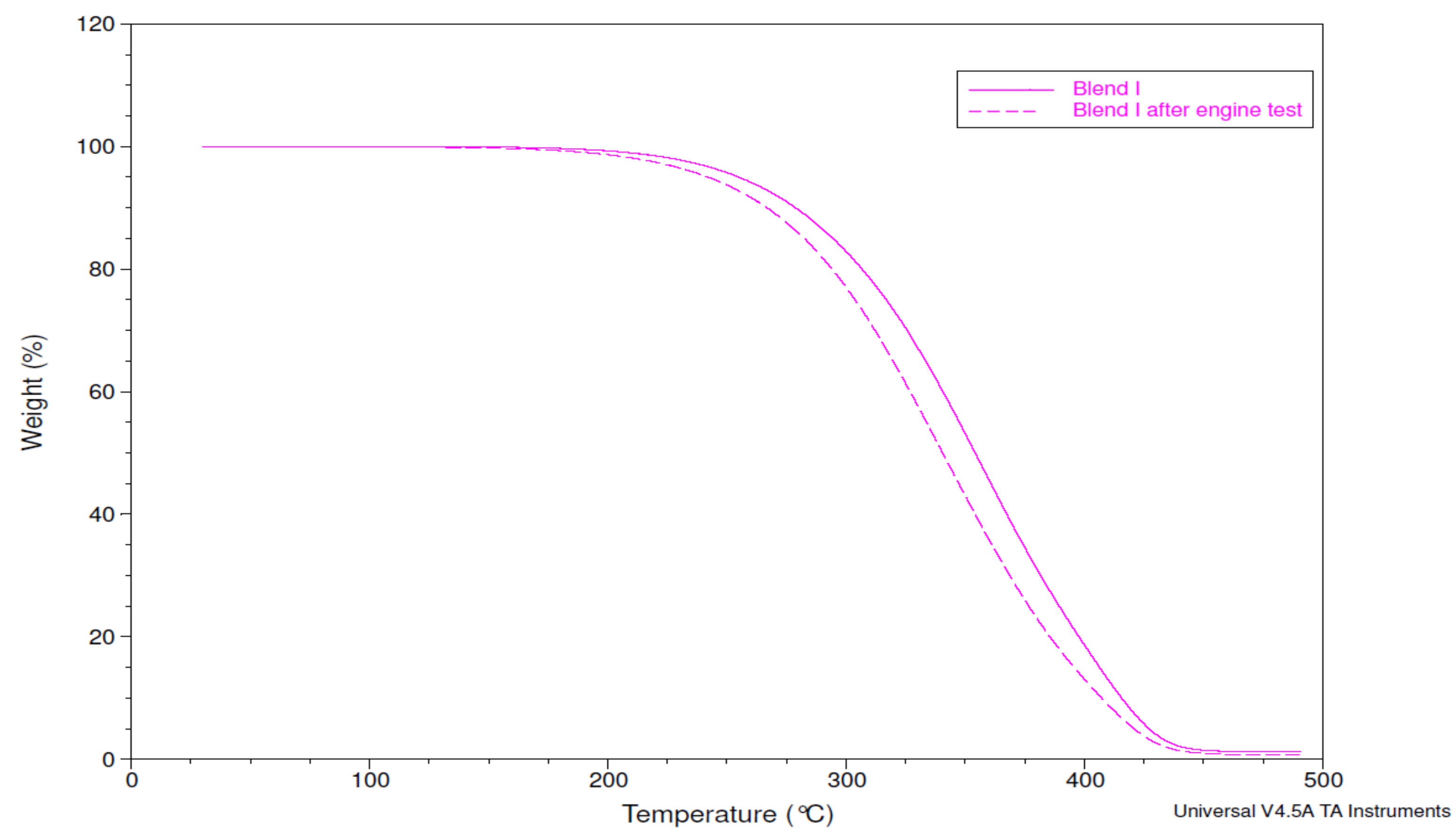

Figure 4.12 (b) Thermal stability curve for sample blend I after engine test by TGA.

