THE GOVERNING ROLE OF PRE-EXISTING LUBRICANT DEPOSITS IN SUBSEQUENT DEPOSIT GROWTH:
A UNIFORM LAYER MODEL

A Dissertation in
Energy and Mineral Engineering

by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2011
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Abstract

Deposit formation on pistons, valves, fuel pumps and injectors is universally recognized as undesirable, because engine performance will degrade. Across several lubricant formulations including mineral, synthetic, bio-based and fully formulated lubricants, the Penn State Micro-Oxidation (PSMO) test has shown that mass deposition, regardless of the nature of the lubricant, follows a similar trend. A lacquer or varnish type of deposit initially forms followed by transformation to a dark carbon deposit. Yet each of these very different deposits (lacquer or dark carbon) results from degradation of the same lubricant.

To provide a reference frame for mass deposition, the standard mass deposition profile was mapped using the PSMO method. Sets of substitutional tests were performed using a second stage of PSMO. Aged film substitution tests were performed using differently aged pre-deposits re-inserted within fresh lubricant to gauge the effect of deposit chemistry upon deposit growth. Similarly, aged oil experiments were conducted to test for any potential synergy between aged oil and evolving deposits. Each test strategy provides a means by which to decouple the lubricant from the deposit so as to gauge the role of deposit chemistry upon continued deposit growth. To provide a baseline for comparison, heat treatments were applied to films extracted from various stages of the mass deposition curve.

To characterize film chemistry and its evolution, FTIR and EDS spectroscopy were applied PSMO deposits formed during the course of this study. The former measures alkyl sp3 C-H and carbonyl C=O bond stretching vibrations and their relative concentration as films/deposits age. The latter provides a more global measure of C- and O-atom content as the deposit undergoes deoxygenation and dehydrogenation reactions.
Results obtained in this study showed a declining activity towards mass deposition with film age. Chemical characterization of these series of films by EDS for global elemental composition and by FTIR for chemically specific bond concentration correlate well with each other, specifically comparison of the chemical composition rates shows correspondence between C and O atom concentration changes. Also mass deposition rates decrease with increasing film age, within the proviso for times past induction and accelerative stages. Aged film studies demonstrate a consistent reactivity decline with increasing film.

The significance of these studies is that they are the first to consider the deposit as not only chemically active, but governing subsequent deposition. Traditionally, deposits have been considered as inert, the end product of a series of complex liquid phase radical driven processes, decoupled from the film. Further distinguishing this work from prior studies, referencing the film is the presumption of homogeneous chemistry, albeit time-varying under heated, oxidizing conditions. Hence in this context, the uniform layer deposition model is advanced.
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Acknowledgement

First and foremost I want to express my sincerest gratitude to my thesis advisor, Dr. Randy Vander Wal, whose guidance, assistance and encouragement on this project helped me complete this dissertation. It has been an honor to be his first Ph.D. student here at Penn State. I appreciate all his contributions of time, ideas, and funding to make my Ph.D. experience productive and successful.

I would especially thank Dr. Yaw Yeboah for his immense support, guidance and understanding at a critical moment of my doctoral work. I wish to express my appreciation to Dr. Andre’ Boehman, Dr. Joseph Perez and Dr. Semih Eser for their valuable advice, help and technical support without which this project will not have been possible.

Furthermore, thanks also to the Department of Energy and Mineral Engineering, the Energy Institute and the Chemical Engineering Department and Infineum Ltd. for providing funding, samples, tools and facilities used in this project.

I would like to show my deepest gratitude to my father, Eugene K. Kouame, my mother Rose T. Koffi (Mrs. Kouame) and all my brothers and sisters for their prayers and support throughout my studies in the United States of America.

Most importantly, I would like to thank God for blessing me and giving me such a great family in America. To Sharon and Peter Campione, no words would be enough to show how much I am thankful for everything you have done for me, not forgetting my brothers Bryan and Scott. To my friends Francis, Emily, Alpha, Roland, Desiree and Gilles, I would say thank you for being there when I needed you the most in my life.
Above all, I would like to dedicate my doctoral dissertation to the memory of my dear father whose sacrifices made my dream come true.

“This is the first year of my life without you, what an incredibly difficult and yet life changing year it has been. No one else believed in me as much as you did; I wish you had lived to see this day.”

Thank you Father.
Nomenclature of Substitution Test

S\{30\text{min}\}, Pan covered with 30 min. PSMO deposit

S\{60\text{min}\}, Pan covered with 30 min. PSMO deposit

S\{90\text{min}\}, Pan covered with 30 min. PSMO deposit

S\{120\text{min}\}, Pan covered with 30 min. PSMO deposit

S\{30 + 30 \text{ min}\}, Pan precovered with 30 min. + 30 min. additional PSMO time

S\{30 + 60 \text{ min}\}, Pan precovered with 30 min. + 60 min. additional PSMO time

S\{30 + 90 \text{ min}\}, Pan precovered with 30 min. + 90 min. additional PSMO time

S\{30 + 120 \text{ min}\}, Pan precovered with 30 min. + 120 min. additional PSMO time

S\{60 + 30 \text{ min}\}, Pan precovered with 60 min. + 30 min. additional PSMO time

S\{60 + 60 \text{ min}\}, Pan precovered with 60 min. + 60 min. additional PSMO time

S\{60 + 90 \text{ min}\}, Pan precovered with 60 min. + 90 min. additional PSMO time

S\{60 + 120 \text{ min}\}, Pan precovered with 60 min. + 120 min. additional PSMO time

S\{90 + 30 \text{ min}\}, Pan precovered with 90 min. + 30 min. additional PSMO time

S\{90 + 60 \text{ min}\}, Pan precovered with 90 min. + 60 min. additional PSMO time

S\{90 + 90 \text{ min}\}, Pan precovered with 90 min. + 90 min. additional PSMO time

S\{90 + 120 \text{ min}\}, Pan precovered with 90 min. + 120 min. additional PSMO time

S\{120 + 30 \text{ min}\}, Pan precovered with 120 min. + 30 min. additional PSMO time

S\{120 + 60 \text{ min}\}, Pan precovered with 120 min. + 60 min. additional PSMO time

S\{120 + 90 \text{ min}\}, Pan precovered with 120 min. + 90 min. additional PSMO time

S\{120 + 120 \text{ min}\}, Pan precovered with 120 min. + 120 min. additional PSMO time
CHAPTER 1 - INTRODUCTION

It is universally recognized that deposit formation on pistons, valves, fuel pumps, and injectors are undesirable, as these can degrade engine performance (Rasberger et al., 1997 and Clarke et al., 1997). Ever since the inception of internal combustion engines, these deposits have been largely unavoidable, despite extensive efforts to develop lubricants to eliminate their formation or minimize their impact (Brown et al., 2004; Coates et al., 1983; Coates et al., 1985 and Hsu et al. 1981). In addition to deposit inhibition, a lubricant performs a number of critical functions: lubrication, cooling, cleaning, and protecting metal surfaces against corrosion damage. So-called “finished lubricants” contain one or more additives that are blended with one or more base oils to enhance the performance characteristics of the base oil (Crema et al, 1996). Lubricant breakdown and polymer formation are well recognized as the main cause of oil thickening, and is evidenced by sludge and varnish formation (Asseff, 1977). The sludge and varnish are presumably the results of free-radical chain reactions consisting of the chain initiation, propagation, branching, and termination steps.

The rate at which a lubricant degrades depends upon a number of factors, the most critical of which is temperature. This is reflected by an Arrhenius rate of overall deposit formation typically characterized by an induction period, growth, and decrease of products formed during the process (Emanuel, 1974). These stages comprise the well known mass deposition curve describing deposit formation as a function of time occurring in four basic stages: (1) an induction period, where minimal deposit is formed; (2) a sharp acceleration in mass deposition; (3) maximal attainment, followed by (4) a period of gradual mass decrease (Figure 1.1). Notably such a curve pertains to isothermal conditions.
Although extensively reported in the literature, there is little consensus among researchers on the physical and chemical factors, such as species and/or phase(s) that give rise to the mass deposit curve and account for the induction, the rapid acceleration, the peak, and the decrease observed during deposit formation. Various systems studied using the Penn State Micro-Oxidation (PSMO) test (including mineral, synthetic, bio-based, and fully formulated lubricants) have shown that mass deposition, regardless of the nature of the lubricants, follows a similar trend (Daly et al., 1994).

A lacquer or varnish type of deposit forms prior to the black carbon deposit, but both of these types of deposits result from degradation of the same lubricant. Varnish/lacquer and carbon occur when hydrocarbons undergo polymerization and deposition to make a tenacious (resin-like) film. Unfortunately, very little has been done to underline possible links between the changing chemical nature of the deposit and its relation to the "universal" mass
deposition curve. Implications of such an investigation would be of great significance in combating undesired deposit formation, since arresting and/or reversing deposition is easier when conducted early in the process. With this goal in mind, various studies have put forth models that attempt to either model the rate or describe a general process for deposit formation and growth. Given the chemical complexities involved, such studies generally focus on one phase or general reaction process, with some experimental support. These models may be categorized as a) a liquid phase deposition model, b) a surface-controlled deposition model and c) a binary layer growth model. These models and their supporting literature are briefly described in the next section.

Controlling temperature and improvement in base oil formulation can help limit the degree and rate of oxidation. The eventual breakdown of the base oil molecules due to oxidative processes is inevitable (Perez, 1960). One common feature of these reaction byproducts is the carbon-oxygen double bonds that comprise the “carbonyl group.” The characteristic property of carbonyl groups is their infrared signature at the 1740 cm\(^{-1}\) region. Consequently, Fourier Transform Infrared spectroscopy (FTIR), which measures the degree of infrared absorption in different parts of the infrared spectrum, is an excellent tool for pinpointing base oil oxidation (Naidu et al., 1984).

Other important by-products of the oxidation process are carboxylic acids. Because oil oxidation results in the formation of carboxylic acids, the acidity of oil increases as oxidation proceeds. Carboxylic acids not only cause acidic corrosion, but also lead to more damaging chemical processes that form sludge and varnish (Cheng, 1996). Sludge and varnish form when oxygenated reaction by-products, such as hydroperoxides and carboxylic acids, combine to form larger molecular species. The general process is termed
polymerization and results in the formation of large molecules of high molecular weight (Gunsel et al., 1988). Because the viscosity of oil is directly related to the size of its molecules, any degree of polymerization will result in an increase in the measured viscosity. As polymerization continues, solid material, sludge and varnish form in the oil. These macromolecules become too large to remain in suspension in the liquid (Rudnick, 2006). They precipitate out of solution and initiate deposit formation. To foresee and eliminate these problems, a fundamental understanding of the process by which deposits are formed during oil oxidation is helpful. The current literature review aims to:

- Provide an overview of the general chemistry of lubricants
- Review current models of the lubricant deposit formation mechanism
- Review analytical techniques most commonly used to characterize lubricant deposits
CHAPTER 2: LITERATURE SURVEY

2.1 General Formulation of Lubricants

Typically lubricants contain up to ninety percent base oil, which can be mineral, bio-based, or synthetic with ten percent or more additives (Rudnick, 2006). Additives are incorporated into lubricants to compensate for the deficiencies of the base oils. Depending on the application, additives may deliver reduced friction, wear, increased viscosity, improved viscosity index, and/or resistance to corrosion and oxidation (Rudnick, 2008). Base oils are produced from refining crude oil (mineral base oil), through chemical synthesis (synthetic base oil) or from natural products (vegetable base oils). They are typically defined as oil with a boiling point between 550° and 1050° F, consisting of hydrocarbons with 18 to 40 carbon atoms. Mineral oils can be either paraffinic, aromatic or napthenic in nature, depending on the chemical structure of the molecules (Mortier et al., 2009).

2.1.1 Categories and Formulation of Base Oils

Five major categories of base oils exist on the market and are classified by API based on their processing and composition:

- Group I oils are mineral oils with less than 90% saturates and/or at least 0.03% sulfur. They are manufactured by distillation, solvent or catalytic dewaxing, and hydro-finishing processes.

- Group II base oils are mineral oils with more than 90% saturates and less than 0.03% sulfur. They are manufactured by hydrotreating and solvent or catalytic dewaxing processes. Group II base oil has superior anti-oxidation properties since virtually all hydrocarbon molecules are saturated.
• Group III base oils are also mineral oils with more than 90% saturates and less than 0.03% sulfur. Unlike Group I and II, which have a viscosity index ranging from 80 to 120, the viscosity index for Group III base oils is over 120. Group III base oils are manufactured by special processes such as isohydromerization and can also be manufactured from base oil or slax wax derived from the dewaxing process.

• Group IV oils contain polyalphaolefin synthetics consisting of artificially made chemical compounds that are created using chemically modified petroleum components rather than whole crude oil.

• Group V oils include all other base oils not included in the four categories listed.

Due to the large number of possible isomers, general composition of Group I-III base oils reported by class of compounds is categorized by:

• % saturates
• % aromatics
• % polars

Or by type of compounds:

• % Paraffinic, % Monocycloparaffin, % Dicycloparaffins, etc...
• % Monoaromatics, % Diaromatics, etc...

Tables 2.1 – 2.3 show a representation of molecular structures for the hydrocarbon types, except that the actual base oil molecular structure would contain a greater number of carbon atoms. A more general discussion on the characterization of petroleum fractions by Mass Spectroscopy is the subject of an excellent review article by Algelt and Boduszynski (1994).
Table 2.1. Typical Saturate Distribution of Base Oils 100N (4cSt). (Totten et al., 2003)

<table>
<thead>
<tr>
<th>Hydrocarbon Type</th>
<th>Relative Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Group I</td>
</tr>
<tr>
<td>Paraffins</td>
<td>23.9</td>
</tr>
<tr>
<td>Monocycloparaffins</td>
<td>14.7</td>
</tr>
<tr>
<td>Dicycloparaffins</td>
<td>11.3</td>
</tr>
<tr>
<td>Tricycloparaffins</td>
<td>8.1</td>
</tr>
<tr>
<td>Tetracycloparaffins</td>
<td>9.9</td>
</tr>
<tr>
<td>Pentacycloparaffins</td>
<td>6.6</td>
</tr>
<tr>
<td>Hexacycloparaffins</td>
<td>4.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>78.7</td>
</tr>
</tbody>
</table>

Table 2.2. Typical Aromatic Distribution of Base Oils 100N (4cSt). (Totten et al., 2003)

<table>
<thead>
<tr>
<th>Hydrocarbon Type</th>
<th>Relative Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Group I</td>
</tr>
<tr>
<td>Monoaromatics</td>
<td>11.7</td>
</tr>
<tr>
<td>Diaromatics</td>
<td>3.1</td>
</tr>
<tr>
<td>Triaromatics</td>
<td>1.1</td>
</tr>
<tr>
<td>Tetraaromatics</td>
<td>0.8</td>
</tr>
<tr>
<td>Pentaaromatics</td>
<td>0.4</td>
</tr>
<tr>
<td>Thiophenaromatics</td>
<td>1.6</td>
</tr>
<tr>
<td>Unidentified Aromatics</td>
<td>2.6</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>21.3</td>
</tr>
</tbody>
</table>
Table 2.3. Molecular Structures for the Hydrocarbon Types in Base Oils (Totten et al., 2003)

<table>
<thead>
<tr>
<th>Hydrocarbon Types</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins (includes isoparaffins)</td>
<td>![Paraffins Structure]</td>
</tr>
<tr>
<td>Mononaphtenes</td>
<td>![Mononaphtenes Structure]</td>
</tr>
<tr>
<td>Dinaphtenes</td>
<td>![Dinaphtenes Structure]</td>
</tr>
<tr>
<td>Trinaphtenes</td>
<td>![Trinaphtenes Structure]</td>
</tr>
<tr>
<td>Monoaramatics</td>
<td>![Monoaramatics Structure]</td>
</tr>
<tr>
<td>Indanes</td>
<td>![Indanes Structure]</td>
</tr>
<tr>
<td>Aromatics/Naphthenes “Hybrid”</td>
<td>![Aromatics/Naphthenes Structure]</td>
</tr>
<tr>
<td>Diaromatics</td>
<td>![Diaromatics Structure]</td>
</tr>
</tbody>
</table>
Adhvaryu et al. suggested that the effect of the composition of a base oil matrix on additive response is an indication of its behavior in a dynamic system. They proposed a novel method involving quantitative $^1$H and $^{13}$C NMR to explain the molecular chemistry of base oil. Their results showed that base oil molecular composition plays a significant role in predicting the extent of oxidative degradation. Adhvaryu et al. also concluded that naphtheno-aromatics, polynuclear aromatics, and long side-chains on benzene rings are susceptible to oxidation. Polar compounds were also found to play a significant role in controlling the rate of oxidation. Richaud et al. proposed that thermal oxidation of hydrocarbon substrates at low-to-moderate temperature, typically $T \leq 150^\circ$ C, results from a radical chain process initiated by hydroperoxide decomposition and displays an induction period.

2.1.2 Lubricant Additives

A lubricant performs a number of critical functions: lubrication, cooling, cleaning, and protecting metal surfaces against corrosion damage (Hsu et al., 2005). Several key factors, such as temperature and oil composition contribute to deposit formation of lubricating oils, but studies have also shown that additive formulation plays a predominant role in the mechanism (Ma et al., 2008; Hermance and Egan, 1958). With the increasing number of requirements imposed by the lubricating oil industry, many types of additives have been designed for specific purposes (Crema et al., 1996; Watanabe, 2008). Lubricating oils with continuous exposure to elevated temperatures are subjected to a breakdown, which results in a decrease in their life expectancy (Rasberger, 1997). Depending on the application, particular additives are incorporated into fully formulated oil to compensate for the base oil
deficiencies. Various combinations of additives are used to meet the required performance level (Watanabe, 2008).

The most common types of additives found on the market are listed in Table 2.4.

Table 2.4. List of Common Types of Lubricant Additives

<table>
<thead>
<tr>
<th>Additive Type</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detergent</td>
<td>Clean and neutralize oil impurities which would normally cause deposits (or sludge) on vital engine parts.</td>
</tr>
<tr>
<td>Friction modifiers</td>
<td>Increase fuel economy by reducing friction between moving parts.</td>
</tr>
<tr>
<td>Viscosity modifiers</td>
<td>Make oil's viscosity lower for cold starts. Multi-weight oils all have viscosity modifiers.</td>
</tr>
<tr>
<td>Deposit control</td>
<td>Prevent the formation of soft sludge and hard deposits of impurities.</td>
</tr>
<tr>
<td>Oxidation inhibitor</td>
<td>Retard the oxidation of metal inside an engine.</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>Retard the decomposition of the stock oil.</td>
</tr>
<tr>
<td>Antiwear</td>
<td>Cause a film to surround metal parts, helping to keep them separated.</td>
</tr>
<tr>
<td>Pour point depressants</td>
<td>Improve the oil's ability to flow at lower temperatures.</td>
</tr>
<tr>
<td>Anti-foam agents</td>
<td>Inhibit the production of air bubbles and foam in the oil which can cause a loss of lubrication, pitting, and corrosion where entrained air contacts metal surfaces.</td>
</tr>
<tr>
<td>Seal conditioners</td>
<td>Cause gaskets and seals to swell so that the oil cannot leak.</td>
</tr>
<tr>
<td>Metal deactivators</td>
<td>Create a film on metal surfaces to prevent the metal from prompting oil oxidation.</td>
</tr>
<tr>
<td>Extreme pressure agents</td>
<td>Bond to metal surfaces, keeping them from touching even at high pressures.</td>
</tr>
<tr>
<td>Dispersants</td>
<td>Cause contaminants (e.g., soot) to be suspended in the oil to prevent them from coagulating.</td>
</tr>
<tr>
<td>Wax crystal modifiers</td>
<td>Dewaxing aids that improve the ability of oil filters to separate wax from oil.</td>
</tr>
</tbody>
</table>
Usage of most lubricating oil additives may be divided into two groups, according to their function:

Oxidation inhibitors, detergents, and dispersants make up the general class of additives called “stabilizers” and “deposit control agents.” These additives are designed to control deposit formation, either by inhibiting the oxidative breakdown of the lubricant or by dispersing harmful products formed in the bulk lubricant. Oxidation inhibitors intercept the oxidation mechanism, while dispersants and detergents perform the suspending part of the process.

**Detergents:** Detergents are metal salts of organic acids that frequently contain associated excess base, usually in the form of carbonate. In contrast, dispersants are metal-free and are of higher molecular weights than detergents. The two types of additives almost always work in conjunction with one other. The final products of combustion and lubricant decomposition include organic and inorganic acids, aldehydes, ketones, and other oxygenated materials (Rudnick, 2003; Newby and Dumont, 1957). The acids have the propensity to attack metal surfaces and cause corrosive wear (Newley et al., 1980). Detergents, especially basic detergents, contain a reserve base that will neutralize the acids to form salts. Although this decreases the corrosive tendency of the acids, the solubility of the salt in the bulk lubricant is still low. The organic portion of the detergent, commonly called “soap,” has the ability to associate with the salts to keep them suspended in the bulk lubricant.

However, in this regard, detergents are not as effective as dispersants because of their lower molecular weight. The soap in detergents and dispersants also has the ability to suspend non-acidic oxygenated products such as alcohols, aldehydes, and resinous
oxygenates. The mechanism by which this occurs is depicted in Figure 2.1. Like most additives, detergents contain a surface-active polar functionality and an oleophilic hydrocarbon group, with an appropriate number of carbon atoms to ensure good oil solubility. The cleaning action of detergent additives is attributed to the chemisorptions processes and formation of metal salts. All detergent additives are made of:

- **Polar Head** (hydrophilic) that reacts with metal oxides or hydroxides
- **Hydrocarbon Tail** that provides oil solubility

![Figure 2.1. Oil Suspension of Polar Oxidation Products (Rudnick, pp. 124, 2008)](image)

Detergents prevent deposit formation by attracting and trapping deposit precursors into micelles, thus preventing precursors to settle onto metal surfaces and form resinous deposits. Detergents insure the protection of metallic surfaces by neutralizing acidic compounds formed during the combustion process.

**Dispersants**: Dispersants are designed to suspend polar oxidation products in the oil phase and to prevent them from agglomerating to form heavier fractions (see Figure 2.2). Unlike detergents, this goal is achieved in a reverse micelle process. Fuel- and lubricant oxidation and degradation products—such as soot, resin, varnish/lacquer, and carbon—are of
low lubricant (hydrocarbon) solubility, with a propensity to separate on to surfaces. The separation tendency of these materials is a consequence of their particle size. Small particles are more likely to stay in oil than large particles. Therefore, resin and soot particles, which are the two essential components of all deposit-forming species, must grow in size through agglomeration before separation. Growth occurs either because of dipolar interaction, as is the case in resin molecules, or because of adsorbed polar impurities such as water and oxygen, as is the case in soot particles.

