SYNERGISTIC AND ANTAGONISTIC EFFECT OF SULFUR-BASED ADDITIVES ON THE PERFORMANCE OF GREASES WITH ZDDP AND PTFE

by

ARUNYA SURESH

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ABSTRACT

SYNERGISTIC AND ANTAGONISTIC EFFECT OF SULFUR-BASED ADDITIVES ON THE PERFORMANCE OF GREASES WITH ZDDP AND PTFE

Arunya Suresh, M.S.

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Supervising Professor: Pranesh Aswath

Lithium-base greases constitute about 50% of the grease market. The current trend is towards developing greases with longer working life and wider application flexibility. To address this concern, greases are blended with antiwear and extreme pressure (EP) additives that serve to reduce wear and increase the operating life of the machinery by creating a low strength, shearable film on the moving surfaces. In the current study, greases were developed to address the need for both performances as prescribed by the ASTM standards D2266 and D2596, respectively.

The actual bearing conditions vary significantly with load, rpm and duration of test. These three factors have important consequences such that the load dictates the activation of chemistries, the rpm controls the entry of grease into the contact point and the durability of grease is governed by the test duration. Accordingly, greases with good antiwear and extreme pressure properties were developed and their behavior studied under both standard ASTM conditions as well as by varying test conditions of load, rpm and test duration. For achieving both wear and load-bearing capacity, a multitude of additives have been investigated with varying

degrees of success. The major among these are MoS_2 and graphite to impart extreme-pressure properties to greases, polytetrafluoroethylene (PTFE) for friction reduction and ZDDP for wear reduction. With the intent to replace MoS_2 in greases, the synergistic combination of ZDDP and PTFE has proven to provide superior wear and EP performance and appear to be more durable than their MoS_2 counterparts. The interactions among these additives have been analyzed through design of experiments using the factorial and response surface design approaches. This approach would give the grease-maker preliminary, yet critical, information about suitable chemistry to employ under specific conditions of load, rpm and duration of test.

To develop greases that provide both wear and weld protection, the sulfur additives probably the earliest known EP compounds in lubricants, were tested for interactions with ZDDP and PTFE combination. Since the wear or EP action involves the interposition of a film between mating metal surfaces in order to prevent metal-to-metal contact, the film was analyzed for compositional and morphological features through extensive SEM/EDS experiments. It was deduced that formation of sulfides was important for wear and phosphate pads for load-bearing characteristics. Through this work, four different aspects of the greases have been identified; (1) the design of experiments approach is used to develop an understanding of the interaction of the role played by various additives singly or in conjunction with other additives, (2) the role played by test conditions on the evaluation of grease properties is dealt with, (3) the role played by sulfur chemistries when used with solid lubricants like PTFE is addressed and (4) an understanding on the interaction of various chemistries is established with the goal of developing a Universal grease.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

With the rapid development of technology there is a growing trend toward reduction of size of machinery, increased speed, closer tolerances of moving parts, higher bearing loads, higher operating temperatures which calls for increased lubrication needs. Lubrication is the use of chemicals to improve of the motion of one surface over another by reducing friction and often wear, and the material that is used in this way is called a lubricant. A lubricant functions by introducing between moving surfaces a layer of material that has lower shear strength than the surfaces themselves. Lubricants may be either liquids or semi-liquids, but may also be solids or gases or any combination of solids, liquids or gases.

Greases- best thought of as thickened oils, are not fundamentally different from oils and are largely used to provide semi-permanent lubrication since greases have the ability to remain in contact with the desired moving surfaces and generally do not leak from the point of application. The lubricating phase in grease is always lubricating oil that is entrapped in minute pockets of soap-thickener fibers that form the internal structure of greases. These thickeners are intended to reduce migration through gravity, pressure or centrifugal action. It is chosen over oils in applications where leakage of lubricant is not desired, where sealing action is needed and when greater film thickness is required. Greases lessen the need to lubricate a specific location often owing to its structure. It is very useful when lubricant is desired in a vertical machine component or at sites that are difficult to access. It acts as a sealant to external contaminants and is effective in protecting machinery that run at high temperature and pressure and under conditions of shock loading.

What appears to be a smooth metal surface to the naked eye is in reality a landscape of microscopic ‘hills’ and ‘valleys’ or asperities, when viewed under high magnification. These asperities on the interacting surfaces begin interacting with each other, and under severe conditions make direct surface contact, resulting in enhanced friction, increased wear and eventually welding. With mechanical systems operating under extreme pressure conditions such as heavy loads, low speed and low lubricant viscosity asperity contact results in a grease-film not sufficient to prevent metal-metal contact. More often than not, greases for such extreme pressure operations cannot prevent wear or reduce friction, thus adversely affecting the performance of the system. To address this quandary, anti-wear and extreme-pressure (EP) additives are blended with the greases, usually in amounts ranging from 0.5-10% of the grease depending on the grease type and application, to prevent wear, reduce fuel consumption and increase the operating life of the machinery by creating a smoother surface on the moving surfaces, thus increasing the true contact area.