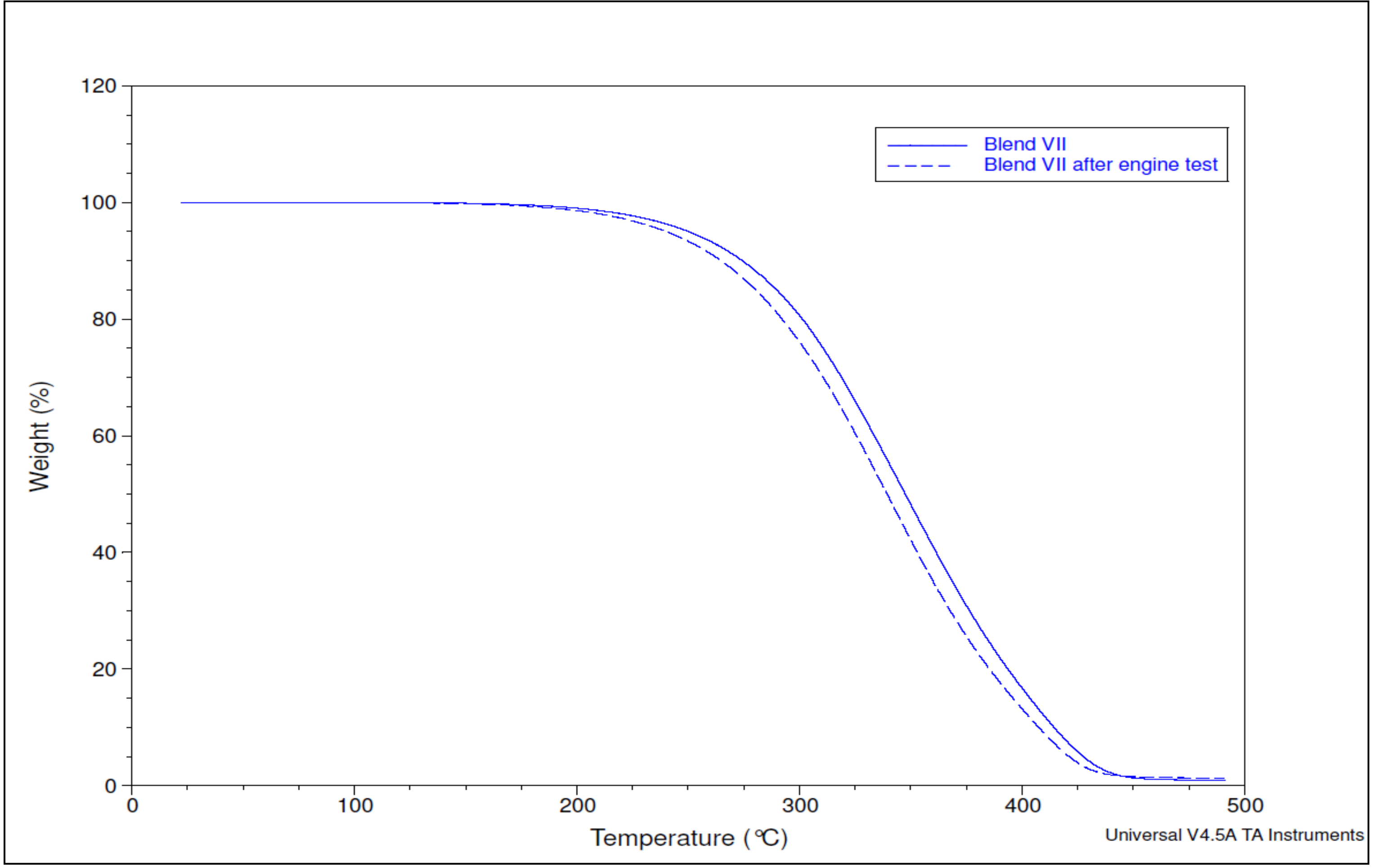

Figure 4.12 (c) Thermal stability curve for sample blend VII after engine test by TGA.