Alternatively, soot particles are caught in the sticky resin. Dispersants interfere in the agglomeration process by association with individual resin and soot particles. The particles with associated dispersant molecules are unable to coalesce because of either steric factors or electrostatic factors. A dispersant molecule consists of three structural features: a hydrocarbon group, a polar group, and a connecting group or link (see Figure 2.2). The polar group is usually oxygen or nitrogen based. The polar group associates with the polar particles, and the non-polar group keeps such particles suspended in the bulk lubricant.

Figure 2.2 Structure of a dispersant (Rudnick, pp 147, 2008)

The mechanism of soot- resin- additive interaction is described as a process in which dispersants associate with individual resin and soot molecules, so as to impede the agglomeration process. Figure 2.3 illustrates how soot particles are caught in resin and how dispersants interfere in agglomeration by associating with individual resin and soot [A-B].
The scheme also presents how polar groups associate with polar particles, and keep non-polar particles suspended in bulk lubricant [C-D].

Figure 2.3. Mechanism of Soot-Resin-Additive interaction (Rudnick, 2006)

Antioxidants: Researchers have come to understand that some oils provide greater resistance to oxidation than others. The difference was eventually identified as stemming from naturally occurring antioxidants present in the oils, which varied depending on crude source-refining techniques. Some of these natural antioxidants were found to contain sulfur- or nitrogen-bearing functional groups. Therefore, it is not surprising that certain additives that are used to impart special properties to the oil, such as sulfur-bearing chemicals, were
found to provide additional antioxidant stability. The discovery of sulfurized additives providing oxidation stability was followed by the identification of similar properties with phenols, which led to the development of sulfurized phenols. Several effective antioxidant classes have been developed over the years and have been used in engine oils, automatic transmission fluids, gear oils, turbine oils, compressors, greases, hydraulic fluids, and metal-working. The main classes of antioxidants include oil-soluble and organo-metallic antioxidant of the following types:

1. Sulfur compounds
2. Sulfur-nitrogen compounds
3. Phosphorous compounds
4. Sulfur-phosphorous compounds
5. Aromatic amine compounds
6. Hindered phenolic (HP) compounds
7. Organo-copper compounds
8. Boron compounds
9. Other organometallic compounds

Antioxidants are designed to delay deposit formation and to inhibit oxidation via the following processes:

1. Radical scavengers donate a hydrogen atom that reacts with alkyl radicals to interrupt the radical chain mechanism.
2. Peroxide decomposers reduce the alkyl hydroperoxides in the radical chain.
3. Metal deactivators coat the metal surface to prevent metal ions from entering the oil and restrict access to corrosives.
Most lubricants, by virtue of being hydrocarbon based, are susceptible to oxidation (Rudnick, 2006). In general, all types of base oil require the addition of an antioxidant depending on the amount of unsaturation and natural inhibition present (Johnson et al., 1983). The refined mineral base oils contain natural inhibitors in the form of sulfur and nitrogen compounds sufficient for many applications. The oxidative stability of such oils shows a distinct, relatively long induction period. In contrast, some oils do not contain these natural inhibitors, or contain them only in small quantities. Besides sulfur and nitrogen compounds, other compounds, such as aromatics or partially oxygenated aromatics and phenolic oxidation products, contribute to the inhibiting effect. Unlike synthetic oils, traditional mineral oils (Group I–III) show moderate oxidative resistance. Oxidation inhibitors can be classified in the following manner:

1. Radical scavengers
   a. Nitrogen-containing inhibitors-aryl amine
   b. Oxygen-containing inhibitors-phenols
   c. Zinc dialkyl dithiophosphates [ZDDPs, (Coy and Jones, 1979 AND Willmermet et al., 1980)]

2. Hydroperoxide decomposers
   a. Sulfur-containing inhibitors-sulfides, dithiocarbonates, and sulfurized olefins
      b. Phosphorous-containing inhibitors-phosphites and ZDDPs

2.2. Oxidative Degradation of Lubricants

The vital input of additives into base oils is associated with unintended side effects, which cause deposit formation on metal surfaces due to lubricant decomposition or reaction.
Degradation by oxygen is common for lubricants. It proceeds according to a radical-chain mechanism, via alkyl and peroxy radicals, in three stages, described in Figure 2.4.

![Degradation of Lubricating Oil Diagram](image)

Lubricating oils can oxidize when exposed to air, particularly at elevated temperatures. The rate of oxidation depends on oil composition, temperature, presence of metal catalysts and operating conditions. Oxidation is the most common chemical reaction, not just in lubrication chemistry, but also in nature as a whole.

In the present context, oxidation is the chemical reaction of an oil molecule with oxygen, which is present due to either ambient or entrained air. Oil oxidation leads to permanent chemical change to the base oil molecules. The reaction results in the sequential addition of oxygen to the base oil molecules and forms a number of different chemicals species, including aldehydes, ketones, hydroperoxides, and carboxylic acids. When lubricants
are subjected to high temperatures, their volatility tends to increase. Over time, the degradation of additives through interaction with metal causes the formation of carbonaceous compounds on the metal’s surface. This degradation of additives and base oil could involve processes as complex as aldol reactions, which are the process of carbon-carbon bond formations, as described below in Figure 2.5.

![Aldol Reaction Diagram](image)

Figure 2.5. Aldol Reaction

2.2.1 Period of Induction

An induction period in chemical kinetics is the initial slow stage of a chemical reaction, which later accelerates. Induction periods are often observed with radical reactions, but may also occur in other systems before steady-state concentration of the reactants is reached (IUPAC, 1997). Often in catalytic reactions, a pre-catalyst needs to undergo a transformation to form the active catalyst, before the catalyst can take effect. Time is required for this transformation, hence the induction period. Many natural processes exhibit a progression from small beginnings that accelerates and approaches a climax over time. For those complex systems a sigmoid function is often used, when a detailed description is lacking. A sigmoid curve is produced by a mathematical function having an "S" shape.
(Figure 1.1). Often, a sigmoid function refers to the special case of the logistic function shown in Equation 1, where \( p(t) \) is the value of the time function at a given time \( t \).

\[
P(t) = \frac{1}{1+e^{-t}} \quad \text{(Eq. 1)}
\]

Similarly, for reactions (often autocatalytic), where one of the reaction products catalyzes further reactions, the rate of reaction is low initially until sufficient products have formed to catalyze the reaction. In general the reaction tends to accelerate with increasing temperatures. Many exothermic reactions often exhibit an induction period as well. In this case, the rate of the reaction is initially low but the heat generated as the reaction proceeds eventually increases the rate of reaction, Figure 2.6 (IUPAC, 1994 & 1996).

![Figure 2.6. Sigmoid curve for an autocatalytic reaction. (IUPAC, 1994 & 1996).](image)

Tseregounis et al. reported linear increase of induction time with increasing thickness of the oil film during oxidation of the base stocks. Tseregounis also describes that induction time decreases exponentially with increasing temperature. Equation 2 was therefore used in
their study to account for the dependence of the induction time on the film thickness and the temperature, (Tseregounis et al., 1987):

\[ t = t_0(T) + a \exp \left( \frac{b}{T} \right) \delta \]  

(Equation 2)

In this equation, \( t \) is the induction time (min), \( a \) and \( b \) are constants (min/\( \mu \)m and K, respectively), \( \delta \) is the thickness of the oil film (\( \mu \)m), \( T \) is the temperature (K), and \( t_0 \) is a time constant which depends on temperature (to account for the fact that the induction time approaches a non-zero value as the oil amount approaches zero).

2.2.2 Deposit Formation Rate

It is well understood that the speed of oxidation and the formation of deposit from the oxidative degradation of lubricants increases with temperature. The increasing rate of oxidation was however described to be limited by a number of factors including the rate of inflow and diffusion of the oxygen in the medium (Maleville et al., 1996).

Tseregounis et al. showed with Arrhenius plots derived from the oxidation process of various base oils that the rate at which deposits are formed appears to depend exponentially on temperature. This indicated that during the formation of the varnish or lacquer-type deposits, a chemical process is taking place rather than a physical one. Figure 2.7 illustrates not only the “S-shaped” standard mass and rate of deposition, but also identifies the major deposit formation parameters of interest.
Along with the rate, stages of deposit formation included stage 1 during which deposit formation is minimal. In this stage, surface discoloration of the substrate occurs and, with some of the heavier oils tested; small amounts of deposits also appear. Rate of deposit formation during this stage is slow. During stage 2, varnish-type deposits accumulate rapidly and cover the substrate surface until the oil sample is consumed. Stage 3 marks a leveling off.
of the deposit amount. At this point, the oil sample has been consumed, and further oxidation results in deposit dehydrogenation and deterioration.

2.3 Current Deposit Formation Models

The rate at which lubricant molecules react with oxygen depends on a number of factors, of which the most critical is temperature. Oxidation rates increase exponentially with increasing temperature, reflecting an Arrhenius rate of overall deposit formation typically characterized by an induction period, and by the growth and decrease of products formed during the process (Naidu et al., 1984 and Tseregounis et al., 1987). The well-established isothermal mass deposition curve describes a deposit formation, which is a function of time and temperature. The process occurs in four basic stages: (1) an induction period, where minimal deposit is formed; (2) a sharp acceleration in deposit mass; (3) the deposit reaches a maximum; and (4) the deposit mass begins to decrease (see Figure 1.1). Although extensively reported in the literature, there is no consensus among researchers on the physical and chemical factors, such as species and/or phase(s), that give rise to the mass deposit curve and that account for the induction, the rapid acceleration, the peak, and the decrease observed during deposit formation. Various systems studied by PSMO, including mineral, synthetic, bio-based, and fully formulated lubricants have shown that mass deposition, regardless of the nature of the lubricants, occurs similarly (Daly et al., 1994).

A lacquer or varnish type of deposit forms prior to the carbon black deposit, but both deposits result from the degradation of lubricants. Varnish/lacquer and carbon occur when oxygenated hydrocarbons, known as oxygenates or resin, separate on hot surfaces and dehydrate (or polymerize) to make a tenacious film with high carbon and oxygen content. Unfortunately, very little has been done to underline possible links between the changing
chemical nature of the deposit and their effect on the “universal” mass deposition curve. Implications of such investigation would be of great significance in combating undesired deposit formation, since arresting and/or reversing deposition tends to be easier when conducted early in the process.

Towards this goal, various studies have put forth models that attempt to either model the rate or describe a general process for the formation and deposition of mass. Given chemical complexities involved, such studies generally focus upon one phase or general reaction process, with some experimental support. These models may be categorized as: a) a liquid phase deposition model; b) a surface-controlled deposition model; and c) a binary layer growth model. These models and their supporting literature are briefly described in the following sections.

2.3.1 Liquid-phase Induced Deposit Model

The liquid phase deposition model presumes base lubricant oxidation as the chemical reaction governing deposit formation and growth. Oxidation is the chemical reaction of an oil molecule with oxygen [or O-bearing species, e.g., H₂O, or radicals (OH)]. This occurs in the combustion environments, such as engine in-cylinder reactions. The reaction results in sequential addition of oxygen to the base oil molecules and forms a variety of chemicals species, including aldehydes, ketones, hydroperoxides, and carboxylic acids (Rudnick, 2006; Ofunme et al., 1989; Ofunme et al., 1991; Stavinoha and Wright, 1969). Controlling temperature and improvement in base oil formulation can help limit the degree and rate of oxidation, but the eventual breakdown of the base oil molecules due to oxidative processes is inevitable.
One common feature of these reaction byproducts is the carbon-oxygen double bond, the “carbonyl group.” This bond configuration is common to both carbonyl and carboxylic acid functional groups. Such groups are well marked by their infrared signatures at approximately 1,700 cm\(^{-1}\) for carbonyls and range from 2,500 to 3,300 cm\(^{-1}\) for carboxylic acids. FTIR has been of high interest for monitoring carboxylic acid formation particularly because carboxylic acids not only cause acidic corrosion, but also lead to more damaging chemical process in the formation of sludge and varnish (Cheng et al., 1994 and Wooton et al. 1984). Models based on liquid phase oxidation consider sludge and varnish to form when oxygenated reaction byproducts, such as hydroperoxides and carboxylic acids, combine to form larger molecular species. The general process is termed polymerization and results in the formation of molecules characterized by high molecular weight. Their early formation and retention in the oil phase is reflected in the increase of oil viscosity. As polymerization continues, solid material, “sludge” and varnish formed in the oil transitions into deposits, as these macromolecules become too large to remain a liquid or in suspension. Beyond this initial deposition, continued increase in deposit mass is considered to still arise through liquid-phase oxidative degradation of the lubricant. In summary, liquid phase oxidation and polymerization processes control the deposit formation, overall path, and extent of the reaction. In support of this argument, the induction period has often been reported to mirror the initiation of liquid-phase species, and cessation of the deposition formation reflects depletion of precursors (Von Fuchs et al., 1942). Experimental support for this mechanism is broad, but varied.

In his pioneering work, N. M. Emanuel (Emanuel et al, 1974) reported a general scheme of chain “liquid-phase” oxidation, in which steps of chain generation, branching,
propagation, and termination were strongly dependent on the substrate to be oxidized. Emanuel et al. also described the possible participation of reaction products in individual elementary events of the process. Fuchs supported the liquid phase-induced reaction theory in their account of an early stage tendency of saturated hydrocarbons to act as autocatalytic oxidation agent, whereas aromatic compounds operate as antioxidants via auto-retardation (Von Fuchs et al., 1942). In an effort to provide a complete and unequivocal explanation to the early optimum aromaticity preceding the initiation of oil oxidation, Fuchs et al. conceived that the amount of oxygen consumed by aromatics during the process was great enough for mask the lesser amount consumed by naphthenes. As an alternative path in the liquid-phase oxidation and deposit formation process, Cerny et al., (2001) proposed that oxidative stability of hydrocracked oils was largely dependent on the deposit promoting sulphur and aromatic hydrocarbon concentration within the oils. Similar liquid phase-induced deposit formation was indirectly described by Maleville et al., (1996) who reported that changes in sulphur and carbon aromatic contents could be correlated to the liquid-phase oxidation of base lubricant. As an amendment to the autoxidation inhibition of aromatic hydrocarbons, Popova et al. suggested that at low concentrations, the contribution of aromatic hydrocarbons to oxidation inhibition increases with the ring content of the molecules (Popova et al., 1968).

Adhvaryu et al., recently conducted a series of PSMO, NMR, DSC and FTIR experiments, where they studied the roles of base oil composition in the oxidation of base oil and associated liquid-phase reaction mechanisms (Adhvaryu et al., 1999). They concluded that saturate content (mainly n-paraffin-type hydrocarbons) increases the activation energy of oxidation, while polar compounds affect the rate of reaction. Adhvaryu et al. observed that alkyl-substituted aromatic rings, naphthenic-aromatics, and polyaromatics were highly
susceptible to oxidation. These results underline the complexity of the liquid-phase processes that lead to primary oxidation product formation and subsequent conversion to high molecular weight oxidation products. During these processes, initiation, let alone growth reactions, is in many instances inferential and limited hydrocarbon classes.

2.3.2 Surface-controlled Deposit Formation Model

Responding to the limitations of the first theory, other groups have introduced a second argument that asserts that the oxidative degradation of lubricants is an all-surface controlled growth process, in which induction depends on activation of surface sites and cessation reflects their coverage (Sheldon and Kochi, 1972; Smith et al., 2002). Lahijani et al., in their study of the effects of metals (copper, brass, aluminum, stainless steel, lead, and low-carbon steel) on lubricant degradation, concluded that metal corrosion and sludge formation are interrelated and are greatly accelerated by intimate contact of air, lubricant, and metal surface (Lahijani et al., 1982). This suggests a metal-catalyzed oxidation. Because the process is mediated and the rate is controlled by surface composition, Naidu et al. indicated that the presence of metals seems to alter the rate of polymeric formation, therefore influencing the overall rate of mass deposition (Naidu et al., 1984). Naidu et al. also reported that solid lead had a strong effect on the secondary oxidation reactions of all of the tested fluids. A number of papers have reported that the general mechanism of lubricant degradation is derived from metal-hydrocarbon interactions [(Charkravarty, 1963); (Klaus et al., 1985); (Hermance et al., 1958); (Klaus et al., 1987); (Clark et al., 1985); (Lockwood et al., 1981) and (Nakayama et al., 1991)]. Maduako et al. reported that the wear metals in lubricating oils, whether as fresh metal surfaces or as organometallic wear products, catalyzed hydrocarbon liquid-phase auto-oxidation. The form of the metal matters: zinc and
nickel were more active as elemental metal surfaces, while aluminum was more active as an organometallic salt (Maduako et al., 1996).

In his study of the effect of metal surfaces on deposits from thermally stressed jet fuels and model compounds, Jun Li reported the formation of 3 types of deposits, depending on reaction conditions and the metal surface: (1) gas-born carbon deposits derived from nucleation of polynuclear aromatic hydrocarbons on metal surfaces; (2) substrate-nucleated pyrolytic carbon with a distinctive cone-structure growth starting on the metal surface; and (3) a catalytic deposit including filamentous and fibrous carbon formation, depending on the metal surface (Li, 1998). Other researchers have reported dangling bonds, emissions of electrons and charged particles describing metal-surface reactivity, which, when combined with heat, produces a variety of chemical reactions (Charkravarty, 1963).

It is well known that many metals such as iron, chromium, copper, and nickel catalytically decompose hydrocarbons. If hydrocarbons yet in the liquid phase react with oxygen to form polar species such as carboxylic acids, these will chemisorb onto the metal surface and react with exposed lattice cations to form metal complexes (Hsu et al., 1988). Altin and Eser, using Temperature-Programmed Oxidation (TPO) and SEM to examine fuel stressing showed variations in the amount and nature of the solid deposits obtained on the different substrates. These authors concluded that activity of the tube surfaces toward carbon deposition decreases in the order nickel > SS 316 > SS304 > Silcosteel > glass-lined stainless steel (Eser et al., 2006). These results were interpreted as reflecting the dependence of deposit formation on the metal’s composition.

In summary, the number of surface reactions includes surface oxidation, surface-catalyzed lubricant degradation, polymerization, and potential contributions from
organometallic chemistry. In recognition of such a dominating role by the surface, Hsu et al. indicated that the lubricant should form a hard-phase film in order to provide successful protection. Usually, such a hard-phase film is supplied as a reaction product from the reaction/decomposition of an anti-wear additive tailored for a specific surface chemistry, and a soft-phase film is supplied as a reaction product formed from surface catalyzation/polymerization of the base fluid.

2.3.3 Binary layer growth Model

Another commonly reported lubricant oxidation process has also been described as a binary layer growth (Daly et al., 1994). Induction reflects “black” carbon coverage and rapid growth is that of the second, polymeric layer upon the carbon layer. Cessation reflects surface coverage of the carbon layer. Eser et al., in their study of the “Utility of Temperature Programmed oxidation for Characterization of Carbonaceous Deposits from heated Jet Fuel”, suggested a binary layer growth consisting of a more ordered, less reactive layer (corresponding to higher elemental carbon content) and a less ordered, more reactive layer (corresponding to higher polymeric content). In sequence, the more ordered carbon initially deposits, followed by a second layer of less ordered carbon (Eser et al., 2006). Notably, this first, more ordered carbon layer served as the “template,” or surrogate substrate, for the deposition of the more organic-like, less ordered layer. Consistent with this model, Altin et al. concluded that solid deposition is usually initiated by catalytic reactions on active metal surfaces that promote a secondary deposition via reactions of reactive species on incipient deposits (Altin et al., 2001). Recently, other authors have expanded this binary layer model to include multiple layers. For example, Lepperhoff initially suggested that four layers exist in the morphology of a combustion chamber deposit (Lepperhoff et al., 1993). Daly et al.
(1994) later postulated without support the existence of two distinct morphological zones in combustion chamber deposits occurring in the following phases of growth (Figure 2.8):

1- The initiation of deposits in Zone 1
2- Growth of Zone 1 deposits
3- The initiation of deposits in Zone 2
4- Growth of Zone 2 deposits
5- Equilibrium is established between Zone 1 and Zone 2 deposits

Figure 2.8. Proposed Mechanism for Binary Layer Deposit Formation

Daly et al. report that during the initiation of deposits in Zone 1, higher boiling components emanating from the fuel, the lubricant, or additive deposit undergo condensation on the metallic surfaces of the combustion chamber (Daly et al., 1994). Once in contact with metal surfaces, these materials become viscous due to vaporization and chemical interaction between the molecules. The growth of deposits in Zone 1 was justified by an intricate web of chemical interactions, observed by Edwards and Chaote (1998). This “lacquer deposit” begins to develop and grows to a given thickness dependent upon the molecular composition of the fuel, lubricant, and additives (Edwards et al., 1998).

According to Daly et al. (1994), as thermal degradation (thermolysis) begins on the flame side surface of the Zone 1 deposit, the thermolized deposit’s surface begins to change chemically and becomes less capable of forming chemical bonds with other deposit molecules. With the initiation of thermolized compounds on the flame-side surface of Zone 1
deposits, the growth of another deposit begins in Zone 2. Zone 2 deposits are described by Daly et al. as carbonaceous in character, having a “soot-like” chemical structure and showed decreasing interconnecting bonds with other deposits.

Daly et al. claim that Zone 2 deposits arise from Zone 1 deposits, grow on top of it, and interfere with and inhibit further addition to Zone 1 deposits (Daly et al., 1994). Cessation was described to reflect the establishment of “equilibrium” between both deposit layers (Zone 1 and Zone 2). Even with such refinements, the overall process remains: the formation of an initial surface layer that serves as a template for subsequent layer formation.

2.4 Summary and Limitations

The liquid-phase-induced deposit model supports the induction period and accelerated growth phase of deposit mass growth. Initiation of oxidative degradation is consistent with the induction period, as pure (non-oxygenated) hydrocarbons are the most inert relative to their oxygenated counterparts. As oxidation proceeds, polymerization reactions begin and lead to mass deposits. Because their rate is non-linearly dependent upon the concentration of oxygenates and derived radical species, their rate of formation rapidly accelerates with increasing precursor concentration. Presumably, the fall-off in deposition rate is due to the depletion of liquid phase precursors. Yet, this model does not account for the changing chemical composition of the deposit.

While it could be argued that heavier (higher molecular) mass polymeric species deposit at later times, such an explanation begs the question as to why the precursors of such species did not contribute to deposition at an earlier stage. The surface-controlled deposit model supports the mass deposition fall-off rather than the initiation and accelerated growth phases. In this model, induction reflects active site formation at the surface, but no specific
chemical process has been offered, let alone definite experimental evidence for such. If, however, activation of surface sites is required, then once formed, the pathway for surface catalyzed deposit formation can begin and an accelerated stage can be realized. As surface coverage continues, the rate at which the surface can catalyze deposits decreases because active surface areas (sites) are decreasing. This model, too, suffers from lack of clarity as to why the deposit chemistry changes with time. Implicit to the model is homogeneous chemistry in the deposit layer.