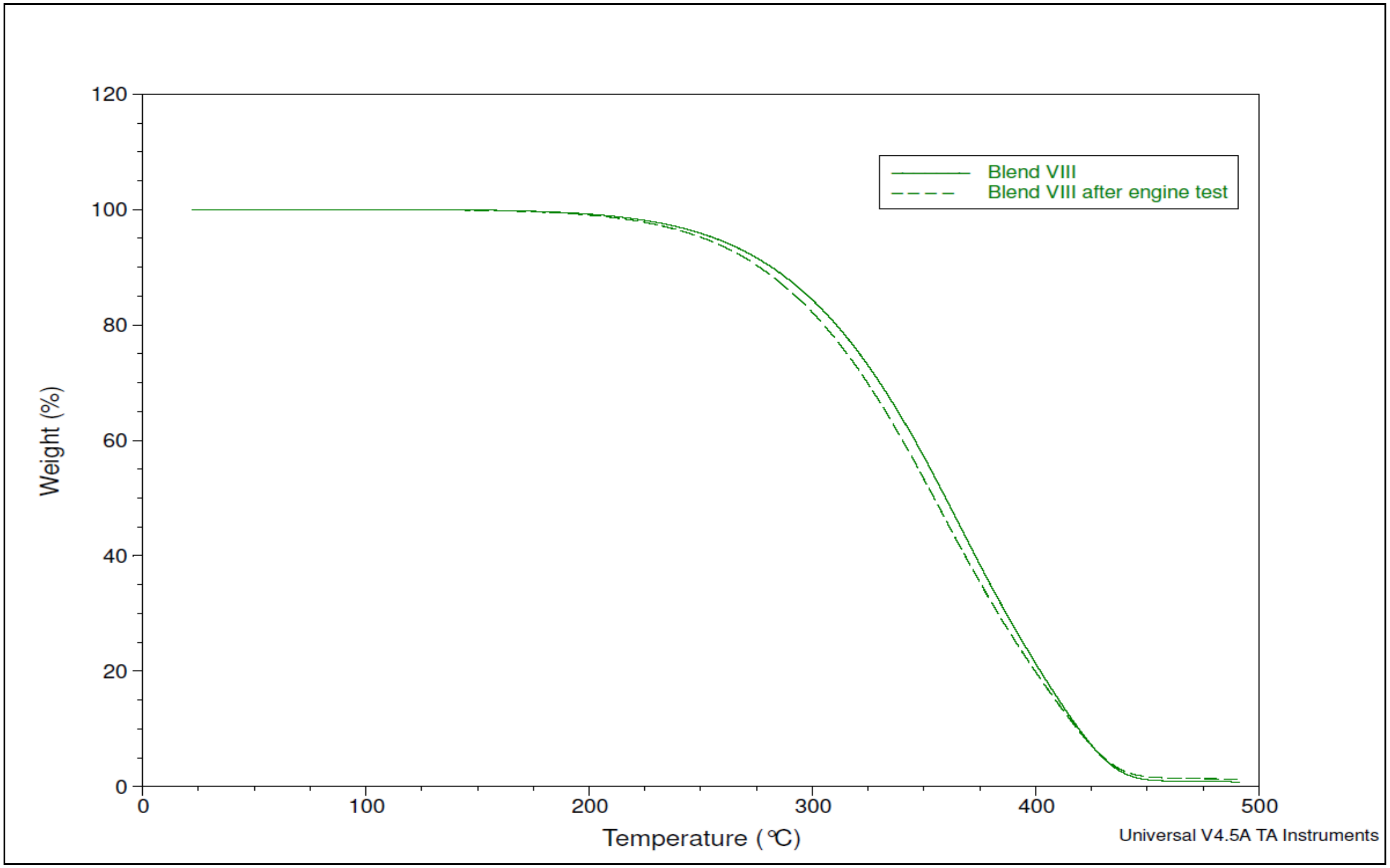

Figure 4.12 (d) Thermal stability curve for sample blend VIII after engine test by TGA.

From the respective traces it is observed that used engine oil after 64 hrs of test run did not show a significant deviation in the properties when compared to these for fresh engine oil. Further the values in the ensuing table revealed that the deviation is least for the blend VIII which is followed by blend VII, blend I and then the industry standard, all the optimized samples having exceeded their performance against the industry standard.

The next chapter will logically conclude the findings of the research study carried out in the development of energy efficient engine oil as illustrated in the earlier chapters.

4.4 Bibliography

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Chapter 5

Conclusion

5.0 Prologue

Thermo-oxidative stability is fundamental to the design of high performance engine oil, addressing the severity associated with the current designs of the engines operating in highly stressed conditions. In this thesis it is shown that synergism in thermal and oxidative stability of engine oil definitely improves its performance in automotive engines. This chapter consolidates the outcome of studies elaborated in the previous chapters of the thesis and presents the landscape of the validation of the laboratory test results in actual performance engine tests. In this context a synergy in identified Viscosity Modifier (VM), Friction Modifier (FM), and Antioxidants (AO) has also been elucidated.

5.1 Base Oils

Base oil should have lower volatility (for control of evaporation loss), high viscosity index and good low temperature properties. Volatility and thermal stability are the inherent properties of base oil and have significant influence on stability at higher temperatures. The reasons behind the selection of Group III base oil is clearly explained in the Chapter 2 of the thesis. The paraffinic content, naphthenic content and the monocycloparaffins present in the base oil plays important role in deciding its properties. The selection of base oil is also based on its compatibility with the antioxidants. From Chapter 2 it is inferred that all the aminic antioxidants selected have given response in the order Group IV~ Group III > Group II > Group I. This conclusion is based on thermal stability response shown by TGA.

5.2 Antioxidant Response

It is observed that antioxidant response in the base oils is based upon the alkylated groups attached with the aminic antioxidants. Aminic antioxidants with higher alkylated group have shown good response in all the base oils. Undecyl and naphthyl group presence in Aminic DPA A_4 has shown the highest response which is followed by the two nonyl groups present in aminic DPA A_3. All the aminic antioxidants have enhanced/increased the thermal stability of the base oils except for the aminic antioxidant A_2. The two Octyl groups present in Aminic DPA A_2 have shown least response in the entire base oils even though having better thermal stability than the Butyl Octyl Aminic DPA. It may be due to the poor solubility of A_2 in the base oil due to its solid state nature. All the other aminic antioxidants are liquid in state and have good solubility with the base oil mixtures.

5.3 Viscosity Modifier Response

Fuel efficiency is the global focal point in the automotive segment and plays an important role in the designing of engine oil, and hence friction control assumes greater focus. However, film thickness playing an important role in controlling the wear of engine parts, also needs to be critically examined. Due to thin film formation at high temperature in current and future generation engines, selection of viscosity modifiers becomes critical. As discussed in Chapter 2 and 3 respectively, lower SSI (shear stability index) VMs in both non-dispersant ethylene-propylene copolymer VM 1 (25 SSI) and dispersant ethylene-propylene copolymer VM 3 (24 SSI) have exhibited higher EHD film thickness. Higher ethylene content (^{13}C NMR; Table 2.7) and lower molecular weight profile (GPC; Table 2.6) may be the plausible reason for such an observation.

5.4 Friction Modifier Response

Friction profile traces (coefficient of friction on the SRV linear oscillating tribometer) for blend containing FM 2 showed lower coefficient of friction than for the blend containing FM 1. The possible reason may be due to the oxidative inhibition characteristic of FM 2 as compared to FM 1 due to the presence of sulphur content in it as explained in chapter 2 and 3 (See Table 2.8).

One of the combinations of Viscosity Modifier and Friction Modifier (VM 3 and FM 2), blend I in chapter 3 reported highest EHD film thickness and lowest coefficient of friction value among the others. This could be due to the dispersant behavior of aromatic polyamine derivative present in the VM 3. This particular combination (VM 3 & FM 2) in addition with additive package and antioxidant combinations is used for developing next generation engine oils in this study.

5.5 VM-FM-AO Synergy

Further 6 antioxidants comprising of 2 phenolic and 4 aminic types were evaluated in the bench laboratory tests in combination with the VM & FM along with an identified additive package in group III base oil as discussed in chapter 3. Total of 8 blends were prepared by taking one Phenolic and one Aminic antioxidant combination at a time (see Table 3.2). These blends were evaluated on different thermal stability and oxidation stability tests for screening out the best performing engine oils.

5.6 Thermo-oxidative Screening Protocol

Various tests selected were TGA for weight loss profile as a function of temperature, DSC for oxidation onset temperature, PDSC for oxidation induction time, TFOUT for oxidation stability under simulated engine operating condition and modulated DSC for heat capacity evaluation. As discussed earlier 4 out of 8 blends formulated contained P_1 and rest 4 contains P_2, the basic difference between these two (P_1 & P_2) being the sulphur content (See Fig. 2.5 a).

5.6.1 Thermal Stability

Higher thermal stability translates into lower oil consumption, an important component of the operational expenses. Thermograms of optimized samples derived from TGA Studies (See Fig. 3.10 and Table 3.3) show all the combinations to have enhanced the thermal stability of the blends against base oil group III. The base line group of test blends containing phenolic antioxidant P_2 (curves with solid lines) have shown higher thermal stability than the group of test blends containing phenolic antioxidant P_1 (curves with dashed lines).

Within these two groups it is also observed that blends with one of the aminic antioxidant A_2 exhibit least stability. The reason behind this may be the solid state nature of aminic antioxidant A_2 and its poor solubility issue with the base oils as discussed above. Within the group of test blend containing phenolic antioxidant P_2, the thermal stability is found to be dependent on the alkylated groups attached to the diphenyl amines. It is observed that the blend containing aminic antioxidant A_4 reported highest thermal stability followed by blend containing A_3 and subsequently by A_1 and then A_2.