The binary layer growth model can well account for an induction phase, reflecting the initial formation of the carbon layer. Surface (active) sites may well be involved in its formation also. Once significant carbon coverage forms, accelerated mass deposition begins, as this layer serves as the template for subsequent deposition of polymeric (organic-like) species. As the initial carbon layer becomes covered, the deposition rate decreases due to the loss of deposition-promoting surface. Yet again, this model lacks support, in that the initial carbon layer has neither been directly observed nor is it consistent with numerous empirical observations of a polymeric oxygenated organic layer. Moreover, the critical (chemistry) link between the carbon layers to cause liquid phase deposition of the polymeric oxo-compounds has not been specified. Recent publications by Pfaendtner and Broadbelt have demonstrated that single phase focused models or process of oxidation tends to be artificial and narrow (Pfaendtner and Broadbelt, 2008). Therefore, I propose the current uniform layer growth mechanism, based on this review of the limitations of previous lubricant degradation theories and of the preliminary results obtained in studying the mechanism by which a lubricant undergoes oxidative degradation in the presence of metallic surfaces.
CHAPTER 3: HYPOTHESIS

My hypothesis, termed the uniform layer deposition model, suggests that lubricant deposit growth is governed by pre-existing deposit age, reflecting its evolving chemistry.

3.1 Objectives

As a means to better understand the mechanism of deposit formation from the decomposition of lubricants on metal surfaces, the current study aims to verify the proposed uniform layer deposition model with the following specific objectives:

1. Demonstrate & determine deposit dependence upon “film” aging.
2. Verify and quantify deposit chemistry at various stages of aging. (Fig 1.1).
3. Compare rates: physical mass deposition and chemical composition towards validating the uniform layer deposition model.
CHAPTER 4: EXPERIMENTAL

The overall experimental approach to support the hypothesis is found in Figure 4.1. The initial tests involved use of the Penn State Microoxidation Test and the Penn State Microautoclave/Tubing Bomb Test. The products of these tests were analyzed and characterized to define the mechanism of lubricant deposit formation.

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Figure 4.1. Illustration of the Structural Approach of the Study
4.1 Thermal and Oxidative Degradation Test

4.1.1 The Tubing Bomb Test

The Penn State Micro Autoclave test, or tubing bomb experiment, is a laboratory-scale test wherein fuel or lubricants’ stability, degradability, and oxidation are evaluated under controlled conditions (temperature, time, pressure, etc.). A small volume of lubricant (approximately 20 cc) is placed inside a sealed reactor and exposed to elevated temperatures in the presence of a piece of metal (304 SS), in order to evaluate the tendency of lubricants to form carbonaceous deposits on the metal surface (liquid or gas phase). The tubing bomb test provides the opportunity to prompt various reactions under different pressurized gas conditions. The reactor is equipped with a pressure gauge to monitor pressure buildup throughout the reaction (Figure 4.2 and 4.3). A fluidized sand bath allows convenient control of temperature (Figure 4.4 and 4.5).

4.1.2 Experimental Design

4.1.2.1 Metal selection

The tubing bomb test was conducted with different stainless steel coupons. 304 Stainless Steel was selected based on its general affinities with piston alloys. Stainless steel has a high oxidation resistance in air at ambient temperatures.

4.1.2.2 Sample Volume

All lubricants were tested in separate reactors in 20 ml volumes, allowing us to monitor reactions in both the liquid and gas phases of the reactor, and on the surface of the metal coupon in each of those phases.

4.1.2.3 Reaction Gas

Air is known to be the gas present in the combustion chamber during engine performance
and was therefore selected as reaction gas for the micro autoclave test, in order to remain as close as possible to engine operating conditions.

Figure 4.2  Schematic of a Tubing Bomb Reactor (Designed at Penn State)

Figure 4.3  Images of Tubing Bomb Reactors
Figure 4.4  Schematic of the Tubing Bomb Experiment

Figure 4.5  Temperature-Controlled Fluidized Sand Bath
4.1.2.4 Experimental Procedure

The desired temperature is initially set on a thermocouple attached to the sand bath. Stainless coupons are cut into equal size, 6 cm x 1 cm. Twenty (20) ml of lubricant or base oil are placed into each reactor with a coupon partially immersed in the lubricants. Each coupon is then marked to indicate the liquid/gas interface.

Once the reaction temperature stabilizes, reactors are simultaneously placed in the sand bath for the duration of the reaction. Once reaction time has elapsed, we proceed with quenching by removing and cooling reactors in water for 10 to 15 minutes. In a well-ventilated room, coupons and oil residues are collected one at the time, under a fume hood (Figure 4.5).

Figure 4.6 Stainless Steel Coupon and Oil Residues
4.1.3. The Penn State Micro Oxidation Test

The Penn State Micro Oxidation (PSMO) Test evolved from oxidation studies at the Petroleum Refining Laboratory and Tribology Group over the past 50 years. The test is a thin-film oxidation test initially developed to evaluate III-D engine oils (Erhan, 2002), and was later expanded to evaluate heavy-duty diesel engines. A modification of the test, The Caterpillar Micro Oxidation Test (CMOT), was adopted by Caterpillar Tractor Company to evaluate large engine piston deposits (Zerla et al., 1989).

4.1.3.1 Principle

Complication of heteroatoms from lubricant additives motivated base oils studies via PSMO. The test involves small samples to avoid the oxygen diffusion limitations of many oxidation tests. The generally accepted mechanism of oxidation is a free radical process (Figure 4.7). At temperatures exceeding $260^\circ \text{C} (500^\circ \text{F})$, the mechanism becomes more complicated as incipient breakdown of molecular bonds occurs due to the thermal instability of the molecules. The rate of breakdown of a compound due to thermal stability increases with temperature. This phenomenon was also demonstrated as shown in Figure 4.8 by Hsu (Hsu et al., 1983). The oxidation mechanism of lubricants is complex and rapid, but can be simplified.

\[
\begin{align*}
\text{Initiation:} & \quad \text{RH} & \rightarrow & \text{R}^* + \text{H}^- \\
\text{Chain Propagation:} & \quad \text{R}^* + \text{O}_2 & \rightarrow & \text{ROO}^- \\
\text{Chain Branching:} & \quad \text{ROO}^- + \text{RH} & \rightarrow & \text{ROOH} + \text{R}^- \\
\text{Chain Termination:} & \quad 2\text{R}^* & \rightarrow & \text{R-R} \\
& & & \text{R}^* + \text{ROO}^- & \rightarrow & \text{ROOR} \\
& & & 2 \text{ROO}^- & \rightarrow & \text{ROOR} + \text{O}_2 \\
& & & \text{H}^* + \text{OH} & \rightarrow & \text{H}_2\text{O} \\
\end{align*}
\]

Figure 4.7 Free-Radical Oxidation Mechanism
The Penn State Micro Oxidation Test simplifies the reaction’s complexity by using a global model approach, wherein the initial sample undergoes primary reactions with both volatiles and oxidation products removed, followed by continued oxidation, resulting in polymer formation and eventually deposits (Figure 4.9). The test unit is shown in Figure 4.10.
4.1.3.2. Experimental Procedure

Samples were weighed and placed on a hot plate that maintained temperature, with air flowing constantly over the sample. After a sequential 30 min time period, the oxidized oil samples are removed from the oxidation chamber and weighed in order to determine the amount of the sample lost due to oxidative volatility. After cooling to room temperature, the sample is soaked in a solvent to dissolve the soluble constituents of oxidized oil, and then weighed to determine the deposit mass.

The test is conducted as follows: A small lubricant sample (20-40 ug) is placed on a metal specimen and weighed. The specimen is then placed in a pre-heated test tube in a temperature-controlled unit or bath. A gas flow is maintained over the sample for selected time periods and the sample removed, rapidly cooled, and analyzed. The unit and a summary of the procedure are found in Figure 4.10 and Figure 4.11.
1- Weigh steel or alumina pan on microbalance

2- Add test fluid and weigh to obtain sample size

3- Insert in PSMO and heat for designated time

4- Remove from PSMO, cool, weigh, and determine volatility

5- Wash, dry, weigh to determine deposits

Figures 4.11 Summary of PSMO Steps (Erhan, 2002)

4.2 Baseline Tests

The baseline tests consist of partial/sequential oxidative degradation tests (tubing bomb test/PSMO), and included a preliminary investigation of piston deposits; the study of the thermal degradation process of additive-free base oils, lubricant additives, and fully formulated lubricants; a series of thermal degradation test/tubing bomb tests; and the micro-oxidation test/PSMO.

The preliminary investigation of pistons consisted of a detailed investigation of piston deposits to gather valuable information on the physical and chemical structure of the deposits. A series of analytical tests were performed to study the thermal behavior of base oils, additives, and fully formulated lubricants, eventually leading to understanding the appropriate thermal conditions for both thermal and oxidative tests (PSMO, tubing bomb reaction). Finally, the thermal degradation test, via tubing bomb reaction and micro oxidation, were conducted on the formation of carbonaceous materials, which was used to probe into the internal structure and properties of deposits formed by lubricants on metal surfaces.
4.3 Substitution Tests

The substitution tests consist of producing polymeric/carbonaceous films at various stages (3) along the mass deposition curve and then substituting them into the same fresh lubricant used during the initial test specimen/surface. In this manner, the effect of the pre-deposit was gauged against the baseline of fresh lubricant apart from potential complications derived from interactions with partially oxidized lubricants or surface sites.

The first surface was prepared by allowing the induction phase to occur, followed by extraction of the resultant surface as the test surface with which to begin measuring the mass deposition rate anew. With an initial polymeric coating, mass deposition should be accelerated (based on the free-radical addition mechanism, according to the proposed uniform layer model) and accelerated mass growth immediately observed, even in fresh lubricant.

The second surface was prepared by allowing a portion of accelerated mass growth to occur, followed by extraction of the surface as the new test piece with which to begin measuring the mass deposition rate. After the inflection point (on the uniform deposition curve), mass deposition begins to slow, presumably reflecting a slowing rate of radical formation sites upon the surface. Observation of such a deceleration was consistent with the radical formation mechanism within the surface bound organic layer governing the rate of mass deposition upon the surface, even when in fresh lubricant, as predicted by the homogeneous chemical transformation of the hypothesized uniform layer model.

The third surface was prepared by allowing cessation of mass growth to occur, followed by extraction of the surface. Then the precovered surface is used as new test piece
with which to begin measuring the mass deposition rate, again in fresh lubricant. With an initial (largely) carbon layer upon the surface, the chemical transformation of the surface deposit is largely complete, and free-radical site formation less energetically favorable. Mass deposition, even upon exposure to fresh lubricant, should be minimal, thereby testing the final stage as predicted by the uniform layer model.

4.3.1. Aging Film Substitution Test

The substitution tests consist of producing polymeric/carbonaceous (aged films) at various stages (3) along the mass deposition curve and then substituting them into fresh lubricant as the initial test specimen/surface. In this manner the effect of the pre-deposited film was gauged against the baseline of fresh lubricant for potential interactions of partially oxidized lubricant or surface sites.

4.3.2. Aging Oil Substitution Test

Metallic pans were pre-covered with polymeric/carbonaceous films at various stages (3) along the mass deposition curve and substituting them into 30, 60, 90, 120 min aged lubricant. In this manner, the effect of the aging oils was gauged against the aging film for potential interactions of partially oxidized lubricant or surface sites.

4.4 Analytical Characterization

Different analytical characterization techniques, including FTIR-ATR were used to probe into the internal structure and properties of carbonaceous films formed during thermal and oxidative degradation tests. During this task, structure, chemical, and elemental properties of lubricants were studied. Analytical characterization techniques were used to measure variations in the oxygen functional groups (e.g., carbonyl concentration) within the films at various times, as well as the relative H-atom content by the C-H bond absorption
intensity. Different FTIR spectra and deconvolution techniques were employed to detect new compounds formed, as well as minor concentration changes in oxidation products. These measurements were recorded along the standard mass deposit curve in order to derive the overall kinetics of the deposit formation mechanism.

4.5 Relation to Current Literature Models

The described tests will starkly contrast differences between the existing models and the proposed hypothesis. For example, carbon coating should lead to minimal growth according to the hypothesis, while it should lead to accelerative growth according to the binary layer model. Carbon and oxygenated polymeric coatings should correspond to the onset of accelerative growth but should shut off mass deposition according to the surface-controlled model. Liquid-phase oxygenates should result in little difference in mass deposition rate compared to fresh lubricant, according to the hypothesis, but should correspond to the period of accelerated mass deposition according to the liquid phase deposition model.
CHAPTER 5 - THERMAL ANALYSIS

5.1 Thermal Analysis of Base Oil, Additives and Fully Formulated Lubricants

Thermal analysis of the lubricant, base oil, and additives was specifically focused on thermo gravimetric analysis to compare changes in sample weight with changes in sample temperature. The test displays a high degree of precision in three measurements: weight, temperature, and temperature change. A derivative weight-loss curve was also used to show the point at which weight loss is most apparent. The technique is often used to determine the characteristics of materials such as polymers, the absorbed moisture content of materials, as well as the level of inorganic and organic components in materials and solvent residues (Hsu and Cummings, 1983). In the current study, TGA analysis was used to determine the thermal behavior of the lubricants and additives based on the changes of the sample mass with respect to temperature. The samples analyzed were base oil samples, lubricant additive samples, and fully formulated lubricants (or lubricants with additives).

5.1.2 Procedure

The analyzer consisted of a high-precision balance with an alumina pan loaded with the sample, as shown in Figure 5.1. The pan was placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere was purged with nitrogen, an inert gas used to prevent oxidation or other undesired reactions. A computer was used to control the instrument. Analysis was carried out by raising the temperature gradually and plotting changes in weight relative to temperature. The data was then collected, curves were smoothed, and other operations such as finding the exact points of inflection were performed.
5.1.2 Thermal Analysis of Lubricant Base Oils

The most common base stocks for lubricants are mineral- or petroleum-based, synthetic oils, and biomass-based oils. Figures 5.2 and 5.3 list the results of series of thermal analyses that investigated the properties of base oils.

Figure 5.1: Thermo-gravimetric Analysis Pans (Canon Powershot A480, 10 Megapixel CCD, 3.3x optical zoom lens, DIGIC III image processor, a 2.5-inch LCD display)

Figure 5.2. Thermo-gravimetric Analysis of Type 1 Base Oil
Figure 5.3. Thermo-gravimetric Analysis of Type 2 Base Oil

The thermal degradation profiles for Type 1 and 2 base oils presented in Fig 5.2 and 5.3 show that the evaporation process of each sample starts around 170° C and ends approximately at 350° C, with almost 100% of lubricant’s mass lost. It is also observable that beyond 250° C, the degradation process is almost linear. The derivative of the weight loss with respect to temperature shows a single peak, reflecting a gradual evaporation of the sample occurring during the process. In the next paragraph, these observations will be compared with the thermal degradation of the additive, since additives have been reported to play a key role in lubricant deposit formation due to thermal degradation.
5.2 Thermal Analysis of Lubricant Additives

A finished lubricant contains one or more additives blended with one or more base oils. The additives are used to enhance the performance characteristics of the base oil. Some additives only affect one aspect of performance; viscosity index improvers, for example, allow the finished lubricant to attain a different viscosity, depending on temperature. Other additives may have multiple effects. For example, zinc dithiophosphate provides wear protection and helps inhibit oxidation. As described previously, under similar experimental conditions, thermo-gravimetric analysis was conducted to measure weight changes in different lubricant additives as a function of temperature and/or time in a controlled atmosphere (nitrogen). The purpose of such an experiment was to evaluate the thermal stability and composition of each additive. The results are listed in Figure 5.4 through Figure 5.10.

![Graph showing weight percent vs. temperature](image)

Figure 5.4. Thermo-gravimetric Analysis of detergent additive A
Results of the thermal degradation profiles for lubricants additives are presented in Figure 5.4 through 5.10. In Figure 5.4, as temperature increases, variation in the mass of detergent A become noticeable at 120° C (green curve), with progressive reduction in the mass of the additive sample observable during thermal degradation. Thermal decomposition of detergent A occurs in two steps, represented by the dual peaks on the curve, demonstrating the derivatives of the weight loss with respect to temperature (blue curve). The first event, with higher amplitude, occurs between 120° C and 375° C and shows a progressive loss of about 50% of mass. The second event has much smaller amplitude. It is observed between 375° C and 500° C and results in the loss of 17% of the sample’s mass. After the reaction stops, 33% of the sample’s initial mass remains on the crucible.

Figure 5.5. Thermo-gravimetric Analysis of soot dispersant A
In Figure 5.5, variations in the mass of the soot dispersant additive are noticeable at 50°C, and at that temperature the thermal degradation begins with a slight increase of the sample’s weight, prior to the progressive decrease in mass. Thermal decomposition of such soot dispersant additive occurs in three steps represented by each peak, which are derivatives of the weight loss with respect to temperature. The first event occurs at 50°C when there is an increase in sample mass; the second event takes place between 200°C and 300°C, when the additive progressively loses 60% of its mass within the heated environment; the third event occurs between 300°C and 450°C, while the sample loses its remaining mass as the temperature increases. At 450°C, the entire sample mass had vaporized.

Figure 5.6. Thermo-gravimetric Analysis of detergent additive B
In Figure 5.6, the variation in the mass of detergent B is noticeable at $80^\circ C$, where the thermal degradation begins with progressive decrease in mass. Thermal decomposition of detergent B occurs in three steps, as shown on the curve indicating the derivatives of the weight loss with respect to temperature. The first event occurs between $50^\circ C$ and $350^\circ C$ and results in the loss of almost 50% of the sample’s total mass, while the second event is observable between $360^\circ C$ and $400^\circ C$ and causes the additive to progressively lose about 5% of its total mass in the heated environment. The third event occurs at between $400^\circ C$ to $500^\circ C$ and causes a loss of about 16% of the sample’s total mass. Importantly, the reaction stops at $500^\circ C$ with almost 23% of the sample mass remaining.

Figure 5.7. Thermo-gravimetric Analysis of detergent Additive C
Changes in mass for detergent C start around 25\(^\circ\)C but are clearly noticeable around 180\(^\circ\)C. For detergent C, thermal decomposition occurs in two steps, demonstrated by the derivatives of weight loss with respect to temperature. The first event is observable between 180\(^\circ\)C and 360\(^\circ\)C with 55% mass lost; the second event, which occurs between 360\(^\circ\)C and 500\(^\circ\)C, results in another 32% mass lost. At 500\(^\circ\)C, 13% of the mass of additive C9380 remained on the crucible.

![Figure 5.8. Thermo-gravimetric Analysis of antioxidant ZDDP](image)

Figure 5.8 shows that changes in mass of antioxidant ZDDP begin around 120\(^\circ\)C. Unlike all other additives tested, thermal decomposition of antioxidants occurs in a single step, as shown by the derivatives of the weight loss with respect to temperature. It is important to mention that the specific class of ZDDP studied was not provided. The event occurs between 200\(^\circ\)C and 212\(^\circ\)C, where we observe the loss of 82% of the sample’s total
mass. The phenomenon tends to show similarities with the event observed during thermal degradation antioxidants at the temperature range of $375^\circ$ C - $400^\circ$ C. This weight lost is followed by another progressive loss of 7% between $212^\circ$ C and $500^\circ$ C. When the reaction stops at $500^\circ$ C, about 10% of the mass still remains on the pan.

Figure 5.9. Thermo-gravimetric Analysis of a dispersant B

In Figure 5.9, the green curve indicates that variations in the mass of dispersant B begins at $50^\circ$ C. As the dispersant degrades, two peaks are observable, as shown in the derivative of weight loss with respect to temperature. Between $200^\circ$ C and $350^\circ$ C, 34% of the sample’s mass is lost. The additive gradually loses the remaining mass between $350^\circ$ C and $500^\circ$ C. At $500^\circ$ C, the entire sample mass had been pyrolyzed.
In Figure 5.10, variations in the mass of dispersant D start at 180° C. As dispersant D degrades, two peaks are observable in the derivative of weight loss with respect to temperature. Between 190° C and 350° C, 42% of the sample’s mass is lost; from 350° C to 500° C, another 27% is lost. At 500° C, 30% of the sample’s mass remains on the pan.

5.3 Thermal Analysis of Fully Formulated Lubricant

Typically, fully formulated lubricants contain up to 90% base oil (synthetic, mineral, or bio-based oils) and “at least” 10% additives. In this study, both base oil and additives were placed under thermal evaluation, followed by the evaluation of samples of fully formed lubricants. Fully formulated lubricants were studied under the same thermal conditions as the base oil and additives. Lubricant samples Sample 1, Sample 2, and Sample 3 are fully formulated lubricants used for thermo gravimetric analysis of fully formulated lubricants.
Figure 5.11. TGA of commercial lubricant subjected to initial blind test

Figure 5.12. TGA of commercial lubricants subjected to initial blind test
As shown in Figures 5.11 and 5.12, the thermal degradation profile of fully formulated lubricants shows similarities with the thermal behavior of base oil. Most base oil shows a thermal profile with a single peak relative to total weight, when most additives show at least two peaks. In case of additives, there is a residue remaining on the pan even at temperature above 500°C degradation. The derivative curves, which indicate mass lost with respect to temperature, are an important aspect of thermal analysis, because they provide quantitative information about not only weight loss, but also the mass of the deposit remaining on the crucible after the thermal analysis. The amplitudes and the number of peaks observed on the derivative curves generally reflect the performance of a lubricant and its ability to form a deposit. The most important observations are made within the thermal region representing the formation and cracking of carbonaceous compounds, above 500 degrees Celsius. A thermo-gravimetric analysis of base oils, fully formulated lubricants, and additives within a nitrogen atmosphere revealed three major temperature regions within which the lubricants behave in distinct manners. In the 100°C to 120°C region, the light fractions of the lubricants evaporate which is to say, the water molecules or low-molecular weight fractions that are generated in engines during the lubricants’ degradation process. From 200°C to 500°C, we observe the evaporation of oil residues and high molecular fractions contained in the lubricants. This secondary phase is the evaporation of high molecular weight fractions and the continuation of the initial phenomenon observed.

Beyond 500°C, we observe the pyrolysis of carbonaceous residues. As with the base oils samples (lubricant without additives), the thermal analysis shows that base oils tends to reach complete evaporation around temperature range of 500°C. On the other end of the spectrum, an additized sample tends to go through several stages.
In summary, the results obtained in this chapter indicate that thermo gravimetric analysis of base oils, fully formulated lubricants and lubricant additives, revealed three major regions and describes thermal behavior of the lubricants.