This leads to conclude that higher alkylated groups like (undecyl & naphthyl) in A_4 and (Nonyl) in A_3 lead to excellent thermal stability. It is observed that some of the blends are stable up to 50 % of the weight over temperature of 350 °C. This could be beneficial in the new generation engines where the operating temperatures are very high. In the group of test blends containing phenolic antioxidant P_1, the test sample containing aminic antioxidant A_1 (butyl & octyl) had reported the highest thermal stability which is followed by blend containing A_3 and subsequently by A_4 and then A_2.

5.6.2 Oxidation Stability

DSC instrument is measures precisely the heat flow changes for a sample either under increasing temperature profile in presence of oxygen or in isothermal condition under pressurized oxygen (the later one is done in PDSC). Higher OOT/OIT determined in DSC/PDSC respectively, represent better oxidation inhibition characteristic at higher temperatures. Oxidative stability determined in DSC (See Fig. 3.11 and Table 3.4) for all the combinations have shown better OOTs against the base oil group III. Some of the blend combinations exhibited OOT values above 280 °C. Such combinations have shown higher OITs in PDSC against the base oil group III (See Fig. 3.12 and Table 3.5). As already discussed in the results on thermal stability by TGA, similar behavior is observed in the optimized blends as seen for oxidation stability in DSC and PDSC.

5.6.3 Thermo-oxidative Stability

The optimized blends when tested for their thermo-oxidative stability by simulating actual engine operating conditions such as fuel content, NOx content, moisture, temperature and pressurized oxygen on thin films of the engine oil in TFOUT instrument, showed oxygen induction times in line with the results obtained from TGA, DSC and PDSC.

5.7 Heat Capacity

As there is a multiple cooling and heating cycles in the engine operation, the engine oil should be compatible to those temperature gradients too. In other words that engine should dissipate heat quickly when the engine oil returns to sump, from higher temperature regions in the engine such as piston rings. This would facilitate retaining original oil properties and hence longer oil drain period. Hence heat capacity of engine oil at different temperatures needs to be calculated as heat capacity gives valuable information on internal energy of the sample.

When the optimized 8 blends were evaluated for heat capacity at different temperatures by modulated DSC method, it is found that the blends which have given good thermal and oxidative stabilities in TGA, DSC, PDSC and TFOUT instruments have reported lower heat capacities at different temperatures. Heat capacities relates to the internal energies stored at particular temperatures. Lower Heat capacities depicts faster cooling of samples as it has to lose smaller amount of energy (internal) at that temperature to the environment. Therefore, optimized engine oils with lower heat capacities have been found to give better thermal and oxidation stabilities.

Therefore it is established that the thermo-oxidative stability is enhanced by the addition of antioxidants while optimizing/designing the engine oils for newer generation.

5.8 Deposits

The results discussed in the preceding segments, have been validated under actual conditions of test of engine oils in high temperature oxidation engine test bench. Deposit forming tendency of the engine oils (selected blends) with industry standard engine oil as baseline has been tested in two conditions as discussed in the Chapter 4. It is observed (Fig. 4.3 & 4.6) that the selected blends have reported lower deposits in both the cases vs the industry standard. Lower deposits depict higher thermo-oxidative stability. Blend VIII having sulphurized phenolic antioxidant and undecylated/napthenic DPA aminic antioxidant has given the lowest deposit among the two other selected blends (VII & I) and the industry standard. Thus the engine oil optimized is found to maintain its useful oil life for a longer time. This translates into its ability in protecting engine components for a longer drain. Hence the basic formulation adds on to the engine endurance at extended drain of the engine oil.

5.9 Tribo-mechanical Validation of Frictional Efficiency

The blends optimized have, also been evaluated for frictional behavior. Coefficient of friction for the selected blends against an industry standard, when measured on a linear oscillating tribometer, (Fig. 4.7 & 4.8) exhibit lower values than that for industry standard. Lower coefficient of friction depicts smooth operations of engine and is likely to manifest into fuel efficiency and durability. It is therefore, logical to infer that Such a formulation, in all probability, is likely to result in higher KMPL i.e., kilometers per liter of engine oil.

5.10 Engine Test Program for final Validation

The selected blends have been validated on the engine tests for their performance in actual engine running condition. Sequence III E engine test evaluated oil performance for their ability to inhibit high temperature oxidation and subsequently control wear formation in cam/lifter area of the engine. The optimized engine oils (Fig. 4.9 & 4.10) have reported lower values in both the parameter of engine test, (average cam lobe wear and percent increase of viscosity at 40 °C) against an industry standard and have passed the engine test with excellent credentials.

The used engine oils after the engine test, showed insignificant variation in both thermal and oxidation stability (Table 4.2, Fig. 4.11 & 4.12).

5.11 Mechanism of Action of Antioxidants

As per the literature sulphurized additives contribute towards extra oxidation stability [1]. Phenolic antioxidants like P_1 & P_2 are called Setrically hindered phenols (phenols substituted with tertiary alkyl groups at 2 & 6 positions) [2]. Hindered phenols are particularly effective, reacting successively with peroxy radicals to form stable cyclohexadieneone peroxides [3]. However hindered phenols are also able to terminate the reaction before the formation of cyclohexadienone peroxide (hydrogen is donated by the R’ group present in hindered phenol). By this process it duplicates itself and generates another hindered phenol. The reactions are illustrated below in Fig. 5.1.

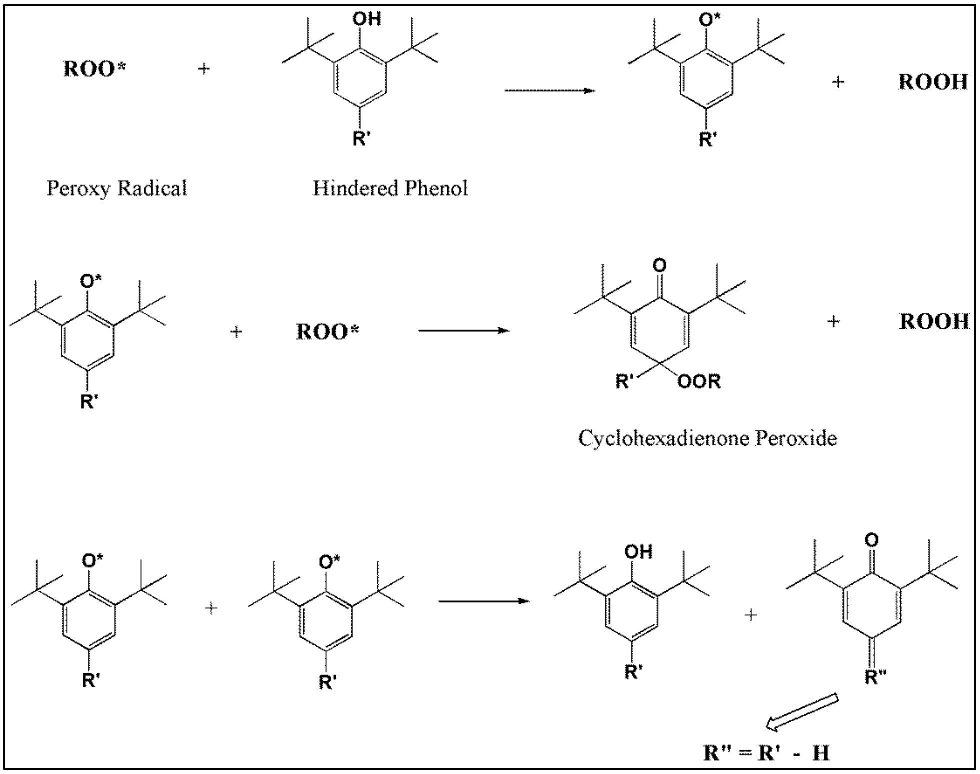

Figure 5.1 Reaction of phenolic antioxidant with alkyl peroxy radicals.

R’ group present in the sterically hindered phenol is responsible for scavenging the number of peroxy radicals. Sulphur presence in this group R’ has a great significance as observed from the results in the previous chapters. P_2 contains sulphur and P_1 doesn’t contain the sulphur. This difference has manifested in the results on the 8 blends. The blends group containing P_2 reported better thermal and oxidative stability than the blends group containing P_1. Further, in the absence of sulphur group as seen for blends containing P_1 it is found that A_4

and A_1 Aminic antioxidants behaved oppositely as seen for the P_1, A_1 combination.

Cyclohexadienone peroxide formed above loses its stability at higher temperatures and forms 2,6-di-tert-butylcyclohexa-2,5-diene-1,4-dione along with alkoxy radical and alkyl radical as illustrated in Fig. 5.2 [4]. This leads to deterioration of the action of phenolic antioxidant at higher temperatures.