- From 100°C to 120°C region, the light fraction of the lubricants first evaporate, water molecules or low-molecular weight fractions generated during the degradation process of lubricants in the engines.

- From 200°C to 500°C, we observe the evaporation of oil residues and high molecular fractions contained in the lubricants. This secondary phase is in fact the continuation of the initial phenomenon observed.

- Beyond 500°C, we observe the pyrolysis of carbonaceous residues. As observed for the base oils samples (lubricant without additives), the thermal analysis shows that base oils, tends to reach complete evaporation around temperature range of 500°C. On the other end, additized sample tends to go through several stages justified by the formation of carbonaceous compounds.
CHAPTER 6. TEMPERATURE PROGRAMMED OXIDATION

6.1 Temperature Programmed Oxidation (TPO) Profile for Deposits from Base Oil and Additive Blends

Different samples (20 ml) of Group I base oil were individually mixed with an antioxidant, detergent, soot dispersant, and viscosity-modifier additives. The blends were thermally stressed using a tubing test at 320° C for 6 hours. Each additive represented ten percent (10%) of the total mass of a 20 ml sample of Group I base oil. Temperature Programmed Oxidation (TPO) was used to analyze carbonaceous deposits that were derived from the thermal decomposition of such mixtures. The carbonaceous structures present were characterized based on the structural characteristics of carbon gasified as a function of temperature. TPO was also used to determine the oxidation reactivity of carbonaceous compounds as a function of temperature. The peaks in TPO profiles were attributed to CO₂ intensity, and indicate differences in the oxidation reactivity of the deposits, which is also related to their structural characteristics.

6.1.1 TPO of Base Oil – Detergents Blend Deposits

The blend consisting of Group I base oil and 10% detergent additives was subjected to thermal stressing, using the tubing bomb test at 320° C for 6 hours. Detergents A and B are two detergent additives commonly used in the formulation of most commercial lubricants. The results listed in Figures 6.1 and 6.2 represent the evolution of TPO profiles for the carbonaceous structures derived from the thermal decomposition of Group I base oil blended with detergent additives. The profile suggests that the oxidation of deposits found on the sample occurs over a wide temperature range (from 200 - 800° C). The more reactive deposits oxidized between 500 and 800° C, and the relatively less reactive deposits oxidized between
200 and 500º C. Clear resolution between the two peaks suggests that two different types of carbonaceous structures are found in the deposits.

Figure 6.1 TPO Profile of Deposit from Base Oil with 10% Detergent A

Figure 6.2 TPO Profile for Base Oil Deposit with 10% Detergent B
6.1.2 TPO of Base Oil – Soot Dispersant Blend Deposits

Figures 6.3 and 6.4 show TPO profiles for carbonaceous structures derived from the thermal degradation of Group I Base Oil with 10% dispersant, using the tubing bomb test at 320°C for 6 hours. Oxidation profiles, in this case, are shown to occur over a narrower temperature range than detergents [250 ºC – 550 ºC]. Careful examination of the profiles reveals two overlapping peaks, evolving at different temperature range. The less reactive deposits oxidize between 250º C and 450º C, and the relatively more reactive deposits oxidize between 480º C and 550º C. The lack of resolution between the two peaks suggests the presence of two types of deposits that are somewhat structurally similar.

A closer look at TPO profiles for both detergent and dispersant blends with Group I base oil shows that low temperature peaks are not only found within the same oxidation temperature range (200º C - 500º C and 250º C – 450º C), but are also the largest peaks in each profile. The most dominant carbonaceous structures constituting these deposits are therefore similar, if not identical. This could be explained by the similarity of the base oil used to dissolve both detergent and dispersant additives. The most dominant peak are attributed to carbonaceous structures resulting from the decomposition of Type I base oil, which represented 90% of the initial mass of the blends. Higher temperature peaks are attributed to carbonaceous compounds derived from the decomposition of the additive package. Deposit control additives such as detergent and dispersant are naturally designed to display thermal and oxidative stability. Whenever it occurs, their thermal or oxidative degradation tends to lead to the formation of more structured and less reactive carbonaceous compounds, seen at much a higher oxidation temperature (TPO) than most hydrocarbon deposits. Differences in the TPO profiles between dispersants and detergents are rationalized
by carbonaceous compound derived from the formulation of the additive packages, beside the oil phase (hydrocarbon).

Figure 6.3 TPO Profile for Base Oil Deposit with 10% Soot Dispersant A

Figure 6.4 TPO Profile for Base Oil Deposit with 10% Soot Dispersant B
6.1.3 TPO of Base Oil – Viscosity Modifiers Blend Deposits

Figures 6.5 and 6.6 show the TPO profile for carbonaceous structure derived from the thermal degradation of Group I Base Oil deposit with a 10% viscosity modifier, using the tubing bomb test at 320ºC for 6 hours. Oxidation profiles show multiple overlapping peaks, evolving at different temperature ranges. The less reactive deposits oxidize between 200º C and 450º C, and the more reactive deposits oxidize between 450º C and 600º C.

Figure 6.5 TPO Profile for Base Oil Deposit with 10% Viscosity Modifier A

Figure 6.6 TPO Profile for Base Oil Deposit with 10% Viscosity Modifier B
6.1.4 TPO of Base Oil – Antioxidant-Blend Deposits

Figure 6.7 shows the TPO profile for carbonaceous structures derived from the thermal degradation of a Group I Base Oil Deposit with 10% of an antioxidant, Zinc Dialkyldithiophosphate (ZDDP), using the tubing bomb test at 320º C for 6 hours. TPO profile shown in Figure 6.7 suggests that carbonaceous structures found in the deposit have a wide range of oxidation reactivity temperature [150º C – 900º C]. Careful examination of the profiles reveals two overlapping peaks, evolving at different temperature ranges. The less reactive deposits oxidize between 150º C and 450º C, and the relatively more reactive deposits oxidize between 450º C and 900º C. Unlike other deposit control additives, carbonaceous structures resulting from the thermal degradation of the antioxidant and Group I base oil mixture presents multiple peaks at both high and low temperature. The resolution between the peaks suggests the presence of different types of carbon structures.

![Figure 6.7](image_url)

Figure 6.7  TPO Profile for Base Oil Deposit with 10% Antioxidant (ZDDP)
Oxidation inhibitors, detergents, and dispersants make up the general class of additives called deposit control agents. These additives are designed to control deposit formation, either by inhibiting the oxidative breakdown of the lubricant, or by suspending harmful product formation in the bulk lubricant. To perform this task, deposit control agents must display a certain level of thermal stability in order to avoid an early breakdown and subsequent further degradation of the base oil due to its interaction with additives. Most deposit control additives consist of a hydrocarbon group, a polar group, and a connecting group. The hydrocarbon group is polymeric in nature (i.e., polyisobutylene, polypropylene, polyalaphaolefins). The polar group is usually nitrogen- or oxygen-derived. The hydrocarbon group of dispersants, for instance, oxidizes in the same manner as the lubricant hydrocarbons: they form a polymeric, highly oxygenated film (oxygenates), and evolve at a relatively lower oxidation temperature during TPO (below 500° C). In order to achieve thermal stability, most detergents, dispersants, and antioxidants contain substances known for their thermal stability in addition to the base lubricant.

Deposits resulting from such substances tend to display both low-temperature and high-temperature oxidation profiles. Less ordered and more reactive carbonaceous structures observable at relatively low temperatures are attributed to deposits derived from base oils, either premixed into the additives or the base lubricant. More ordered and less reactive carbonaceous structures observable at relatively high temperatures are attributed to deposits derived from additives. Carbonaceous materials found in most lubricant deposits are mainly from oil degradation, since additives account for only a small fraction of the lubricant and tend to form deposits with much higher oxidative temperatures.
6.2 TPO Profile for Deposits from Formulated Lubricants

Additional evidence supporting the uniform layer growth model is the result of a TPO test conducted on deposits from the degradation of base oils and fully formulated lubricants.

Figure 6.8 TPO Profile of Fully Formulated Lubricant deposit (Canon Powershot A480, 10 Megapixel CCD, 3.3x optical zoom lens, DIGIC III image processor, a 2.5-inch LCD display).
6.2.1 Processing of TPO Signals

TPO signals were detected and quantified using CO₂ concentrations formed during the carbon analysis test. Lack of resolution in TPO peaks due to similarities in the carbonaceous structures lead to the use of mathematical methods to deconvolute TPO profiles involved in the current study. This was conducted with the software OriginPro which provided a number of tools suited to general signal processing tasks. These include tools for filtering, convolution, deconvolution, correlation, coherence, smoothing, etc. Deconvolution is usually used to restore a signal from a known convolution with a known response, and can be mathematically illustrated as follow:

\[
\text{Equation 6.1}
\]

\[
f = \text{ifft}\left[ \frac{\text{fft}(y)}{\text{fft}(g)} \right]
\]

where \( \text{fft}(\cdot) \) and \( \text{ifft}(\cdot) \) denote fast Fourier transform and its inverse respectively. Results are listed in Figure 6.9 and Figure 6.10.
Figure 6.9. Deconvolved TPO profiles for fully formulated lubricant deposits. (a) 2 hours and (b) 4 hours test tubing bomb test time.
Figure 6.10. Deconvolved TPO profiles for fully formulated lubricant deposits. (c) 8 hours and (d) 12 hours test tubing bomb test time.
All four stainless steel coupons shown in Figure 6.8 were submerged in a fully “additized” lubricant and thermally stressed at a constant temperature (320°C) for 2 hours, 4 hours, 8 hours and 16 hours respectively. After 2 hours of reaction, the beginnings of a lacquer film are observed. Following 4 hours of reaction, a lacquer film is visible on the entire surface of the coupon. After 8 hours, the initial lacquer begins transitioning into a dark carbon deposit. Beyond 16 hours, a homogeneous layer of dark carbon has covered the entire surface of the coupon. Figure 6.9 and 6.10 represents a more detailed analysis of the deconvolved the TPO graphs showing evolutions of separate peak intensities and associated integrated areas. The first peak evolves from the initial deposition of a polymeric film and seems to be inversely related to the second peak’s intensity.

Figure 6.11 represents a global analysis of the TPO profiles from lubricant deposits to determine the oxidation reactivity of carbonaceous compounds as a function of temperature. The evolution of the TPO profile width and the average oxidation temperature reflect the heterogeneity and reactivity of carbonaceous deposits, respectively, present on the metal coupons as a function of oxidation temperature. Figure 6.11 relates oxidation reactivity across a tubing bomb test to the physical structure characteristics of the carbonaceous deposits. The variation in average temperature signals structural changes in the deposit characteristics due to aging, while the width reflects chemical transformation. Increasing peak breadth reflects the composite of dehydrogenation and deoxygenation reactions occurring within the film. The increasing mean temperature of oxidation, though globally averaged, suggests an evolution towards elemental carbon, away from the organic/polymeric initial lacquer.
Results obtained from the peak deconvolution process were used for a secondary stage of TPO signals processing, involving the width of the peaks and the average weighted peak temperatures.

6.2.2 Peak Widths

Normalized widths were defined as the linear extent of the total TPO profile or each deconvoluted peak at a defined baseline CO$_2$ intensity of 10. Normalized widths values represented temperature ranges characterizing the variation of carbonaceous structures present on each deposit. Peak widths were computed as follow;

$$n = T_2 - T_1 \quad \text{Equation 6.2}$$

Where $n$ is the width; $T_1$ is the intensity of CO$_2$ at the lowest temperature on the baseline and $T_2$ is the intensity of CO$_2$ at the lowest temperature on the baseline.

6.2.3 Average Peak Temperatures

Average peak temperatures were calculated for each TPO corresponding to the most representative temperature value for each TPO profile. TPO profiles were determined by weighted average across the peak’s temperature profile, Eqn. 6.3, for single peaks or by the integrated area of each deconvolved peak and maximum peak temperature as expressed by Eqn. 6.4 when deconvolution was applied.

$$T_{avg} = \frac{\sum_{n=1}^{n}(In \times Tn)}{\sum_{n=1}^{n}(Tn)} \quad \text{Equation 6.3}$$

or

$$T_{avg} = \frac{[(\%A1 \times T1) + (\%A2 \times T2)]}{100\%} \quad \text{Equation 6.4}$$

Where; $T_{avg}$ is the average weighted peak temperature; $Tn$ is the temperature at any given point $n$ and $In$ is the CO2 intensity at any given temperature. A1 and A2 are percentage of
deconvoluted peak 1 and peak areas. T1 and T2 are corresponding temperatures for Peak 1 and Peak 2.

Figure 6.11. Evolution of TPO profile breadth and Average Temperature for Fully Formulated Lubricant deposits

Figure 6.12. Percentage of Peak Area 1 vs. Peak Area 2
This relation is attributed to the transition of the polymeric film into an “elemental” dark carbon deposit: initially, the dominant first peak decreases intensity throughout the reaction, while the second peak undergoes a steady increase in intensity, as plotted in Figure 6.12. Past studies have revealed that carbonaceous solids containing heteroatoms such as oxygen tend to have a relatively disordered internal structure (Franklin et. al., 2008). However, polyaromatic hydrocarbons that do not have heteroatoms form relatively ordered planar layers. This indicates that the varying composition and structure of the carbonaceous deposits studied shows a gradual transition from a highly oxygenated—hence more reactive—polymeric film (Peak 1), to a less reactive and more structured “elemental” dark carbon deposit (Peak 2).

6.3 TPO Profile for Deposits from Base Oil Deposits

TPO analysis can also be conducted on deposits derived from PSMO test using base oils. Differences in the oxidation reactivity of the deposits once again relates to their different chemical and structural characteristics. Low temperature peaks are attributed to the presence of less ordered (more reactive) carbon, while the high temperature peaks indicate the presence of more ordered (less reactive) carbonaceous species.

Low-temperature, more reactive carbonaceous structures are clearly distinguishable from high-temperature and less reactive carbon structures. The temperature range and number of peaks indicate that deposits derived from deposit-control additives are more complex and varied in their carbonaceous structure than deposits emanating from additive-free base oils.
Figure 6.13. TPO Profile for Additive-Free Base Oil Deposit

Most importantly, these observations reveal that additive-free base oils tend to form carbonaceous deposits that are much more reactive, despite possessing a more homogeneous chemistry (lesser heteroelements content) than deposits from additives such as antioxidant, dispersants, detergents and viscosity modifiers, as presented in Figures 6.14 – 6.17 with images of the corresponding pan deposits for series of PSMO test involving type 1 - 4 base oils.
Figure 6.14. TPO Profiles for Type 4 Base Oil PSMO deposits (Canon Powershot A480, 10 Megapixel CCD, 3.3x optical zoom lens, DIGIC III image processor, a 2.5-inch LCD display)
Figure 6.15. TPO Profiles for Type 2 Base Oil PSMO deposits. (Canon Powershot A480, 10 Megapixel CCD, 3.3x optical zoom lens, DIGIC III image processor, a 2.5-inch LCD display).
Figure 6.16. TPO Profiles for Type 3 Base Oil PSMO deposits. (Canon Powershot A480, 10 Megapixel CCD, 3.3x optical zoom lens, DIGIC III image processor, a 2.5-inch LCD display).
Figure 6.17. TPO Profiles for Type 1 Base Oil PSMO deposits. (Canon Powershot A480, 10 Megapixel CCD, 3.3x optical zoom lens, DIGIC III image processor, a 2.5-inch LCD display).
TPO data of Base oil deposits from PSMO tests presented in Figures 6.14 – 6.17 may also be analyzed using evolved CO$_2$ as the oxidative reactivity metric, as illustrated in Figure 6.18 for the global change in film chemistry. Consistent with the prior results, as the deposit undergoes visible changes over time (lacquer deposit transforming into dark carbon), the average temperature (mass-weighted, mean oxidation temperature) monotonically increases, as described in Figure 6.18. This reflects the global (homogeneous) change in film composition, hence the terminology “uniform layer model”.

As film chemistry evolves, it apparently becomes more complex (varied) as indicated by the increasing breadth of the TPO peak. The breadth of the TPO peaks may be considered to reflect a superposition of TPO profiles of polymeric species with varied degrees of thermo-oxidative stability (nominally different oxidation temperatures), again a manifestation of changing film chemistry through loss of O and H atoms during a carbonization type process, illustrated pictorially in Figure 6.18.

Plots describing the evolution of TPO breadth and average temperature against reaction time seem to display either partial sections of the overall chemical transformation or the full range of a pattern depending on the nature and thermal oxidative stability of the lubricant and additives, as seen in Figure 6.19. This is coupled with monotonic increasing average peak temperatures, reflecting the gradual transformation of the deposit, as described above.
Figure 6.18. Illustration of Global Change in Film Composition

Step 1. Initiation of Polymeric Film (Lacquer/Varnish)

Step 2. Growth of Polymeric Film (Transition to dark carbon)

Step 3. Formation of dark “elemental” carbon deposit
Figure 6.19. Average Oxidation Temperature for Group 1–4 Base Oils

Figure 6.20. Evolution of TPO profile breadth and Average Temperature for Type 1-4 Base Oil
As shown in Figure 6.20, because film chemistry becomes more complex (through aging) TPO profiles undergo an increase of breadth, reaching a maximum and then decreases gradually to a width near their initial range reflecting the evolution of film composition [Fig. 6.20 (a)]. In most cases, Figs 6.20 (b), (c) and (d), only portions of the pattern could be observed. Plot (c) displays the initial two stages (gradual increase, followed by maximum attainment in TPO breadth) and plot (d) displays the two final stages (maximum attainment and gradual decrease). In summary, these observations are supporting evidence of the uniform layer model and the proposal hypothesis.

In summary, results of TPO analysis showed that as film chemistry evolves, it apparently becomes more complex (varied) due to loss of O and H atoms during a carbonization type process. As the deposit undergoes visible changes over time (lacquer deposit transforming into dark carbon), the average peak temperature (mass-weighted, mean oxidation temperature) monotonically increases. The characterization of PSMO deposits by TPO indicate that the global change in carbonaceous structure proceed uniformly across the PSMO deposits in support of the uniform layer deposition model.
CHAPTER 7. SUBSTITUTION TEST

7.1 Principle of the Substitution Test

The Penn State Micro-oxidation test (PSMO) has long been used to evaluate the oxidative stability of lubricants and additives. PSMO was used in a substitutional test to pre-cover metallic pan surfaces with polymeric, transitioning, and carbonaceous films produced by the oxidizing lubricant at various stages along the mass deposition curve, and to substitute the films into the same fresh or aging lubricant as the initial test specimen/surface. In this manner, the effect of the pre-deposit was gauged against the baseline of fresh and partially oxidized films. Different substitution tests conducted for the purpose of this investigation included: Inert Environment Substitution Test (Nitrogen), Aging Film Substitution Test, and Aging Oil Substitution Test.

7.2 Nature of Thin Film Oxidation Deposits

The oxidative degradation of lubricants can be classified into two main reactions: bulk oil oxidation and thin-film oxidation. Bulk oil oxidation usually takes place in larger oil bodies at a slower rate. Exposure to air (oxygen) is regulated by the surface contact kinetics, and the gas diffusion is limited. Bulk oxidation leads to increased oil acidity, oil thickening, and, to a more severe extent, oil-insoluble polymers that may manifest as sludge when mixed with unburned/oxidized fuel components, water, and other solids. Thin-film oxidation describes a more rapid reaction in which a small amount of oil, usually in the form of a thin-film coating on metal surfaces, is exposed to elevated temperatures and air (oxygen). Under these conditions, hydrocarbons decompose much more quickly and the polar oil oxidation products formed at the oil-metal interface can rapidly build up on the metal surface, leading to the formation of highly polymeric lacquer or dark carbon deposits. Thin film oxidation
(PSMO) is governed by the well documented free-radical chain reaction consisting of four distinct steps: Chain initiation, propagation, branching, and termination, as illustrated in Figure 7.1.

1. **Initiation**

\[ R - H + O_2 \rightarrow R \cdot + HOO \cdot \]

\[ R - R \xrightarrow{\text{Energy}} R \cdot + R \cdot \]

2. **Propagation**

\[ R \cdot + O_2 \rightarrow ROO \cdot \]

\[ ROO \cdot + RH \rightarrow ROOH + R \cdot \]

3. **Chain Branching**

   a. **Radical Formation**

   \[ ROOH \rightarrow RO \cdot + HO \cdot \]

   \[ RO \cdot + RH \rightarrow ROH + R \cdot \]

   \[ HO \cdot + RH \rightarrow H_2O + R \cdot \]

   b. **Aldehyde and Ketone Formation**

   \[ RR'HCO \cdot \rightarrow RCHO + R' \cdot \]

   \[ RR'R''CO \rightarrow RR'CO + R'' \cdot \]

4. **Chain Termination**

\[ R \cdot + R' \cdot \rightarrow R - R' \]

\[ R \cdot + R'OO \cdot \rightarrow ROOR' \]

Figure 7.1. Free-Radical Chain Reaction
Series of repeated pan precoverage PSMO tests, shown in Figure 7.2 lead to the generation of the standard mass deposition curve listed in Figure 7.3. Aging deposits formed during the process represent various types of carbonaceous deposits produced during PSMO, starting with an initial polymeric film (a) which transitions into a varied lacquer/dark carbon film (b); which further transforms into lacquer/dark carbon film (c). The final stage is the formation of a dark more-elemental carbon deposit (d). The next section discusses in more details the type of deposits found at each stage of the precoverage steps described in Figure 7.2.

**Figure 7.2.** Precoverage Test (30, 60, 90, and 120 minutes)
Figure 7.3. Standard Mass Deposition Curve

7.2.1 Polymeric “lacquer” deposits

Thirty minutes of oxidation (PSMO) using Type 1 base oil led to the formation of two very different types of products (see Figure 7.4 and 7.5). The first is a soft and sticky resin-like deposit that is easily washed away by a solvent during the rinsing process; the second is polymeric film, also referred to as a “lacquer deposit.” Lacquer deposits are formed as oxygenates created in the oil phase polymerize on hot surfaces, the nature of which depends on the severity of the test conditions. The quantity and nature of the deposit seems also to depend on test conditions such as time and temperature. Oxygenated hydrocarbons are either the basic component in or the precursor to most, if not all, types of deposits.
Figure 7.4. Condensation and polymerization reactions of primary oxidation products

Lacquer and varnish deposits are formed under mild conditions, such as short reaction time and/or low temperature. The difference between lacquer and varnish is that lacquer is lubricant-derived and varnish is largely fuel-derived. In addition, lacquer is water-soluble and varnish is acetone-soluble. In engines, lacquer usually forms on piston skirts, cylinder walls, and in the combustion chamber, whereas varnish occurs on valve-lifters, piston rings, piston skirts, valve covers, and crankcase ventilation valves.