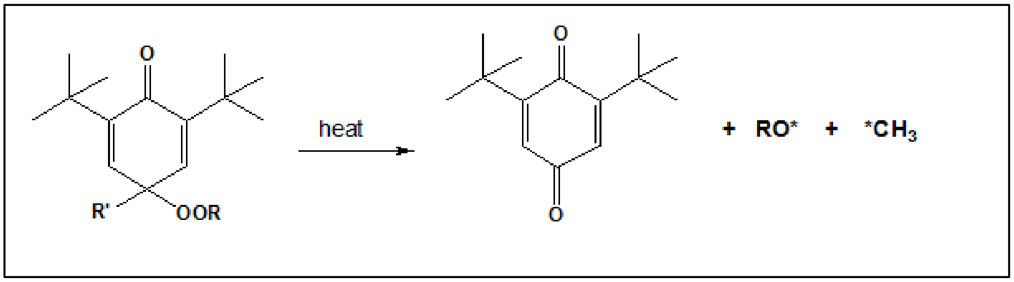

Figure 5.2 Decomposition of cyclohexadienone peroxide at higher temperatures.

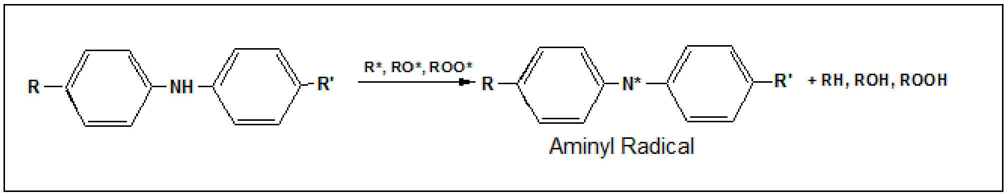

Figure 5.3 . ADPA acting as hydrogen donor.

Considering aminic antioxidant used alkylated diphenyl amines (ADPA), the oxidative inhibitive characteristic depends on the substituent, mainly alkyl groups, in the para position of diphenyl amines. The higher the alkyl group present in the DPA the higher is the oxidative stability of the DPA as it is observed from the results. These aromatic amines act as a hydrogen donor which reacts with alkyl radicals, alkoxy radicals and alkyl peroxy radicals as given below and forms aminyl radical as illustrated in Fig. 5.3 [4].

The reactivity of the aminyl radical formed can proceed in various pathways which depend on concentration of peroxy radical's present, temperature, chemical (alkyl) groups present in itself [5]. Under temperatures below 120 °C aminyl radical formed further reacts with more alkyl peroxy radicals to form nitroxyl radical and an alkoxy radical [6, 7]. This reaction further proceeds to form nitoxyl peroxide and finally forms 1,4 benzoquinone and alkylated nitrosobenzene on getting dissociated from intermediate nitroxyl cyclohexadienone peroxide as illustrated in Fig 5.4.

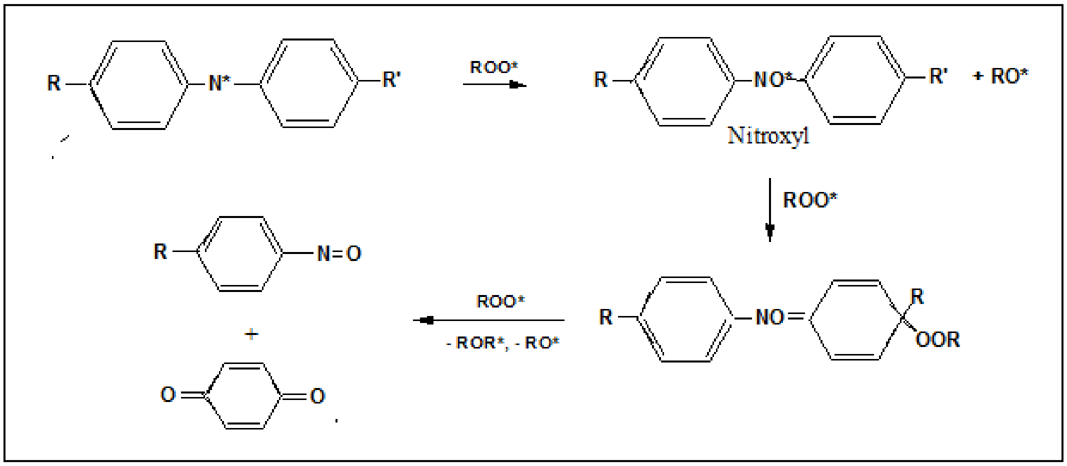

Figure 5.4 . Low temperature reaction for aminyl radicals

At temperatures above 120 °C nitroxyl radical reacts with secondary alkyl radical and rearranges to form ADPA (regeneration) as illustrated in Fig. 5.5 which can further react with more and more alkyl peroxy radicals. It can be said that stoichiometric factor will be higher for those DPAs whose alkyl group attached in the para position is high as is observed from the experimentation discussed in the study. Stoichiometric factor is the count of peroxy radicals/hydroperoxides inhibited or scavenged [8]. Therefore as we see in the selected antioxidants from A_1 to A_4 the alkyl group is increasing from butyl to octyl to nonyl to naphthyl and undecyl. The possible reason for antagonistic action of aminic antioxidant A_2 is discussed earlier.

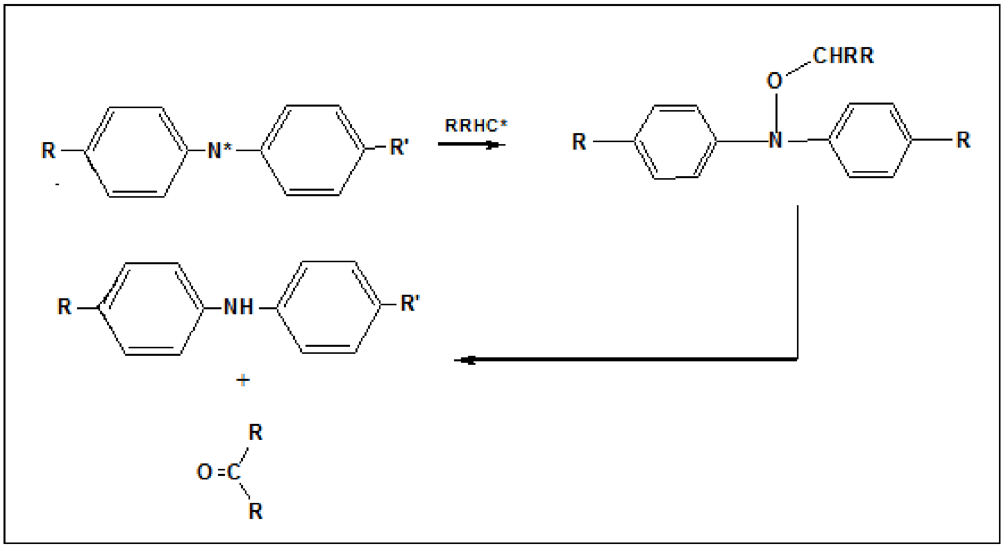

Figure 5.5 . High temperature reaction for aminyl radicals.

5.12 Inference

Thermal stability and oxidation stability are enhanced by the addition of antioxidants. The optimized engine oils with Phenolic and Aminic antioxidant combination have reported synergized results in controlling thermo-oxidation of engine oil. The presence of sulphur group in phenolic antioxidants is responsible for better thermo-oxidative stability of blends. Higher alkyl group present in the aminic antioxidants is responsible for good synergism in oxidative stability. Heat Capacity values of engine oils are found to be additional tool for screening of optimized engine oils giving valuable information on internal energy of the samples. The results are validated on the performance engine test. Engines durability can be increased by usage of energy efficient engine oils with good thermo-oxidative stability. Synergism among the thermal stability and oxidation inhibition characteristic of oil plays a vital role in the durability of next generation engines

Future scope of the research is very huge due to the new chemistry of additives evolving day by day for the better performance of engine oil. This has better and wider scope since the other options of baseline engine modification, after treatment devices and other vehicle design factors appear to reach the stagnation level.

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Publications, Conferences & CV

Publications

Paper 1 :

Title Study of Tribo-Chemistry in Establishing Synergy of Friction Modifiers and Viscosity Modifiers in Engine Oils.

Authors Shiv Kumar Vabbina, Anil Bhardwaj, Sanjiv Kumar Mazumdar and Mukesh Saxena.

Publication Indian Journal Of Tribology (ISSN 2347-3037), Vol. 7, No. 1, July 2015, Page 16-20.

Paper 2 :

Title Role of Oxidation Inhibition & Thermal Stability for the Development of Next Generation Engine Oils.

Authors Shiv Kumar Vabbina, Anil Bhardwaj, Sanjiv Kumar Mazumdar and Mukesh Saxena.

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Conferences & Symposiums

1. SAE NIS Conference on Future Trends in Passenger Car Engine and Lubricant Technology : 4th December 2012, Gurgaon.
2. National Tribology Conference, Bangalore, December 15-17, 2014.
3. 4th National Symposium on Recent Advances in Analytical Sciences, Jamia Hamdard University, New Delhi, February 9-10, 2015.
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