Figure 7.5. Polymeric “Lacquer” Deposits on PSMO pans (30 minutes PSMO)

7.1.2 Transitioning deposits

Sixty and ninety minutes of oxidation (PSMO) using Type 1 base oil led to the formation of two somewhat similar transitioning deposits (Figure 7.6). The similarities between the 60-minute and 90-minute coatings lie in the heterogeneity of carbonaceous material found on the pan as oxidation proceeds. Transitioning deposits are formed as
previously formed polymeric deposits separate and dehydrate on hot surfaces, and so make a variety of tenacious films. As a result, both polymeric and dark carbon deposits are observable on the substrate. The extent of the transformation depends on the severity of oxidative reactions. Transitioning deposits, such as those formed after 60 minutes, although more varied in nature tend to be more polymeric than 90 minutes transitioning deposits. Similarly 90-minute transitioning are more carbonaceous in nature due to their longer oxidation times.

![Transitioning Deposits on PSMO pans](image)

a. 60-minute “more polymeric” transitioning deposits

b. 90-minute “more elemental carbon” transitioning deposits

**Figure 7.6.** Transitioning Deposits on PSMO pans

7.1.3 Dark Carbonaceous Deposit

Dark carbonaceous deposits resulted after 120 minutes of oxidation (PSMO) using Type 1 base oil, as shown in Figure 7.7. Dark carbonaceous deposits are formed when polymeric deposits on hot surfaces undergo severe dehydrogenation. These deposits are constituted mostly of elemental carbon and are indicative of the final stage of lubricant oxidation; such
deposits are the most common consequences of lubricant degradation. As the deposit ages, its physical appearance changes from a lacquer to dark carbon. It is believed that this physical transformation reflects an underlying chemical morphogenesis that results from a sequence of dehydrogenation and deoxygenation reactions.

![Figure 7.7. Dark carbon deposits on PSMO pans](image)

A detailed characterization of lacquer, transitioning, and dark carbon deposits to help quantify the changes will be presented later. This would enable a verification of the uniform layer model, since in the model the deposit film is projected to undergo a homogeneous transformation over the temporal course of the standard mass-deposition curve.

7.2. Inert Environment Substitution Test on Metal Substrate

7.2.1 Inert Environment Control Test (on clean pan surface)

Inert environment substitution tests were conducted with high-purity nitrogen on stainless-steel pan surfaces. An initial set of standard PSMO tests were conducted to assess the deposit formation tendency of Type I base oil (a control Inert Environment PSMO Test). Forty mg of type base oil was placed on 4 different pans and were oxidized in sequence of 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Results shown in Scheme 7.1 illustrate the deposition process. The standard PSMO test conducted under nitrogen showed significant aging of oil due to thermal degradation and a light coating/discoloration of pan surface. No
mass deposition was recorded in the standard PSMO test conducted under nitrogen (Figure 7.8 and 7.9).

**Scheme 7.1.** Standard PSMO Test under Nitrogen

**Test Conditions:** Test temperature: 225°C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: Clean stainless-steel pan surface. **Gas:** (Nitrogen). (Canon Powershot A480, 10 Megapixel CCD, 3.3x optical zoom lens, DIGIC III image processor, a 2.5-inch LCD display)
**Figure 7.8.** PSMO Test conducted under Nitrogen

**Figure 7.9.** Repeated 60 min Duration Tests

**Figure 7.9.** Repeated 60 min PSMO Test conducted under Nitrogen
7.2.2 Inert Environment Test (on aging deposit films)

In the Substitution test (under nitrogen), polymeric, transitioning, and carbonaceous films were sequentially produced to pre-cover sets of four (4) pans by oxidizing Type I base oil for 30 minutes, 60 minutes, 90 minutes, and 120 minutes (Schemes 7.1 – 7.6). A pre-coverage step was conducted in air (oxygen) to ensure normal oxidation of the lubricant. The different films formed, corresponded to 3 various stages along the mass deposition curve. Each specimen (pre-covered pan) was further oxidized in the presence of freshly supplied or aging lubricant. The oxidation temperature was set at 225°C for all samples. Air was supplied at a rate of 20 cc, and the initial oil mass was approximately 40 mg. The test temperature was increased to 250°C. The effect of the pre-deposit was then gauged against the baseline of fresh lubricant. The first surface (30-minute precoverage), was prepared by allowing the induction phase to occur, followed by the extraction of the resultant surface as the new test surface with which to begin measuring the mass deposition rate anew. The second surface, (60-minute precoverage) was prepared by allowing a portion of accelerated mass growth to occur, again followed by extraction of the surface as the new test piece with which to begin measuring the mass deposition rate. The last surfaces, (90-minute and 120-minute precoverage) were prepared by allowing maximum deposit and cessation of mass growth to occur, followed by extraction of the surface. Each set of 4 samples (4 of the 30-minute group, 4 of the 60-minute, 4 of the 90-minute, and 4 of the 120-minute) was further oxidized for subsequent deposition under similar conditions. The graphs below represent mass deposition profiles for layers formed during initial precoverage and after 30, 60, 90, and 120 minutes of subsequent deposit formation (the second layer), along with sets of control tests shown in Figure 7.8 and 7.9.
Scheme 7.2. 30 minutes Precoverage and Subsequent Oxidation

Precoverage test Conditions: Test temperature: 225° C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: Clean stainless-steel pan surface. Gas: (Air) Overlayer test Conditions: Test temperature: 225° C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: 30-minute precovered lacquer deposit. Gas: (Nitrogen).
Scheme 7.3. 60-minute Precoverage & Subsequent Oxidation

Precoverage test Conditions: Test temperature: 225° C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: Clean stainless-steel pan surface. Gas: (Air) Overlayer test Conditions: Test temperature: 225° C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: 60-minute pre-covered lacquer/dark carbon transitioning deposit. Gas: (Nitrogen)
Scheme 7.4. 90-minute Precoverage & Subsequent Oxidation

Precoverage test Conditions: Test temperature: 225°C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: Clean stainless-steel pan surface Gas: (Air)

Overlayer test Conditions: Test temperature: 225°C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: 90-minute more transformed lacquer/dark carbon transitioning deposit. Gas: (Nitrogen)
Scheme 7.5. 120-minute Dark Carbon Precoverage & Subsequent Oxidation

Precoverage test Conditions: Test temperature: 225°C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: Clean stainless-steel pan surface; Gas: (Air) Overlayer test Conditions: Test temperature: 225°C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: 120-minute dark carbon deposit. Gas: (Nitrogen)
Scheme 7.6. Inert Environment Substitution Test [4 x 4 Experimental Matrix]

**Row 1:** 30-minute lacquer precoverage and subsequent oxidation; **Row 2:** 60-minute lacquer/dark carbon transitioning precoverage and subsequent oxidation; **Row 3:** 90-minute more transformed lacquer/dark carbon transitioning precoverage and subsequent Oxidation; **Row 4:** 120-minute dark carbon precoverage and subsequent oxidation. (Canon Powershot A480, 10 Megapixel CCD, 3.3x optical zoom lens, DIGIC III image processor, a 2.5-inch LCD display)
Figure 7.10. PSMO conducted with pans precovered for 30, 60, 90, and 120 minutes
As described, sets of 4 precovered pans were further tested in 30-minute sequences (30 minutes to 120 minutes) with freshly supplied oil in a nitrogen environment. In this manner, the effect of the pre-deposit was gauged against the fresh lubricant over-layer for potential interactions between the initial substrate and the newly deposited film (Figure 7.10 & 7.11). With an initial coating, mass deposition even under nitrogen was observable on all precovered films, except the dark more elemental carbon deposit. PSMO conducted under nitrogen with 30-minute precovered samples showed mass growth immediately in fresh lubricant. Maximum deposition is observed after 90 minutes, characterized by an inflection point (on the uniform deposition curve). Beyond this point, mass deposition begins to diminish. A similar pattern was observed for the 60-minute and 90-minute precovered pans. The largest deposit (7%) was recorded after 90 minutes of oxidation on a 90-minute
precovered pan. Otherwise, deposition observed under nitrogen on precovered pan-surfaces was minimal (<8%), and decreased as with aging substrate (Figures 7.10 and 7.11).

7.3. The aged film substitution test

Polymeric and carbonaceous films were sequentially produced to precoat each pan surface by oxidizing Type I base oil for 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Precoverage and subsequent oxidation steps were conducted in air (oxygen) to ensure normal oxidation of the lubricant. As discussed previously, different films corresponded to various stages (3) along the mass deposition curve. Each specimen (precovered pan) was further oxidized in the presence of freshly supplied or aged lubricant.

- Test temperature 225°C
- Air supply rate: 20 cc/min
- Initial oil mass: 40 mg
- Test times: 30 minutes, 60 minutes, 90 minutes, and 120 minutes.

The first surface was prepared by allowing the induction phase to occur, followed by the extraction of the surface as the new test surface with which to begin measuring the mass deposition rate anew. The second surface was prepared by allowing a portion of accelerated mass growth to occur followed, by the extraction of the surface, again as the new test piece with which to begin measuring the mass deposition rate. The third surface was prepared by allowing cessation of mass growth to occur, followed by the extraction of the surface as the new test piece, again in fresh lubricant (Scheme 7.7 – 8.11). Three (3) different substitution tests were conducted for the purpose of this investigation.
Scheme 7.7. Aging Film Substitution Test. 30-minute Lacquer Precoverage & Subsequent Oxidation

**Precoverage test Conditions:** Test temperature: 225°C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: Clean stainless-steel pan surface; Gas: (Air)

**Overlay test Conditions:** Test temperature: 225°C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: 30-minute dark carbon deposit. Gas: (Air)
Scheme 7.8. Aging Film Substitution test. 60-minute Transitioning Lacquer/Dark Carbon Precoverage & Subsequent Oxidation

**Precoverage test Conditions:** Test temperature: 225°C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: Clean stainless-steel pan surface. **Gas:** (Air) **Overlay test Conditions:** Test temperature: 225°C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. **Substrate:** 60-minute transitioning deposit. **Gas:** (Air)
Scheme 7.9. Aging Film Substitution Test. 90-minute More Transformed Lacquer/Dark Carbon Precoverage & Subsequent Oxidation

**Precoverage test Conditions**: Test temperature: 225° C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: Clean stainless-steel pan surface; Gas: (Air) **Overlay test Conditions**: Test temperature: 225° C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. **Substrate**: 90-minute dark carbon deposit. Gas: (Air).
Scheme 7.10. Aging Film Substitution Test. 120-minute Dark Carbon & Subsequent Oxidation

**Precoverage test Conditions**: Test temperature: $225^\circ$ C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Substrate: Clean stainless-steel pan surface. **Gas**: (Air) **Overlayer test Conditions**: Test temperature: $225^\circ$ C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. **Substrate**: 120-minute dark carbon deposit. **Gas**: (Air).
Scheme 7.11. Aging Film Substitution Test (4x4 Experimental Matrix)

Row 1: 30-minute lacquer precoversage and subsequent oxidation; Row 2: 60-minute lacquer/dark carbon transitioning precoversage and subsequent oxidation; Row 3: 90-minute more transformed lacquer/dark carbon transitioning precoversage and subsequent oxidation; Row 4: 120-minute dark carbon precoversage and subsequent oxidation. (Canon Powershot A480, 10 Megapixel CCD, 3.3x optical zoom lens, DIGIC III image processor, a 2.5-inch LCD display)
With an initial polymeric coating, mass deposition should be accelerated (based on the free-radical addition mechanism, according to the proposed uniform layer model) and accelerated mass growth was immediately observed, even in fresh lubricant. After the inflection point (on the uniform deposition curve), mass deposition begins to slow, presumably reflecting a slowing rate of radical formation sites upon the surface.

Observation of such a deceleration would provide further confirmation of the radical-formation mechanism within the surface-bound organic layer, governing the rate of mass deposition upon the surface, even when in fresh lubricant, as predicted by the homogeneous chemical transformation of the hypothesized uniform layer model. With an initial (largely) carbon layer upon the surface, the chemical transformation of the surface deposit is largely complete and free-radical site formation less energetically favorable. Mass deposition, even upon exposure to fresh lubricant should be minimal, thereby testing the final stage as predicted by the uniform layer model.

Test Conditions were as follow: 225° C, 40 mg of Type I oil. Time: 30 minutes, 60 minutes, 90 minutes, and 120 minutes. The graphs indicate the percentage of mass deposited during each of the quadrupled PSMO tests (repeated four times).
Figure 7.12. Mass Deposition Profile for PSMO Aging Film Substitution Test

Plotted parametrically with pre-deposit age, as a function of additional PSMO duration, Figure 7.12 shows the first stage results of the aging film substitution tests over pre-deposited films (namely for the 30-, 60-, 90-, and 120-minute pre-deposits). The practical relevance of such plots is that they reveal the effect of additional aging of pre-existing deposits. Across the graphs, as the initial deposit age increases, the rate of mass deposition slows. This will be further detailed in Chapter. 10.

Results shown in Figure 7.12 (a) indicates that when further oxidation is conducted with fresh oil on 30-minute lacquer pre-deposited films, mass deposition increases gradually from 9.75%, to 14.6%, to 17%, and 19.5%, after 30, 60, 90, and 120 minutes of further oxidation, respectively. The monotonic increase in graph (a) is a snapshot of the standard mass deposition curve and represents the phase of sharp acceleration in mass deposition,
without the initial induction period and the final decrease in mass deposition. In Figure 7.12 (b), when further oxidation is conducted with fresh oil on 60-minute transitioning (lacquer/dark carbon) pre-deposited films, mass deposition increases gradually from 0%, to 9.89%, to 14.38%, and 17.01%, after 30, 60, 90, and 120 minutes of further oxidation, respectively. Graph (b) is also a snapshot of the standard mass deposition curve, representing the final stage of the rapid acceleration in mass deposition and initial stage of the gradual decrease in mass deposition. In Figure 7.12 (c), additional oxidation conducted with fresh oil on 90-minute (more transformed lacquer/dark carbon deposits) pre-deposited films indicates that mass deposition increases from 0%, to 7.5%, to 12%, and 12%, after 30, 60, 90, and 120 minutes of further oxidation, respectively. Graph (c) further illustrates the final stage of the rapid acceleration in mass deposition and the inflection point that precedes the gradual decrease in mass deposition. No additional mass deposition is observed on 120-minute (dark carbon) pre-deposited film for the time sequences involved in this study. Such deposits appear to be chemically inert towards facilitating further mass deposition. Replotting the data as shown in Fig. 7.13 provides better comparison to the hypothesis. Data are plotted parametrically with additional PSMO duration and as an explicit function of initial deposit age. As observed, film age markedly controls the deposited mass and its rate, for any given duration of 2nd stage PSMO duration. Deposited mass declines with initial film age. Based on panel a, the 30 minute film appears to be most active relative to the other films at the short testing duration of 30 minutes. Graph [a] corresponds to all 30-min additional PSMO data points (x-axis) in Figure 7.12 plotted against pre-deposition time.
Figure 7.13. Mass Deposition Profile for Aging Film Additional PSMO Times

Beyond an initial mass deposition observed after 30 minutes of additional PSMO on 30-minute aging film, no additional mass deposition was observed when the films’ age exceeded (2 times or more) oil oxidation time in the presence of fresh oils. For each additional PSMO time of 60, 90, and 120 minutes, the mass deposition profile of the aging films decreases as film ages increases. As shown before, all deposits with an initial time of 120 minutes are inactive. These observations are also consistent with the hypothesis (as results in graphs [b], [c] and [d] indicate), such that when additional oxidation time is kept constant (60, 90, or 120 minutes), as film age varies from nascent to aged to severely aged, overall mass deposition decreases from the nascent and more active lacquer film, to the aged and less active dark carbonaceous deposits.
7.4. The Aged Oil Substitution Test

Motivation for these complimentary tests was based on observations with the aged films. Though in all cases mass deposition amount declined with film age, additive (1st and 2nd stage) PSMO duration times did not behave as single PSMO duration times. For example, films with a pre-age of 120 minutes were inactive but films with lesser 1st round ages were yet active in the 2nd round tests even when the total PSMO clock time exceeded 120 minutes. Such differences prompted further examination of oil age effects upon mass deposition of the various pre-aged films. As described in the aging film substitution, polymeric and carbonaceous films were sequentially produced to precoat each pan surface by oxidizing Type I base oil for 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Precoverage and subsequent aging steps were both conducted under air ambient to ensure a consistent environment for the lubricant. Each specimen (precovered pan) was further aged via the PSMO procedure in the presence of sets of aging oils, preoxidized for 30 minutes, 60 minutes, 90 minutes, and 120 minutes. The process of oil preoxidation was conducted as follows. Two hundred mg of Type I base oil were weighed and preoxidized in a PSMO test at 225°C for 30 minutes, 60 minutes, 90 minutes, and 120 minutes. Forty mg of the oxidized oil were then collected and further oxidized on 30-, 60-, 90-, and 120-minute aging deposits films. Oil pre-oxidation conditions were as follows:

- Test temperature 225°C
- Air supply rate: 20 cc/min
- Preoxidized oil mass: 40 mg
- Preoxidized oil times: 30 minutes, 60 minutes, 90 minutes, and 120 minutes.
- Pre-deposit (production) times: 30 minutes, 60 minutes, 90 minutes, and 120 minutes.
The first set of tests were conducted by combining the 30-, 60- 90- and 120-minute aged deposits with 30-minute oxidized oil for an additional PSMO duration of 30 minutes. The second set of tests proceeded similarly but using 60-minute aged oil as a starting point for the additional 30-minutes of PSMO oxidation. Likewise the third set of tests used 90-minute oxidized oil while the fourth round utilized 120-minute aged oil. All subsequent PSMO durations were 30 minutes to maintain as close a differential measurement while yet providing for sufficient measureable mass deposition.

![Graphs](image)

**Figure 7.14.** Mass Deposition Profile for Aged Oil Substitution Test

Plotted as a function of initial film age towards testing the fundamental hypothesis, the first plot (Fig. 7.14.a) is consistent as it shows a marked decline in activity with increasing film age. The fall off is steep and monotonic. Symmetrical with the aged film.
results, though affording no further support of the hypothesis, Fig.14.d at least verifies that aged oil does not contribute to further deposits.

However of particular interest are the results with intermediate aged oils and respective films. There appears to be a synergy between an aged deposit and equally aged oil towards facilitating mass deposition. Such synergy points to chemical similarity of film and oxygenated liquid phase precursors.

![Graphs showing mass deposition profile for aged oil substitution test](image)

**Figure 7.15.** Mass Deposition Profile for Aged Oil Substitution Test (second stage plots)

Plotted parametrically with initial pre-deposit age and as an explicit function of oil oxidation time, Figure 7.15 shows first-stage results of the substitution test conducted with aged or preoxidized oils on pre-deposited aged films (see, Figure 7.14). Results shown in
graph (a) indicate that when further oxidation is conducted with 30-minute preoxidized oil on 30-minute pre-deposited films, mass deposition decreases gradually from 17% for the nascent pre-deposit to 0% for the aged carbonaceous pre-deposits. As observed in the aging film substitution test, results in graph (a) suggest that when further oxidation is conducted with 30-minute preoxidized oil on 30-, 60-, 90-, and 120-minute pre-deposited films, the highest deposition rate is observed with 30-min pre-deposited films, and decreases monotonically as the film ages. As illustrated in graph (d), no additional mass deposition is observed when 120-min preoxidized oils are further oxidized with 30-, 60-, 90-, and 120-minute pre-deposited films. Once more, these sets of data support and confirm that existing deposits govern the mass deposition derived from the oxidative degradation of the lubricant by becoming less capable of binding with additional deposits as the film chemistry changes due to aging. Graphs (b) and (c) suggest a synergy between the aging oil and the aging film. These results do not necessarily disprove the uniform layer deposition model but could point to possible specific conditions, such as oil and film chemistry, under which both oil and film properties together could lead to maximum deposition. An overview of the aging film and aging oil substitution test is provided in Scheme 7.12 and illustrates all sections of the substitution test, including the Extended Mass Deposition Profile (Section 1); the Base PSMO Profile (Section 2); the Aging Oil Substitution Test (Section 3); lacquer & carbon deposits from the Aging Film Substitution Test (Section 4); and transitioning deposits from the Aging Film Substitution Test (Transitioning Deposits).
**Section 1:** Standard Mass Deposition Curve (Extensive PSMO Test)  
**Section 2:** Base PSMO Test  
**Section 3:** Aging Oil Substitution Test  
**Section 4:** Aging Film Substitution Test (Lacquer & Carbon Precoverage)  
**Section 5:** Aging Film Substitution Test (Transitioning Deposits)

**Scheme 7.12** Overview of the Aging Oil and Aging Film Substitution Test. (Canon Powershot A480, 10 Megapixel CCD, 3.3x optical zoom lens, DIGIC III image processor, a 2.5-inch LCD display)
7.5. Role of Metal Surface in Thin Film Oxidation

During precoverage and/or the standard thin film oxidation test, the presence of metals has a major effect on the deposit-forming properties of most lubricants. Results have clearly shown that lubricant oxidation reactions can be catalyzed by metal surfaces. In the process, metal surfaces promote lubricant degradation by accelerating hydroperoxide decomposition, and affect the condensation of oxidation products to form lacquer or dark carbon deposits (Colclough, 1987). The initiation step is therefore catalyzed by metal ions as well as hydroperoxide decomposition in the chain-branching step through a redox mechanism, illustrated in Figure 7.16. The required activation energy for this mechanism, and thus the initiation and propagation steps, can commence at much lower temperatures.

a. Initiation Step

\[ M^{(n+1)+} + \text{RH} \rightarrow M^{n+} + H^+ + R \cdot \]

\[ M^{n+} + O_2 \rightarrow M^{(n+1)+} + O_2^- \]

b. Propagation Step

\[ M^{(n+1)} + \text{ROOH} \rightarrow M^{n+} + H^+ + \text{ROO} \cdot \]

\[ M^{n+} + \text{ROOH} \rightarrow M^{(n+1)+} + \text{HO}^- + \text{RO} \cdot \]

Figure 7.16. Redox Mechanism

The rate of catalytic activity on oxidation rate in decreasing order of activity has been reported to be: low-carbon steel > stainless steel > lead > aluminum > brass > copper (Lahijani et al., 1982). Also the rate of catalytic activity on the deposit formation in decreasing order of activity was found to be: low-carbon > stainless steel > aluminum > brass > copper > lead (Rudnick, 2008). To steer away from such effects, tests here were conducted
with pre-deposited films. With this pre-coverage, underlying metal effects upon deposit growth are eliminated.

7.6. Role of Film Chemistry in Thin Film Oxidation

Lubricant deposits have a complex chemistry that results from various complex factors including chain reactions, chemistry of the aging lubricant, and nature of the substrate in the oxidative environment. Deposit growth is dynamic and film chemistry is time-dependent until a “maximum” point in the growth/degradation is reached. Initial polymeric growth on metal substrate gives a deposit composition that contains significant oxygen and hydrogen content, reflecting a largely organic composition. As the reaction continues, the film chemistry changes as oxygen and hydrogen are lost through deoxygenation and dehydrogenation reactions. Corresponding carbon content increases, on an atomic percentage basis. Occurring in the condensed phase, the reactions are varied and complex. Essentially the film is undergoing a low temperature carbonization process and its final chemistry will be highly temperature dependent. At temperatures far lower than normal carbonization temperatures or gasification temperatures (Harris et al., 2008) film hydrogen and oxygen content will be governed by thermodynamics and reach a limiting value, different than zero. Results of both “Aging Oil” and “Aging Film” Substitution tests show that film chemistry does affect the deposition process via the attachment of liquid phase species (which could be oxygenated) to pre-deposited carbonaceous films. Though physical adsorption is possible and likely, mass deposition as defined and measured for these studies is based on chemically adsorbed species, i.e. reactive bonding. Such chemistry is believed to occur via the formation of free radicals. Traditionally, as outlined by the mechanism in Figure 4.7 of Chapter 4., such species have been considered to be formed in the liquid. This is not disputed here nor directly
tested. The hypothesis only went so far as to state that the film governed mass deposition based upon film chemistry. While it is likely that loss of heteroatoms in the film lead to radical sites that facilitate, indeed promote reactive mass addition, the hypothesis could yet be valid without invoking such reactions. The same radical formation processes occurring in the liquid phase and by which oxygenated species are formed, could yet contribute to chemisorptions. In this manner the film and its chemistry would yet control mass deposition. While contributions from radicals in both phases (liquid and solid) are likely, it is speculated that radical sites in the film are in fact those that contribute to mass deposition; first, because such sites are localized to the film thereby fostering only mass increase and secondly, being stabilized by the film matrix may have a longer lifetime than free radicals in the liquid lubricant phase to facilitate the former process.

Undoubtedly the liquid phase contributes and its effect is most clearly observed for the aged oils which match the film age in the aged oil substitution tests. The uptick in mass deposition with these “matched” paired systems hints at synergy and the possibility of concerted reactions between similar oxygenated polymeric species for lubricant and film. Why such synergy is not observed for standard PSMO testing or other aged film substitution tests may be due to their start with fresh lubricant which does have an induction period for formation of reactive species. More likely, at later test durations some non-bonded oligomers may form a boundary layer preventing reactive mass deposition. Upon removal and rinsing of the test coupon in the substitution tests, such a protective film is removed, being non-bonded, now exposing the yet reactive, underlying film. This explanation also accounts for the seemingly longer “active” lifetime of films in the substitution tests than observed in the straight PSMO procedure. It should be noted that lubricants and additives are commonly
engineered to create “protective” films. Confirmation of such physically adsorbed films would require in situ measurements, or very different experimental procedures. It is noted that during washing of the coupons that the leachate was colored and unlike the original oil exhibited visible absorbance. As a final note, the practical relevance of such data with aged oils and aged films and their mutual synergy towards mass deposition is that such synergy is lost with fresh oil for the reasons outlined above. The moral is then to frequently change the oil.

In summary, different substitution test were conducted to decouple the lubricant-deposit system. Across the set of aged films, the substitution tests show a declining activity towards mass deposition with film age. For each increment of 2nd stage PSMO duration each individual film of the set and the set as a whole exhibit a decrease in mass deposition, interpreted as decline in reactivity. The Chemical characterization of PSMO deposits by EDS and FTIR are discussed in the next chapters and provide additional supporting evidence to the uniform layer deposition model.
CHAPTER 8. FTIR SPECTROSCOPY STUDY OF LUBRICANT DEPOSITS

8.1 Introduction

Infrared spectroscopy is a widely used technique for investigating chemical processes and structure. In the most basic terms, the infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds from within a molecule. In this chapter, the principles behind Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) Spectroscopy and its application to the uniform layer deposit formation process are discussed.

Equation 8.1 reflects the distribution of energy possessed by a molecule at any given moment, and is defined as the sum of the contributing energy terms.

\[ E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}} \]  

(Equation 8.1)

The translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter. Rotational energy, which gives rise to its own form of spectroscopy, is observed as the tumbling motion of a molecule, which is the result of the absorption of energy within the microwave region. The vibrational energy component is a higher energy term and corresponds to the absorption of energy by a molecule as the component atoms vibrate about the mean center of their chemical bonds. The electronic component is linked to the energy transitions of electrons as they are distributed throughout the molecule, either localized within specific bonds, or delocalized over structures, such as an aromatic ring. In order to observe such electronic transitions, energy \((E)\) is applied in the form of visible and ultraviolet radiation, as shown in Equation 8.2.
\[ E = h\nu \] (Equation 8.2)

Where \( E \) is the energy of a photon, \( h \) the Planck constant and \( \nu \) the frequency of its associated electromagnetic wave.

The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study. From Hooke’s law, the fundamental vibrational frequency of a molecular ensemble is expressed in Equation 8.3:

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \] (Eq 8.3)

Where \( \nu \) = fundamental vibration frequency, \( k \) = force constant, and \( \mu \) = reduced mass, given by \( \mu = m_1 m_2 / (m_1 + m_2) \), where \( m_1 \) and \( m_2 \) are the component masses for the chemical bond under consideration. Specific infrared (IR) reflectance techniques may be divided into the areas of specular reflectance, diffuse reflectance, and internal reflectance. The latter is often termed as “attenuated total reflectance,” and is used in this study to characterize PSMO deposits as they undergo chemical transformation from the initial lacquer type deposit to dark carbonaceous deposits.

8.2 Principle of ATR spectroscopy

The fundamentals of attenuated total reflection (ATR) spectroscopy date back to the initial work of (Harrick, 1973), who independently devised the theories of ATR spectroscopy and suggested a wide range of applications. The concept of internal reflection spectroscopy originates from the fact that radiation propagating in an optically dense medium of refractive index \( n_1 \) undergoes total internal reflection at an interface of an adjacent medium of lower optical density (refractive index \( n_2 < n_1 \)). This wave is termed \textit{evanescent} and is derived from
the Latin root *evanescere*, meaning “to tend to vanish or pass away like a vapor.” The above phenomenon occurs only when the angle of incidence exceeds a critical angle $\Theta$. Figure 8.1 shows a transverse standing wave totally reflected at the interface, and is best described as the interference wave of the incident and reflected waves.

![Image of evanescent wave formation](image_url)

**Figure 8.1.** Evanescent wave formed at the internal reflection element sample surface (Harrick, 1973).

8.3 Peak Identification

Carbonaceous deposits formed during the micro oxidation test were analyzed by FTIR-ATR, and various peaks evolving at different wavelengths were attributed to characteristic functional groups formed during the oxidative degradation of base lubricants. IR peaks were assigned to chemical groups according to the peak assignments shown in Table 8.1. Functional groups composed of a carbon atom double-bonded to an oxygen atom (carbonyl groups or C=O), such as aldehydes, ketones, carboxylic acid, and esters are known to absorb at IR wavelengths of 1690–1750 cm$^{-1}$. Other functional groups composed of a carbon atom attached to a hydrogen atom (C-H) absorbed at IR wavelength of 2922 cm$^{-1}$.
Figure 8.2 is a spectral snapshot of the “fingerprint regions” for most common base oil deposits. The defined spectral regions (CH and C=O functional groups) hardly change from lubricant to lubricant (on the horizontal axis). The amount present will, however, affect the amplitude of the peaks (on the vertical axis). It is not uncommon for additives in fully or partially formulated lubricants to also create new bands depending on the oxidative state of the lubricant. Proof of the oxidation state of a deposit film is indicated by the concentration of the above-mentioned functional groups in a set of sequential micro oxidation tests.

Table 8.1 Typical FTIR functional groups’ peak assignments.

<table>
<thead>
<tr>
<th>Absorbance</th>
<th>Wave number, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretch of carboxylic acid</td>
<td>3300-2800 (strong, broad, centers at ~3000)</td>
</tr>
<tr>
<td>N-H stretch</td>
<td>3400-3250 (medium intensity, often broad)</td>
</tr>
<tr>
<td>sp(^2) C-H stretch</td>
<td>3100-3020</td>
</tr>
<tr>
<td>sp(^3) C-H stretch</td>
<td>2960-2850</td>
</tr>
<tr>
<td>aldehyde C-H stretch</td>
<td>2830-2695</td>
</tr>
<tr>
<td>aromatic overtones</td>
<td>2000-1600</td>
</tr>
<tr>
<td>C=O stretch</td>
<td>See Table 8.2</td>
</tr>
<tr>
<td>aromatic C=C stretch</td>
<td>1600-1585</td>
</tr>
<tr>
<td>alkene C=C stretch</td>
<td>1680-1620</td>
</tr>
<tr>
<td>C-O stretch</td>
<td>1150-1050</td>
</tr>
<tr>
<td>aromatic ring bends</td>
<td>770-730 and 710-690</td>
</tr>
</tbody>
</table>

(Carbonyl region)  
C=O stretch mode  
(sp\(^3\) hybridized Carbon)  
CH stretch mode
Figure 8.2. FTIR Spectrum for Base Oil Deposits

8.4 FTIR Spectra for Standard PSMO Deposits

FTIR was used to determine the aging of PSMO produced deposits by the response in the alkyl and carbonyl stretching modes. In the first region, infrared energy is absorbed due to a symmetrical CH stretch from sp$^3$ hybridized carbon atoms. In the second region, infrared energy is absorbed due to the C=O stretch from ketones, esters, carboxylic acids, aldehydes, and anhydrides. Monitoring these two regions for both the oil phase and the deposit film enables a direct comparison of the oxidation level of deposits formed during PSMO from the degrading base oil.

Figure 8.3. FTIR-ATR Spectra of Standard PSMO deposits.

The degree of oxidation of PSMO deposits was determined by monitoring the concentration of carbonyl and sp$^3$ hybridized carbon species across the PSMO deposits. As shown in Figure 8.3, peak intensities decrease gradually as deposit nature and chemistry
changed from the initial lacquer deposit (30 minutes) to dark carbonaceous deposits (120 minutes). Sixty- and 90-minute transitioning deposits, however, show less resolution in sp$^3$ hybridized carbon peak intensities. This points to the similarities in film chemistry, and also to the uniformity of the chemical changes occurring as the film gradually transforms.

8.5 FTIR Spectra of Oxidized Oil

Infrared spectra of the preoxidized oil oxidation are shown in Figure 8.4 on an expanded scale from 0 to 4000 cm$^{-1}$. The preoxidation tests were conducted with 200 mg of fresh oils on a low-carbon steel (Fe) metal cup at 225°C. In Figures 8.5 and 8.6, the most dominant absorption peaks were observed respectively at 2978 cm$^{-1}$, 2870 cm$^{-1}$, 1068 cm$^{-1}$, and 912 cm$^{-1}$ for the esters. Other less pronounced but moderate absorption bands were observed at 1470 cm$^{-1}$ and 1374 cm$^{-1}$, and from 1300 to 1200 cm$^{-1}$, as shown in Figure 8.6. These spectra are significantly different from PSMO deposit spectra and showed no absorbance band in the 1700 cm$^{-1}$ carbonyl absorbance range, which were the most pronounced peaks of the deposits’ spectra.

![Figure 8.4. FTIR-ATR Spectra of Oxidized Oil Samples](image-url)
Figure 8.5. FTIR-ATR Spectra of Oxidized Oil Samples (C-H stretch 2978 and 2870)

Figure 8.6. FTIR-ATR Spectra of Standard PSMO deposits. [C-O 1068 at cm⁻¹ and C-H stretch at 912 cm⁻¹]
8.6 FTIR Spectra of Aging Film Substitution Test

Overall, spectra derived from FTIR analysis of PSMO produced deposits were generally complex with several overlapping peaks, but a set of three main characteristic absorption bands were accessible for analysis, namely hydroxyl, alkyl and carbonyl stretching modes. Other different functional groups associated with the oxidative degradation of lubricants were observed, including carbonyl groups, unsaturated compounds, hydroxyl groups, organics, etc. Figures 8.7–8.10 represent a series of PSMO deposits from the aging film substitution test. Aging deposits consisted of polymeric/carbonaceous (aged films) at various stages (3) along the mass deposition curve, substituted into fresh lubricant as the initial test specimen/surface. Gradual chemical transformation of the pre-deposited films was determined via changes in functional groups and gauged against the baseline of fresh lubricant for potential interactions with the partially oxidized lubricant. Infrared spectra of the aging film oxidation deposits are presented on an expanded wavelength scale from 0 to 4000 cm$^{-1}$. Micro-oxidation tests were conducted with 40 mg fresh oils on 30-minute, 60-minute, 90-minute, and 120-minute aged lacquer, transitioning, and dark carbonaceous deposits. IR spectra of aging film oxidation products showed the three distinct absorption peaks related to hydroxyl [-OH, 3600-3500], alkyl, sp$^3$ hybridized carbon [C-H, 2950] and carbonyl groups [1725-1715 cm$^{-1}$]. An important piece of evidence that supports the uniform layer deposition model is the consistency (uniformity) in the above-mentioned functional groups found in PSMO produced deposits as they undergo physical and chemical transformation from highly polymeric lacquer deposits to dark carbonaceous deposits. Although lacquer and dark carbonaceous deposits are clearly different physically and chemically, the difference only lies in the intensity or the concentration of their characteristic
functional groups, since no new peaks appear, and existing peak disappearance is observed only during the transformation process.

**Figure 8.7** FTIR Spectra of Aging Film Sub. Test showing evidence of [C-H and C=O] for 30 minutes of additional PSMO time on aging films using 40 fresh oil samples, on stainless steel pans.

**Figure 8.8** FTIR Spectra of Aging Film Sub. Test showing evidence of [C-H and C=O] for 60 minutes of additional PSMO time on aging films using 40 fresh oil samples, on stainless steel pans.
Figure 8.9  FTIR Spectra of Aging Film Sub. Test showing evidence of [C-H and C=O] for 90 minutes of additional PSMO time on aging films using 40 fresh oil samples, on stainless steel pans.

Peak intensities decreasing from 30 to 120 minutes initial PSMO time.

Figure 8.10  FTIR Spectra of Aging Film Sub. Test showing evidence of [C-H and C=O] for 120 minutes of additional PSMO time on aging films using 40 fresh oil samples, on stainless steel pans.

Peak intensities decreasing from 30 to 120 minutes initial PSMO time.
Organics and Hydrocarbons – Absorptions in the Region 3200–2700 cm\(^{-1}\)

Well-defined and characteristic absorptions were observed within the region of hydrocarbon absorption, typically characteristic of carbon- and hydrogen-containing species assigned to various forms of C-H stretching. Minimal absorptions above 3000 cm\(^{-1}\) suggest that the main compounds present in these deposits are unlikely to be unsaturated or aromatic while the region between 900 – 1000 cm\(^{-1}\) is too overlapped to allow definitive inference. As observed, the main absorption bands were observed below 3000 cm\(^{-1}\) and suggest the presence of aliphatic compounds. Furthermore, the existence of long linear aliphatic chains is indicated by peaks evolving at 2935 and 2860 cm\(^{-1}\), and at 1470 and 720 cm\(^{-1}\).

Hydroxy Groups – Absorptions in the Region 3650–3250 cm\(^{-1}\)

A low-intensity and broad peak was observed within the absorption range of 3650–3250 cm\(^{-1}\). Hydroxy groups mainly dominate this region, both giving rise to very characteristic band profiles. The presence or absence of hydrogen bonding is well delineated in this region. Another characteristic vibration that is observed in this region, which is unlikely to be confused with any other functional group, is the C-H stretch of a terminal alkyne (acetylenic compound). The broadening of the main absorption band in this region broadly suggests heterogeneous broadening of the hydroxy groups. Additional moderate to intense bands in the ranges 1600–1300, 1200–1000, and 800–600 cm\(^{-1}\) confirm that the compounds mentioned above were simple hydroxyl compounds. Simple hydrogen-bonded OH absorption of a hydroxy (alcohol) function has a very characteristic shape. When the feature is relatively sharp and occurs between 3670 and 3550 cm\(^{-1}\), then the compound contains a non-hydrogen-bonded hydroxy group, often an alcohol or phenol with a sterically
hindered OH group. Here the low intensity and miniscule dynamic range eradicate potential information from this band.

*Carbonyl Compounds – Absorptions in the Region 1850–1650 cm\(^{-1}\)*

A major band in the carbonyl absorption region (1850–1650 cm\(^{-1}\)) indicates the presence of a carbonyl group, although other minor groups may interfere. Absorption at the high end of the range (1775 cm\(^{-1}\)) hint that carbonyl compounds found on PSMO deposits may include reactive carbonyl, such as an anhydride; acid halide (acyl halide); a strained-ring carbonyl, such as a lactone; or an organic carbonate. More importantly, strong absorption in the middle of the range (1750–1700 cm\(^{-1}\)) confirmed the dominance of simple carbonyl compound, such as a ketone, an aldehyde, an ester, or a carboxylic acid, reported as lubricant oxidation products. In addition, medium or weak absorption at the low end of the range (1700 cm\(^{-1}\)) suggests the presence of a carboxylate (carboxylic acid salt), although conjugated aldehydes, ketones, esters, and carboxylic acids may also fall into this lower-end category. Due to conjugation with a double bond, a second absorption is observed between 1650 and 1600 cm\(^{-1}\). This could potentially be explained by the involvement of an aromatic ring, as discussed in the characteristic aromatic absorptions section.

*Unsaturated Compounds – Weak to Moderate Absorption in the Region 1670–1620 cm\(^{-1}\)*

A relatively narrow, weak-to-moderate absorption, normally centered on 1650 cm\(^{-1}\), was indicative of olefinic unsaturation. A lowering of this frequency, accompanied by intensification of the band, is characteristic of conjugation with another double-bond structure, such as an aromatic ring. Confirmation of such unsaturation is typically indicated by C-H peaks above 3000 cm\(^{-1}\), and a pair of absorptions at 3085 cm\(^{-1}\) and/or 3025 cm\(^{-1}\).
Table 8.2. Characteristic Infrared Carbonyl Stretching Frequencies

<table>
<thead>
<tr>
<th>General Structure</th>
<th>Functional Group</th>
<th>Wave number, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Aliphatic acids</td>
<td>1725-1700</td>
</tr>
<tr>
<td>R−C=O−OH</td>
<td>α,β-unsaturated acids</td>
<td>1700-1680</td>
</tr>
<tr>
<td>Ar−C=O−OH</td>
<td>Aryl acids</td>
<td>1700-1680</td>
</tr>
<tr>
<td>R−C=O−Cl</td>
<td>Aliphatic acid chlorides</td>
<td>1815-1785</td>
</tr>
<tr>
<td>Ar−C=O−Cl</td>
<td>Aryl acid chlorides</td>
<td>1800-1770</td>
</tr>
<tr>
<td>O</td>
<td>Aliphatic aldehydes</td>
<td>1725-1700</td>
</tr>
<tr>
<td>Ar−C=O−H</td>
<td>Aryl aldehydes</td>
<td>1715-1695</td>
</tr>
<tr>
<td>R−C=O−H</td>
<td>α,β-unsaturated aldehydes</td>
<td>1705-1685</td>
</tr>
<tr>
<td>O</td>
<td>Primary amides</td>
<td>1694-1650</td>
</tr>
<tr>
<td>R−C=O−NH₂</td>
<td>Secondary amides</td>
<td>1700-1670</td>
</tr>
<tr>
<td>R−C=O−NHR'</td>
<td>Tertiary amides</td>
<td>1670-1630</td>
</tr>
<tr>
<td>R−C=O−NR₂</td>
<td>Acyclic anhydrides (2 peaks)</td>
<td>1840-1800 and 1780-1740</td>
</tr>
<tr>
<td>R−C=O−OR</td>
<td>Aliphatic esters</td>
<td>1740</td>
</tr>
<tr>
<td>Ar−C=O−OR</td>
<td>Aryl esters</td>
<td>1730-1715</td>
</tr>
<tr>
<td>R−C=O−OR'</td>
<td>α,β-unsaturated esters</td>
<td>1730-1715</td>
</tr>
<tr>
<td>H−C=O−OR</td>
<td>Formate esters</td>
<td>1730-1715</td>
</tr>
<tr>
<td>R−C=O−R</td>
<td>Aliphatic ketones</td>
<td>1725-1705</td>
</tr>
<tr>
<td>Ar−C=O−R</td>
<td>Aryl ketones</td>
<td>1700-1680</td>
</tr>
<tr>
<td>R−C=O−R'</td>
<td>α,β-unsaturated ketones</td>
<td>1685-1666</td>
</tr>
</tbody>
</table>
Table 8.3 Peak Intensities for Chemical Groups for standard PSMO deposits

<table>
<thead>
<tr>
<th>Nascent Film Identification</th>
<th>[C=O]</th>
<th>[C-H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min oxidation</td>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td>60 min oxidation</td>
<td>0.19</td>
<td>0.076</td>
</tr>
<tr>
<td>90 min oxidation</td>
<td>0.11</td>
<td>0.075</td>
</tr>
<tr>
<td>120 min oxidation</td>
<td>0.03</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Standard PSMO test conditions**: temperature, 225°C; sample size, 40 mg fresh oil.

Table 8.4 Peak Intensities for Chemical Groups for pre-deposits subjected to 30 minutes of additional PSMO exposure.

<table>
<thead>
<tr>
<th>Nascent Film Identification</th>
<th>[C=O]</th>
<th>[C-H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min oxidation</td>
<td>0.328</td>
<td>0.199</td>
</tr>
<tr>
<td>60 min oxidation</td>
<td>0.180</td>
<td>0.074</td>
</tr>
<tr>
<td>90 min oxidation</td>
<td>0.134</td>
<td>0.046</td>
</tr>
<tr>
<td>120 min oxidation</td>
<td>0.055</td>
<td>0.047</td>
</tr>
</tbody>
</table>

**Aging film substitution test conditions**: temperature, 225°C; sample size, 40 mg; substrate, 30-, 60-, 90-, and 120-minute pre-deposits further oxidized for 30 minutes with 40 mg fresh oil.

Table 8.5. Peak Intensities for Chemical Groups for pre-deposits subjected to 60 minutes of additional PSMO exposure.

<table>
<thead>
<tr>
<th>Nascent Film Identification</th>
<th>[C=O]</th>
<th>[C-H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min oxidation</td>
<td>0.267</td>
<td>0.134</td>
</tr>
<tr>
<td>60 min oxidation</td>
<td>0.088</td>
<td>0.081</td>
</tr>
<tr>
<td>90 min oxidation</td>
<td>0.056</td>
<td>0.047</td>
</tr>
<tr>
<td>120 min oxidation</td>
<td>0.036</td>
<td>0.028</td>
</tr>
</tbody>
</table>

**Aging film substitution test conditions**: temperature, 225°C; sample size, 40 mg; substrate, 30-, 60-, 90-, and 120-minute pre-deposits further oxidized for 60 minutes with 40 mg fresh oil.
Table 8.6. Peak Intensities for Chemical Groups for pre-deposits subjected to 90 minutes of additional PSMO exposure.

<table>
<thead>
<tr>
<th>Nascent Film Identification</th>
<th>[C=O]</th>
<th>[C-H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min oxidation</td>
<td>0.203</td>
<td>0.074</td>
</tr>
<tr>
<td>60 min oxidation</td>
<td>0.109</td>
<td>0.062</td>
</tr>
<tr>
<td>90 min oxidation</td>
<td>0.081</td>
<td>0.052</td>
</tr>
<tr>
<td>120 min oxidation</td>
<td>0.032</td>
<td>0.028</td>
</tr>
</tbody>
</table>

**Aging film substitution test conditions:** temperature, 225°C; sample size, 40 mg; substrate, 30-, 60-, 90-, and 120-minute pre-deposits further oxidized for 90 minutes with 40 mg fresh oil.

Table 8.7 Peak Intensities for Chemical Groups for pre-deposits subjected to 120 minutes of additional PSMO

<table>
<thead>
<tr>
<th>Nascent Film Identification</th>
<th>[C=O]</th>
<th>[C-H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min oxidation</td>
<td>0.327</td>
<td>0.107</td>
</tr>
<tr>
<td>60 min oxidation</td>
<td>0.075</td>
<td>0.033</td>
</tr>
<tr>
<td>90 min oxidation</td>
<td>0.038</td>
<td>0.017</td>
</tr>
<tr>
<td>120 min oxidation</td>
<td>0.010</td>
<td>0.006</td>
</tr>
</tbody>
</table>

**Aging film substitution test conditions:** temperature, 225°C; sample size, 40 mg; substrate 30-, 60-, 90-, and 120-minute pre-deposits further oxidized for 120 minutes with 40 mg fresh oil.

Although many peaks or bands could be associated with sets of functional groups or classes, their high overlap, reflecting diversity in local environments precludes their utility for monitoring changes in film chemistry with aging. This, coupled with a lack of specificity rendered their analysis and interpretation problematic. Hence attention was focused upon the three largely separable and identified groups of –OH, -C-H and –C=O stretching modes.
The relative intensities for these peaks from the presented spectra were extracted by deconvolution using Origin™ and these values are summarized in Tables 8.3 – 8.7.

Figure 8.11. Intensity of [C=O] and [C-H] for standard PSMO deposits

Figure 8.12  Aging Film Sub. Test: Carbonyl peak intensities for additional PSMO
8.7 Decreasing Carbonyl content of PSMO deposits

In the context of the uniform layer deposit formation model, carbonyl compounds are important as contributing to radical site formation via deoxygenation reactions. The carbonyl absorption was one of the most common characteristics in the entire spectrum, and also the most intense spectral feature, as shown in Figure 8.3. Table 8.2 provides an example of some of the common carbonyl frequencies as a function of the particular type of carbonyl group. As shown in Figure 8.11 for standard PSMO deposits and in Figure 8.12, the decreasing carbonyl peak intensities suggest a loss of oxygen atoms as the deposits undergo deoxygenation and dehydration.

Since the oxygen content of carbonyl groups represents only a portion of the film’s total oxygen content, the overall rate of deoxygenation may differ from the trend reported in the elemental analysis section (see Tables 8.3–8.7). The relationship between carbonyl content...
and oxidation state is used as evidence for the deoxygenation of the film at different stages of age. As such, it represents a valid metric of the chemical changes throughout the film as the micro-oxidation reaction proceeds.

8.8 Decreasing sp\(^3\) hybridized carbon content of PSMO deposits

The aliphatic C-H stretch occurs between 2800 and 3000 cm\(^{-1}\) and is typically exhibited as a strong band, compared to a multiplicity of weak-to-moderate C-H bands. As shown in Figure 8.11 for standard PSMO deposits and in Figure 8.13, sp\(^3\) hybridized carbon peak intensity decreases monotonically as PSMO deposits undergo transformation from lacquer to dark carbon. The decline in peak intensity suggests an increasing degree of unsaturated C-C bonding within PSMO deposits, reflecting the loss of terminal H-atoms. Increased carbon-carbon bonding (along with higher fractional C-atom content) also explains the darkening of the deposit, since increasing carbon concentration and decreasing oxygen concentration as described in the uniform layer deposition model accounts for such a phenomenon. As summarized in Tables 8.3–8.7, the consistency in declining concentration of sp\(^3\) hybridized carbon and carbonyl groups provide direct chemical mechanistic support of the hypothesis, which linked deposit reactivity to deposit chemistry and changes therein over time. Traditionally such changes in reference to the universal mass deposition curve has been referenced qualitatively as a shift from a highly oxygenated and polymeric film, to a more carbonaceous and less oxygenated film chemistry.

8.9 Other functional groups associated with chemical transformation of PSMO deposits

There are very large numbers of different organic compounds that are associated with gradually and homogeneous chemical transformation of deposits. These also incorporate the
sp³ hybridized carbon compounds and carbonyl groups that have already been covered, in addition to a number of others, as mentioned at the beginning of this chapter. Alternative analytical techniques with higher resolution would be needed to access this richer and more convoluted chemistry.

To sum up, chemical characterization of series of films by FTIR indicated loss of H atom and O atom based on functional groups associated with alkyl chains, losing hydrogen – dehydrogenation and carbonyl groups decomposing – deoxygenation. Further characterization of the films by EDS for global elemental composition, as discussed in the next chapter, would provide valuable insight on existing correlation between FTIR and EDS results toward confirming or validating the gradual deoxygenation and dehydrogenation of the deposits.
CHAPTER 9: ELEMENTAL CHARACTERIZATION OF PSMO DEPOSITS

Energy-dispersive x-ray spectroscopy (EDS or EDX) was used to determine the amount (weight percent) of carbon and oxygen in various carbonaceous deposits formed during degradation lubricant. Energy-dispersive x-ray spectroscopy relies on interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter. During EDS, a sample is exposed to an electron beam supported by an electron microscope. These electrons collide with the core-shell electrons within the sample, causing some of them to be knocked out of their orbits. The vacated positions are filled by higher-energy electrons which emit x-rays in the process. By analyzing the emitted x-rays, the elemental compositions of the sample were determined.

9.1 Characterization of Piston Skirt Deposits

Preliminary analysis of engine skirt deposits and deposits derived from the thermal degradation of lubricants on stainless steel coupons provides the following evidence that supports the uniform layer growth model. Figure 9.1 illustrates the heat distribution in cast- and forged-aluminum pistons. The forging process densely packs the grains, allowing the forged pistons to quickly conduct heat away from their tops.

**Crown Center**: 430 – 450°C

**Crown**: 260°C – 300°C

**Skirt**: 150°C – 165°C

**Bottom Skirt**: 130°C – 150°C

*Figure 9.1* Temperature Distribution on Piston (Ganesan, 2008)
Pistons, commonly made of a cast aluminum alloy designed to withstand elevated temperatures, slide back and forth in the cylinder bore, propelled by forces produced during the combustion process (Figure 9.1).

9.1.2 Characterization of Piston-Skirt Deposits

The lubricant deposits observed in this study tend almost always to undergo a transition from a lacquer/varnish type to a carbon black deposit. General observations show that temperature and time are the two most influential variables in the formation of either lacquer/varnish or dark carbonaceous deposits, which result from the degradation of lubricants on metal surfaces. Varnish or lacquer deposits form under mild conditions (short time and/or low reaction temperature). Such deposits therefore commonly form during the early stages of the lubricant degradation process, or on surfaces exposed to mild temperatures (< 300° C) such as piston skirts. Dark carbon deposits are observed under severe conditions (high temperature and/or extended reaction times). Such deposits then form during the late stages of the degradation process, or on surfaces that are subjected to high temperatures (>300° C) such as piston rings, see Figure. 9.2.

![Figure 9.2. Piston Skirt Deposit Formation Sequence](image)

**Phase 1.** Time of Induction. No deposit formed on Piston Skirt; **Phase 2.** Initiation Lacquer/Varnish Deposit **Phase 3.** Growth of Lacquer deposit and initiation of dark carbon deposit; **Phase 4.** Growth of Dark Carbon Deposit and Initiation of lacquer deposit.
Figure 9.2 shows deposit formations, ranging from lacquer to dark carbon at the same location on different piston skirts. The deposit seems to develop in a specific pattern. Initially, no visible deposit is observed on the skirt (phase 1). Then a lacquer/varnish type of deposit is initiated on the skirt (phase 2). The lacquer/varnish deposit expands to other areas of the skirt, while the initial deposit site sees a transition of the original lacquer deposit into a dark carbon film (phase 3). The process continues until the entire varnish layer transitions into a uniform/homogeneous layer of dark carbon deposit (phase 4). These observations suggest that the initial lacquer/varnish deposit undergoes a (homogeneous) chemical transformation over time, leading to a dark carbonaceous film.

The elemental composition of the varnish (early-stage) deposit or dark carbonaceous (late-stage) deposit remained similar throughout the deposit formation process, with carbon at ~60% and oxygen ~20%. Other metallic elements such as magnesium, silicon, phosphorous, zinc, and sulfur are also present in noticeable concentration in both the varnish and dark carbon deposits (Figures 9.3 – 9.5). These results also support the uniform (homogenous) layer model. The varnish layer and the dark carbon layer seem to be the same deposit at different stages of the standard deposition curve.

Figure 9.3 shows the morphology of piston deposits at a magnifying power of 1500 and 1000. The image shows a cracked aspect for the deposits. The surface seemed to be polished by the movements of the skirt in the combustion. These deposits were formed by the agglomeration of fine particles on the surface the piston skirt.
Figure 9.3. SEM Images of Piston Deposit (Piston Sample 6). FEI Quanta 200 ESEM (environmental SEM +5° to 1,000°C temperature controlled stage, lateral resolution: 3.5 nm)
Table 9.1. Elemental Composition of Lacquer Deposit from Formulated Lubricant

<table>
<thead>
<tr>
<th>Elt</th>
<th>App</th>
<th>Intensity</th>
<th>Weight %</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc.</td>
<td>Corrn.</td>
<td>Sigma</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C K</td>
<td>61.53</td>
<td>0.5065</td>
<td>42.74</td>
<td>1.24</td>
<td>57.48</td>
</tr>
<tr>
<td>O K</td>
<td>37.88</td>
<td>0.4348</td>
<td>30.64</td>
<td>1.13</td>
<td>30.93</td>
</tr>
<tr>
<td>Mg K</td>
<td>5.74</td>
<td>0.7664</td>
<td>2.63</td>
<td>0.21</td>
<td>1.75</td>
</tr>
<tr>
<td>Al K</td>
<td>1.58</td>
<td>0.8940</td>
<td>0.62</td>
<td>0.13</td>
<td>0.37</td>
</tr>
<tr>
<td>P K</td>
<td>19.17</td>
<td>1.2776</td>
<td>5.28</td>
<td>0.24</td>
<td>2.75</td>
</tr>
<tr>
<td>S K</td>
<td>5.81</td>
<td>0.9018</td>
<td>2.26</td>
<td>0.16</td>
<td>1.14</td>
</tr>
<tr>
<td>Cl K</td>
<td>2.14</td>
<td>0.7856</td>
<td>0.96</td>
<td>0.11</td>
<td>0.44</td>
</tr>
<tr>
<td>Ca K</td>
<td>25.74</td>
<td>0.9865</td>
<td>9.18</td>
<td>0.34</td>
<td>3.70</td>
</tr>
<tr>
<td>Fe K</td>
<td>2.21</td>
<td>0.9915</td>
<td>0.79</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>Zn K</td>
<td>10.71</td>
<td>0.7677</td>
<td>4.91</td>
<td>0.47</td>
<td>1.21</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 9.4. EDS Spectrum of Lacquer Deposit (Piston Sample 6)
Table 9.2. Summary of Elemental Analysis of Dark Deposit

<table>
<thead>
<tr>
<th>Elt</th>
<th>App</th>
<th>Intensity</th>
<th>Weight Conc.</th>
<th>Weight Corrn.</th>
<th>Weight Sigma</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>85.62</td>
<td>0.5552</td>
<td>52.56</td>
<td>1.27</td>
<td>66.77</td>
<td></td>
</tr>
<tr>
<td>O K</td>
<td>28.60</td>
<td>0.4027</td>
<td>24.20</td>
<td>1.26</td>
<td>23.08</td>
<td></td>
</tr>
<tr>
<td>Mg K</td>
<td>10.39</td>
<td>0.8150</td>
<td>4.35</td>
<td>0.28</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>Al K</td>
<td>1.26</td>
<td>0.9071</td>
<td>0.47</td>
<td>0.15</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>P K</td>
<td>17.41</td>
<td>1.2817</td>
<td>4.63</td>
<td>0.26</td>
<td>2.28</td>
<td></td>
</tr>
<tr>
<td>S K</td>
<td>7.25</td>
<td>0.9050</td>
<td>2.73</td>
<td>0.20</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td>Ca K</td>
<td>19.43</td>
<td>0.9813</td>
<td>6.75</td>
<td>0.33</td>
<td>2.57</td>
<td></td>
</tr>
<tr>
<td>Zn K</td>
<td>9.62</td>
<td>0.7596</td>
<td>4.31</td>
<td>0.50</td>
<td>1.01</td>
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</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 9.5.** EDS Spectrum of Dark Deposit (Piston Sample 6)

9.1.3 Characterization of PSMO deposits

The characterization process of Penn State Micro Oxidation pans was centered on changes in carbon and oxygen content throughout PSMO tests. The series of deposits analyzed by EDX included sets of pans from: the standard PSMO test; direct oxidative degradation of deposits due to “heat treatment”; and PSMO conducted on the set of 30, 60, 90 and 120 minute-aged films exposed to fresh oils (aged film substitution tests); and PSMO conducted with 30 minute-aged oils on 30, 60, 90, and 120 minutes aged films (aged oil substitution tests). A combined plot of the EDS data for the standard, PSMO and thermal treatment studies is
found in Fig. 9.6. For standard PSMO deposits, Carbon content increases monotonically from 68% in a 30-minute lacquer deposit to 84% in 120 minute-dark carbon deposit. Sixty-minute and 90-minute transitioning deposits were found to have 74% and 79% carbon, respectively. Oxygen content, on the other hand, decreased monotonically from 32% in a 30-minute lacquer deposit to 16% in 120-minute dark carbon deposit. Sixty-minute and 90-minute transitioning deposits were found to have 26% and 21% oxygen, respectively.

Figure 9.6 also shows the evolution of carbon and oxygen content within deposits formed during thermal treatment of dry deposits; performed with the standard PSMO after rinsing with THF. Carbon content increases monotonically from 75% in a 30-minute lacquer deposit to 86% in 120-minute dark carbon deposit. Sixty-minute and 90-minute transitioning deposits were found to have 80% and 82% carbon, respectively. Oxygen again decreased monotonically from 24% in a 30-minute lacquer deposit to 14% in a 120-minute dark carbon deposit, while 60-minute and 90-minute transitioning deposits were found to have 19% and 17% oxygen, respectively. Due to air exposure in the absence of oxygenated species deposition, overall oxygen content in heat treatment samples after 30, 60, 90 and 120 minutes of film oxidation is slightly lower, and carbon content slightly higher, than those of standard PSMO deposits for similar oxidation times. Plotted are the C- and O- atom concentrations for films as extracted from the standard PSMO test and from thermal treatment study. The high correspondence between these plots supports the hypothesis by indicating that the measured chemistry changes predominantly reflect those within the film and are not offset or otherwise skewed by lubricant deposition during the course of the standard mass deposition curve. Therein focusing upon the film and associated chemistry as a governing factor in deposit growth is justified.
Figure 9.6. Carbon and Oxygen Content for Standard PSMO and Thermal treatment Deposits

Figure 9.7. Carbon and Oxygen Content for 30-minute Aged Film Substitution Test Deposits
Figure 9.8. Carbon and Oxygen Content for 60-minute Aged Film Substitution Test Deposits

Figure 9.9. Carbon and Oxygen Content for 90-minute Aged Film Substitution Test Deposits
Figure 9.10. Carbon and Oxygen Content for 120-minute Aged Film Substitution Test Deposits

Figure 9.11. Carbon and Oxygen Content for 30-minute Aged Oil Substitution Test Deposits
Figure 9.7- 9.11 shows the evolution of carbon and oxygen content for the series of aging film substitution test deposits. For aging film substitution tests conducted with 30 min additional PSMO duration, carbon content increases monotonically from 72% on a 30-minute pre-deposited lacquer film to 84% in a 120-minute pre-deposited dark carbon. On sixty-minute and 90-minute transitioning pre-deposits, subsequent 30 min PSMO duration led to 80% and 82% carbon, respectively. Oxygen content, on the other end of the spectrum, decreased monotonically when further aged for 30 min from 28% on a 30-minute pre-deposited lacquer film to 16% in 120-minute pre-deposited dark carbon. Sixty-minute and 90-minute transitioning deposits were found to have 23% and 18% oxygen, respectively.

For aging film substitution test conducted with 60 min additional PSMO, carbon content increases monotonically from 72% on a 30-minute pre-deposited lacquer film to 83% in a 120-minute pre-deposited dark carbon. On Sixty-minute and 90-minute transitioning pre-deposits, subsequent 30 min PSMO led to 74% and 78% carbon, respectively. Oxygen content, on the other end of the spectrum, decreased monotonically when further oxidized for 30 min from 27% on a 30-minute pre-deposited lacquer film to 17% in 120-minute pre-deposited dark carbon. Sixty-minute and 90-minute transitioning deposits were found to have 23% and 20% oxygen, respectively.

Also in Figure 9.10, for aging film substitution tests conducted with 90 min additional PSMO duration, carbon content increases monotonically from 74% on a 30-minute pre-deposited lacquer film to 83% in a 120-minute pre-deposited dark carbon. On sixty-minute and 90-minute transitioning pre-deposits, subsequent 30 min PSMO times led to 79% and 81% carbon, respectively. Oxygen content, on the other end of the spectrum, decreased monotonically when further oxidized for 30 min from 26% on a 30-minute pre-deposited
lacquer film to 17% in 120-minute pre-deposited dark carbon. Sixty-minute and 90-minute transitioning deposits were found to have 21% and 19% oxygen, respectively.

Finally in Figure 9.11, for aging films substitution tests conducted with 120 min additional PSMO duration, carbon content shows a slight increase of 83% on a 30-minute pre-deposited lacquer film to 86% in a 120-minute pre-deposited dark carbon. On sixty-minute and 90-minute transitioning pre-deposits, subsequent 120 min PSMO led to 82% and 85% carbon, respectively. Oxygen content, on the other end of the spectrum, decreased monotonically when further oxidized for 120 min from 17% on a 30-minute pre-deposited lacquer film to 14% on a 120-minute pre-deposited dark carbon. Sixty-minute and 90-minute transitioning deposits were found to have 18% and 15% oxygen, respectively.

Figure 9.7 shows the evolution of carbon and oxygen content for 30-minute aged oil substitution test deposits. Carbon content increases monotonically from 71% in a 30-minute lacquer deposit to 82% in 120-minute dark carbon deposit. Sixty-minute and 90-minute transitioning deposits were found to have 76% and 79% carbon, respectively. Oxygen again decreased monotonically from 29% in a 30-minute lacquer deposit to 18% in 120-minute dark carbon deposit, while 60-minute and 90-minute transitioning deposits were found to have 23% and 20% oxygen, respectively. Due to further oxidation, overall oxygen content in “heat treated samples” after 30, 60, 90 and 120 minutes of film oxidation is slightly lower, and carbon content slightly higher, than those of standard PSMO deposits for similar oxidation times. These results suggest an oxygen loss from the film, initially being highly oxygenated. There is also an associated increase in carbon content as the film transitions into a more carbonaceous chemistry.
Though necessarily increasing based on elemental composition, carbon could be lost commensurate with the O-atom loss reflecting gasification reactions. Therein an increase, let alone at a comparable rate is not guaranteed. To examine the correspondence between the C and O-atom film content, a non-parametric statistic analysis can be performed upon the ranked data. A non-parametric measure is chosen so as to not presume any particular relation and using the ranked data affords freedom from differences in absolute quantities. Spearman’s rho (ρ) as define in Equation 9.1 provides a measure of the correlation or anti-correlation between data pairs (Myers et. al., 2003).

\[
\rho = 1 - \frac{6 \sum d_i^2}{n(n^2 - 1)}.
\]

Equation 9.1

Where, \(d_i\) is the difference between \((x_i \text{ and } y_i)\), \(x_i\) and \(y_i\) are the corresponding conversion of raw variables or data \(X_i\) and \(Y_i\) into ranks and \(n\) represents the number of raw scores.

For the standard PSMO data, as presented in Fig. 9.6, a value of -0.9 is derived, suggesting that little carbon is lost through direct gasification. Such an analysis is best applied with carbon and oxygen being the dominant elements.

In summary, the significance of these results is that they provide a foundational understanding and chemical basis for the empirical physical mass deposition rates and dependencies upon film age. These chemical analyses provide the rationale for the hypothesis of film age controlling mass deposition. As films age, they do so via dehydrogenation and deoxygenation processes. The O-atom decrease confirms the latter. To test the former requires more specific information on the kinetics behind these reactions, as provided by reaction kinetics analyses found in the next chapter.
CHAPTER 10 - REACTION KINETICS

This chapter describes a study of the reaction kinetics involved in the uniform layer deposition model. The goal was to determine the overall kinetics of the deposit formation mechanism and more specifically the surface effect and the impact of lacquer and the carbon layer on the overall deposition rate. This involves on one end, the well known liquid-phase (oil phase) reactions responsible for oil degradation, leading to deposit formations and on another end the subsequent reaction of the deposited film manifested in series of deoxygenation and dehydrogenation reactions.

10.1 Oil Phase Reactions

The oxidative degradation of oils begins the formation of organic peroxides with continued oxidation producing alcohols, aldehydes, ketones, and organic acids. These species are further oxidized to form high molecular weight, oil insoluble polymers. To determine the kinetics of base oil oxidation in comparison with data reported in the literature, series of PSMO tests were conducted with four base oils at 175 °C, 200 °C and 225 °C for 30, 60, 90 and 120 min. All deposits produced as part of this study were used to generate a series of “S-shaped” standard mass deposition curves.

Figures 10.1 – 10.4 show such results for the four base oils at 225 °C and identify the major stages of deposit formation, including the induction time, the accelerated growth phase and leveling off stage of the deposition.
Figure 10.1 Isothermal Plot for Oil 1 at 225°C

Figure 10.2 Isothermal Plot for Oil 2 at 225°C
Figure 10.3 Isothermal Plot for Oil 3 at 225°C.

Figure 10.4 Isothermal Plot for Oil 4 at 225°C.
Isothermal plots at 175 °C, 200 °C and 225 °C were made by plotting percent deposit vs. time to establish the induction time for each oil. Induction times were graphically determined from the standard mass deposition curves as illustrated in Figures 1.1 and 2.6. The reaction which takes place in the micro-oxidation correlates with the theory that deposit is formed more quickly as temperature increased. The controlling rate constant for the isothermal reaction is the inhibition portion of the isotherm, that is, the linear portion up to the end of the induction period. Assuming a very small amount of deposit forms up to this point, that is, when the uninhibited oxidation reaction begins to occur. The slope is then calculated as follows:

\[ k = \frac{y^2 - y^1}{x^2 - x^1} \quad \text{Equation 10.3} \]

Linear plots suggested that the reaction follows a first order kinetics and more so, similar slopes shows that the degradation process has roughly the same activation energy. A more explicit analysis of the induction time reported by Tseregounis et al. (1997). Since induction time increases linearly with an increasing thickness of the film; it also decreases exponentially with temperature. The dependence of induction time on film thickness and temperature can therefore be expressed as follows:

\[ t = t_0(T) + a \exp \left( \frac{b}{T} \right) \sigma \quad \text{Equation 10.1} \]

In this equation, \( t \) is the induction time (min), \( a \) and \( b \) are constants, \( \sigma \) is the thickness of the oil film (pm), \( T \) is the temperature (K), and \( t_0 \) is a time constant which depends on temperature (to account for the fact that the induction time approaches a non-zero value as the oil amount approaches zero). The induction times of fully formulated lubricant reported by Zerla et al. (1989) in Table 10.1 were plotted on a log scale against
as shown in Fig. 10.2, along with the induction times of the base oils involved in this study. Given the differences in fully formulated lubricants versus base oils, these two groups of samples separated naturally, as shown in Fig. 10.2. The general linear relationship established by this Arrhenius plot substantiates the semi-empirical relation between the deposit formation and temperature, as described in Equation 10.1. Moreover, it suggests the natural interpretation of the constant “b” as the activation energy, $E_a$.

Table 10.1 Lubricant induction Times (Zerla et al., 1998)

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>210 °C</th>
<th>230 °C</th>
<th>240 °C</th>
<th>250 °C</th>
<th>260 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID4855</td>
<td>375</td>
<td>140</td>
<td>80</td>
<td>57</td>
<td>42</td>
</tr>
<tr>
<td>ID4858</td>
<td>150</td>
<td>54</td>
<td>40</td>
<td>21</td>
<td>18</td>
</tr>
<tr>
<td>ID4859</td>
<td>150</td>
<td>65</td>
<td>40</td>
<td>29</td>
<td>16</td>
</tr>
</tbody>
</table>

As shown in Figure 10.5, Arrhenius plots give a relative ranking of how fast each oil degrades under these PSMO conditions. This shows that fully formulated lubricants which are more stable due to deposition inhibiting additives take much more time to form deposits than base oils less stable ones at a given temperature.
As stated in the hypothesis, the deposit formation mechanism is explained by the formation of a single “layer” of uniform composition whose overall chemical composition gradually changes (uniformly) from a highly oxygenated lacquer deposit to a dark carbonaceous deposit. This is essentially governed by a continuous process of dehydrogenation and deoxygenation of the deposited film, rarely reported in the literature. This section focuses on the kinetics of the subsequent degradation (deoxygenation and dehydrogenation) of the deposits derived from the oxidative degradation of lubricant during the process. Since subsequent degradation (dehydrogenation/ deoxygenation) of deposits occur according to the general equation:

$$\frac{1}{T^*}(1000) \quad (T=\text{Absolute Temperature})$$

Figure 10.5 Arrhenius plot for Fully Formulated Lubricants and Base Oils

10.2 Solid Phase Reactions
A → P reaction where A is a reactant and P is a product, the reaction rate was assumed to be proportional to the change in concentration of oxygen or hydrogen during the oxidative degradation process. The rate of such first order reaction can therefore be expressed as:

\[ r = - \frac{d[A]}{dt} = k[A] \]  
Equation 10.4

Where \( r \) is the rate of the reaction \([A]\) is the concentration of oxygen or hydrogen in the deposit at time \( t \). Separation of variables in Equation 10.4 leads to:

\[ -k dt = \frac{d[A]}{[A]} \]  
Equation 10.5

Equation 10.5 is then integrated to obtain:

\[ \int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = -k \int_{t_0}^{t} dt \]  
Equation 10.6

This finally yields to the following expression:

\[ \ln[A] = -kt + C \]  
Equation 10.7

Initial conditions where defined by the chemical properties (sp3 carbon content, oxygen content, hydrogen content) of the nascent deposit at time \( t_0 \). The constant of integration \( C \) can be evaluated by using boundary conditions. Therefore, when \( t = 0 \),

\[ [A] = [A]_o \]  

\([A]_o \) represented initial concentration of \( A \).

Substitution of the initial conditions above into equation 10.7 leads to:

\[ \ln[A]_o = -k(0) + C \]  
Equation 10.8

The integration constant is then defined as:

\[ C = \ln[A]_o \]  
Equation 10.9

Finally the integrated rate is obtained by substituting Equation 10.9 into 10.8:
\[
\ln \frac{[A]}{[A]_0} = -kt
\]

\( \ln [A] \) or \( \ln \frac{[A]}{[A]_0} \) was then plotted against time to obtain the rate of degradation of the film, as shown in Figure 10.6 base data presented in Table 10.2 and 10.3.

Table 10.2 Aging Film sp3 carbon content (from Figure 8.7 – 8.10)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>(-\ln \frac{[A]}{[A]_0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.04 0.39 0.98 0.62 0.04</td>
</tr>
<tr>
<td>60</td>
<td>0.9   0.89 1.16 1.79 0.89</td>
</tr>
<tr>
<td>90</td>
<td>1.46  1.443 1.34 2.46 1.341</td>
</tr>
<tr>
<td>120</td>
<td>1.44  1.96 1.96 3.50 3.50</td>
</tr>
</tbody>
</table>

Table 10.3 Aging film carbonyl content content (from Figure 8.7 – 8.10)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>(-\ln \frac{[A]}{[A]_0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.02 0.20 0.47 0.003 0.003</td>
</tr>
<tr>
<td>60</td>
<td>0.60 1.31 1.10 1.47 1.31</td>
</tr>
<tr>
<td>90</td>
<td>0.89 1.76 1.39 2.15 1.39</td>
</tr>
<tr>
<td>120</td>
<td>1.78 2.20 2.32 3.49 3.49</td>
</tr>
</tbody>
</table>
Figure 10.6 Rate of Change for Aging film sp3 carbon content

Figure 10.7 Rate of change for Aging film carbonyl content.
The linear relation established by these plots confirms the analysis using first order kinetics. In the oil phase, oxidation begins with formation of organic peroxides leading to alcohols, aldehydes, ketones, and organic acids through a series of radical driven reactions. Further oxidation of such species forms high molecular weight, oil insoluble polymers. These reactions explain the similarity the degradation process of all oils and the dependence of the rate of reaction on temperature, with very few exceptions.

The relationship between the rate constant, $k$, for a given reaction and temperature was first proposed by Arrhenius:

$$k = Ae^{-E/RT} \quad \text{Equation 10.2}$$

Where $k =$ rate constant

$A =$ frequency factor

$E =$ activation energy

$R =$ gas law constant

$T =$ temperature (absolute)

Of course a caveat is that this analysis is for an overall rate expression involving many individual elementary reactions. As such it reflects the composite mechanism with weighting by the rate controlling/limiting reaction. That step is likely the formation of the radical site on the deposit surface that is reflected in the activation energy $E_a$.

The standard PSMO test provides a baseline by which to gauge the decline in film reactivity. With increasing test duration, as shown in Fig. 7.3, the rate of mass deposition decreases. As seen from the derivative of the standard PSMO mass deposition curve, the rates for the set of 4 test times are remarkably similar, largely reflecting their position relative to the induction and accelerative phases of the profile. This constancy of physical rate (i.e.
mass deposition) is also reflected in the rates for the corresponding EDS and FTIR chemical data.

Comparison of physical mass deposition rates may be made across the set of aged films. These data were plotted parametrically as a function of additional (2\textsuperscript{nd} stage) PSMO duration (Figure 7.13). By comparison of the rates of mass deposition for the differently aged films, (Fig. 7.13, aged films), the average rate decreases with successive film age, for each succession of additional PSMO duration. From such data rates may be calculated. This succession of rates plotted in Fig. 10.8, where the average rate was calculated as an unweighted average, using linear least square fit applied to the data of Fig. 7.13. For any particular initial film age, the rate decreases monotonically with additional PSMO time. The plot of rates in Fig. 10.8 allows comparison across the set of films as 2\textsuperscript{nd} stage PSMO duration increases. Not surprisingly, the relative rates of mass deposition across the film sets decreased with increasing age. Staying in relation to each other, the films become less active towards further mass addition with aging.
10.4 Rates of chemical composition change

10.4.1 Correspondence of physical/chemical changes

The substitution tests with the differently aged films clearly demonstrate that the substrate governs the mass deposition, i.e. film formation for fresh lubricant. Parallel tests using lightly aged oil further confirm the hypothesis. Neither set of experiments however provides evidence of a mechanism, the causative factors that are responsible for the observations. Indeed, without identification of the underlying film chemistry changes, the second part of the hypothesis is left untouched. The focus of this chapter is the film chemistry and its changes upon film aging. Chemistry compliments the physical changes as monitored by mass deposition.

10.4.2 EDS versus FTIR

Two physical measures of film chemistry were sought, elemental composition and specific functional groups. The former was measured using energy dispersive X-ray (EDS)
analysis, within an electron microscope. Further details are conveyed in the experimental chapter. As a broad metric, the totality of chemical groups containing oxygen, as deoxygenation proceeded would be expected to decline in concentration and this aggregate effect would be manifested as a global change in elemental oxygen content. Complimenting this measure of changing film composition is an enrichment of elemental carbon, which was also measured during the EDS scan.

10.4.3 Standard PSMO

Representing all oxygen functional groups, such elemental measures provide an encompassing metric of film elemental composition and changes during aging. However, light elements, such as hydrogen are not detectable by EDS. Yet hydrogen is a clear participant in changing film chemistry as the proposed dehydrogenation reactions occur. These EDS rate data, for standard PSMO deposits are summarized in Table 10.4 in comparison to the same rate data as derived from the thermal treatment studies. For both standard PSMO and Heat treatment studies, rates were compared on the basis of time. As shown in Table 10.4 within error limits, these rates agree and were comparable. Although, standard PSMO rates reflected continuous deposition of nascent film and Heat treatment reflected loss of material. As stated in Chapter 9, the correspondence of the qualitative trends and quantitative rates for these two tests provides foundational support to the hypothesis that film chemistry is the governing factor in deposit growth.

Table 10.4 Summary of EDS rate for Standard PSMO and Heat Treatment Deposits

<table>
<thead>
<tr>
<th>Deposit type</th>
<th>Std. PSMO</th>
<th>Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rates*</td>
<td>0.1</td>
<td>0.15</td>
</tr>
</tbody>
</table>

* Rates listed represent changes in film atomic content with respect to time.
10.4.4 Film substitution

Other comparisons across the various aged film substitution tests can be made, but are offset to varying degrees by differences in film and lubricant clock time. This desynchronization can obscure comparisons, though support for the hypothesis is yet found by their examination as well, as next described.

For the EDS plots shown in Figures. 9.7-9.11 of Chapter 9, of particular note is that by cursory comparison of the rates of mass deposition for the differently aged films, the average rate decreases with successive film age. (As discussed, this is most apparent for the nascent films of the standard PSMO test). Secondly, for any particular initial film age, the rate decreases monotonically with additional PSMO time.

Third, within experimental error, each succeeding aged film begins with an oxygen composition similar to that of the preceding aged film with subsequent aging to the same nominal total PSMO run time. Such order gives confidence in data consistency and validity of comparison. As expected, the magnitude of the change in oxygen and carbon content decreases with increasing film age, both across different starting aged films and with additional PSMO duration for any particular film of given initial age, as shown in Figs. 10.9 – 10.11. These rates mirror monotonically the physical mass deposition rates, both their initial value and their decrease in time.
Figure 10.9. Average rate of change in oxygen and carbon for Aging Film Substitution test deposits

Figure 10.10. Average rate of change in sp3 hybridized carbon content for Aging Film Substitution test deposits
10.5. Comparisons - Chemistry

Somewhat surprisingly the mass deposition rate for the film goes to zero while the chemical composition, as measured by EDS, though approaching a steady-state, does not exhibit a commensurate loss of oxygen as measured by EDS. This compliments the FTIR data that do in fact show a near total loss of oxygen as found in the carbonyl group signature. This disparity marks the complementary nature of both measures and highlights the need for chemically specific analyses for future identification of the film carbonization mechanism.

Nevertheless, this difference may be understood as follows. The EDS O-atom content includes all oxygen functional groups, many of which may not be active towards decomposition at this temperature. Indeed TGA measurements of oxygenated carbons have shown evolution of CO and CO2 at temperatures ranging from 300 °C (Soto-Garrido et. al., 2003). Moreover, even if a particular C-O bond breaks, competing reactions with
neighboring groups within the film may result in other side reactions that reincorporate oxygen into the evolving polymeric film. Finally it should be remembered that these film composition measurements look at one part of the system whereas lubricant species deposited at different times would re-introduce additional oxygen content into the evolving film. The the chemical composition measurements reflect a balance of the rate of incoming versus outgoing oxygen (in the form of oxo-polymeric species). The FTIR plot shows that the carbonyl group is fully engaged in deoxygenation reactions as exhibited by its full loss over the course of film aging at this temperature.

In summary the difference between the EDS and FTIR measurements shows that not all oxygen is involved in radical formation for further mass addition. Clearly the rates of the film polymerization reaction set will be highly temperature dependent and so too, the final oxygen content of the aged film.

10.6. Comparisons: Physical Mass Deposition vs. Chemical Composition Rates

Comparison of the chemical composition rates shows correspondence between C and O atom concentration changes. As best illustrated by the standard, PSMO data, they anticorrelate, indicating little carbon loss due to gasification during deoxygenation. Reflecting the parallel nature of the H atom and O atom loss, functional groups associated with alkyl chains losing hydrogen – dehydrogenation and carbonyl groups decomposing – deoxygenation are illustrated by the concerted trends manifested in the FTIR data.

In parallel, the physical mass deposition rates decrease with increasing film age, within the proviso for times past induction and accelerative stages. Aged film studies demonstrate a
consistent reactivity decline with increasing film age. These trends are consistent across a
nominal set of varied age films and subsequent increments of additional PSMO duration.
Each measure, physical or chemical supports the hypothesis as being consistent with its
prediction. While the physical mass deposition data validate it, the chemical rate data provide
an understanding for its accuracy. Necessarily then the chemical rate data trend with the
physical data and as such, suggest a causative factor for film activity decline. While
correlative data does not guarantee cause and effect, the visible and quantifiable change in
film chemistry suggest this inference is valid.

Figure 10.12 compares the rates for the standard mass deposition curve as normalized
by the corresponding rate of chemical composition change as measured by the O-atom
content of the EDS data. As the derivative plot of the standard PSMO test shows, the rates at
the reference time points of 30, 60, 90 and 120 minutes are nearly constant. The
corresponding EDS data likewise show nearly constant rates or equivalently a uniform
increment of change (decrease) between each time increment. As then anticipated, as
observed in Fig 10.12, both plots are nearly flat, horizontal lines, illustrating that the rate of
mass deposition is nearly normalized and hence directly related, i.e. proportional to the
chemical change. Clearly there are many assumptions in this simple analysis. First and
foremost is that the depositing species are in fact identical throughout the course of the
experiments. Moreover, that the C=O bond if not dominating the film reactive site
formation, is directly proportional to their totality.
Figure 10.12. Average rate of carbon and oxygen for standard PSMO deposits.

Figure 10.13. Ratio of C-H and C=O to mass deposit for aging film substitution test deposits.
Figure 10.14 Ratio of Carbon and Oxygen Content to Mass Deposit for Aging Film Substitution Test Deposits.

Finally, implicit in all the work is that the film chemistry is uniform in depth. A similar comparison can be made across the aged film substitution tests. To facilitate comparison, the percentage change in mass deposition across each set of aged films for the different successive increments of PSMO duration are ratioed or normalized in the same manner as for the standard PSMO data described above. Similarly, qualitative inspection of the mass deposition data in Figure 7.13 and corresponding chemical composition data (FTIR, of Figures. 8.13) and EDS data (Figures. 9.7-9.10) exhibit similar trends, i.e. they show monotonic declines. As observed in Figures 10.12 - 10.14, the change of mass deposition divided by the corresponding chemical content change yields nearly a constant across the different 2nd stage PSMO durations. This constancy strongly links the change in film chemistry as being responsible and in fact governing the mass deposition, confirming the hypothesis of this thesis.
In this chapter, a study of the reaction kinetics involved in the uniform layer deposition model is conducted to determine the surface effect and the impact of lacquer and the carbon layer on the overall deposition rate. Results obtained clearly indicate that, the rate of change in film chemistry is strongly dependent on temperature. It was also observed that pre-existing deposit chemistry governs the rate of subsequent deposit growth in fresh and moderately aged oils. It was more specifically showed that direct correlation exist between mass deposition rates and changes in film chemistry.
Deposit formation has a long history of study (Barcelo et al., 1964). General consensus exists regarding the peroxy radical formation process, formation of oligomers and their subsequent deposition. The goal of this work was to challenge this paradigm by the hypothesis that the pre-existing deposits actually played the leading role once deposit formation occurred. This radically departs from the traditional view, since the lubricant and deposit form a highly coupled system. Based on the current study, the following conclusions can be made:

- Across the set of aged films, the substitution tests show a declining activity towards mass deposition with film age. For each increment of 2nd stage PSMO duration each individual film of the set and the set as a whole exhibit a decrease in mass deposition, interpreted as decline in reactivity.

- Chemical characterization of these series of films by EDS for global elemental composition and by FTIR for chemically specific bond concentration correlate well with each other, specifically comparison of the chemical composition rates shows correspondence between C and O atom concentration changes. Reflecting the parallel nature of the H atom and O atom loss, functional groups associated with alkyl chains losing hydrogen – dehydrogenation and carbonyl groups decomposing – deoxygenation are illustrated by the concerted (loss) trends manifested in the FTIR data.

- The physical mass deposition rates decrease with increasing film age, within the proviso for times past induction and accelerative stages. Aged film studies demonstrate a consistent reactivity decline with increasing film.

- Finally, the change of mass deposition divided by the corresponding chemical content change yields nearly a constant across the different 2nd stage PSMO durations. This
constancy strongly links the change in film chemistry as being responsible and in fact governing the mass deposition, confirming the hypothesis of this thesis.

- As for broader applications of this research, at short times, deposits govern further mass addition with the lubricant playing little role. Hence deposit prevention by frequent lubricant change (so as maintain fresh lubricant) retains control of the process by the lubricant. Given the observed synergy between aged oils and aged deposits, the tactic to break such synergy is by maintaining fresh lubricant, i.e. change the oil often.
RECOMMENDATIONS FOR FUTURE STUDIES

As different from previous research work, this study has focused on investigating the governing role of pre-existing lubricant deposits on subsequent deposit growth. Further studies could focus on others aspect of the subject such as:

1. **Surface effects**

To lend further credence to lubricant degradation and film formation in real engines, supplementary tests are warranted. Surface topography may play a role if only to increase potential surface area. Varying roughness by degree of polishing should influence deposit mass as surface area should increase with deposit mass. Therein roughness will be varied by degree of polishing. As a further check of surface sites contributing to film formation, surface composition will also be varied in a subset of tests. While most engines using steel or steel liners, the transition metals can catalyze hydrocarbon decomposition, though literature documentation suggests only at much higher temperatures. Still, Au as an inert metal would further test the roles played by such metals, if any. Surface finish and composition will be tested using fresh lubricant over the timeframe of the standard mass deposition curve, as further baseline comparisons.

2. **Model (lubricant) compounds**

As further extension of the studies on uniform layer model, model oxygenates, likely formed in the lubricant should be added to fresh lubricant with this same set of substitutional tests. Such comparative measures will directly assess and quantify the role played by specific oxygen functional groups in contributing to the mass deposition as there admittedly is the possibility that given their more reactive nature, these species preferentially add to the free radical sites within the organic film. A model oxygenated lubricant facsimile, added to fresh
lubricant as in the substitutional tests would further gauge potential synergies between film radical sites and partially oxidized lubricant intermediates. Variations in lubricant formulation could be considered based on compound classes of paraffins, cyclic paraffins, unsaturated compounds and aromatics. Given the disparate results and claims associated with additives, neat lubricants should be the focus of these tests.

3. Model deposit films

In this test, model compounds such as elemental carbon, partially oxygenated carbon (or equivalently partially carbonized polymeric compound), and a polymeric oxygenated organic, compounds known to play key roles in the deposit formation process should be pre-coated upon the surface. With well-defined composition, mass deposition rates upon each of these three coatings should be measured using fresh lubricant to provide additional confirmatory evidence for the free radical, surface-coating driven mass deposition curve. As before, each coating represents a different stage of the standard mass deposit curve and corresponding rates.

Reciprocal tests should be performed using model films/deposits:

a. Pre-coverage of surface with carbon film, followed by heat treatment should be conducted to determine the effect of surface and most importantly the impact of the carbon layer on the overall deposition rate. This experimental step would help elucidate the limitations of the binary growth mechanism.

The formation of lacquer deposit during the early phases of the deposition process seems to be paired with an increase in deposit formation rate, justified by the increase of deposit forming species.
b. Pre-coverage of surface with high molecular weight polyethylene glycol to simulate lacquer followed by heat treatment would help determine the effect of the role of the initial lacquer deposit in the overall deposition rate. This experimental step would also help elucidate the limitations of the binary layer growth mechanism.

4. Temperature effects

Varying temperature should influence rate of deposition and help determine the activation energy of the uniform layer deposition model.
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VITAE

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While at Penn State, he served as President of the African student Association from 2006 to 2007 and was recognized by the Paul Robeson Center for outstanding services to the student program advisory board. He also received several other research and leadership awards such as the AESEDA fellowship Award, the Penn State bio-energy research Awards and the Above and Beyond achievement Award.