For materials to be classified as EP/AW additive, they should be able to interact with the metal surface forming a film that prevents direct contact between the moving surfaces. These film are formed through either reaction with the contacting surfaces or physical deposition of a shearable film. In the former case, the elements that could form iron compounds could be either sulfur, phosphorus, chlorine or other halogens. Sulfur additives are probably the earliest known EP additives with extent of load bearing capacity without seizure being proportional to the amount of the sulfur in the additive. Phosphorus-containing additives provide EP protection through a totally different mechanism than sulfur-based additives and have very good corrosivity control, unlike sulfur additives. Chlorine-containing additives act by forming a metal chloride film on the metal surface under conditions of high pressure and presence of traces of moisture. In the latter case where physical deposition of shearable layers are deposited at contacting surfaces MoS_2 has found application. Molybdenum disulfide has found applications in extreme pressure conditions through a layered lattice structure, strong bonds between S-Mo-S layers and relatively weak bonds between adjacent S layers. Other layer-lattice compounds include graphite and WS_2.

1.2 Foundation of research work

The current grease market aims to satisfy two major concerns- longer grease life and wider application versatility without compromising on the performance. The establishment of an Universal grease would reduce the number of different greases to achieve performance characteristics like service life, shock resistance, high heat, extreme pressure, wear and pumpability along with providing longer grease life. In addition, the use of fewer greases would enable the end-users to simplify their inventory and eliminate greasing mistakes. With this foundation, the present study analyzes the performance and scientific rationale behind the use of traditional and novel grease chemistries. Since multi-service greases contain a variety of additives (like extreme-pressure (EP) agents, antiwear (AW) additives, friction modifiers, anitoxidants, detergents/dispersants and rust inhibitors) of different chemical functionalities to meet the various service requirements, it is important to learn the compatibility and synergism/antagonism of these additives with one another.

In real-world applications, the grease may be subjected to a variety of test conditions rather than the standard conditions prescribed by ASTM D 2266 [reference] to evaluate the EP/AW performance of the greases such that the pumpability of grease to the contact point is governed by the RPM, different loading conditions may have an effect on the activation of chemistries and the duration may have an effect on the grease life. Thus, it was reasonable to evaluate the performance of the grease properties under variable conditions of load, RPM and duration of test.

The use of sulfur in the grease chemistries forms an important part of this work. The lubrication properties of sulfur have been known to mankind since the era of Greeks and Romans. Today, sulfur additives are known for their versatility in their chemistry and the range of applications they are put to use in. An important aspect of the literature since 1950 until today [reference] concentrates around the synergies of the sulfur additives with other additives and we, aim to develop an insight into the role played by the different sulfur chemistries when used with other solid lubricants like polytetrafluoroethylene (PTFE).

1.3 Outline of the thesis

Chapter 1: Provides a brief introduction on the use of wear and extreme pressure additives in lubricating oils and greases.

Chapter 2: Discusses the background needed to understand the components, functions and types of lubricating greases and the need to introduce anti-wear and extreme pressure additives in greases.

Chapter 3: Discusses the testing protocols followed and a brief background of the chemistries used.

Chapter 4: Provides a Design of Experiment approach for the development of a high-performance grease.

Chapter 5: Deals with the role of sulfur and non-sulfur carriers on the wear and EP performance of greases with emphasis on the one-, two- and three- factor interactions between the additives.

Chapter 6: Deals with the morphological and elementary compositional analysis of the tribofilms formed by the various additives

Chapter 7: Provides a few achievements and conclusions

Chapter 8: Provides some suggestions for future work

CHAPTER 2

BACKGROUND

2.1 Tribology

In 1966, Peter Jost, chairman of a working group of lubrication engineers, published the Department of Education and Science Report wherein he defined the word ‘Tribology’ as ‘…The science and technology of interacting surfaces in relative motion and the practices related thereto.’ ‘Tribology’ is derived from the Greek word ‘tribos’ meaning rubbing or sliding. The reason why this field has attracted the attention of engineers, scientists and economists alike is that the surface interactions control or dictate the functioning of practically every device developed by man to enhance the quality of life through his inventiveness and the utilization of resources of the physical world [4]. It comes of great economic significance since estimated losses from tribology account for ~6% of the GDP in the US. Suh and Saka [5] propose that probably more failures are caused by tribological problems than fracture, fatigue, plastic deformation etc. In terms of criticality, tribology affects industry in the following areas:

1. Tribology is critical to the reliability and efficiency of mechanical and certain electrical products.
2. Tribology directly affects the “maintainability” of a product.
3. Tribology affects a company’s financial statement, both directly and indirectly. [5]

Tribology relates directly to the combination of all sciences and technologies associated with the three areas of *friction, lubrication and wear* and is specifically concerned with the elements as shown in the following schematic:

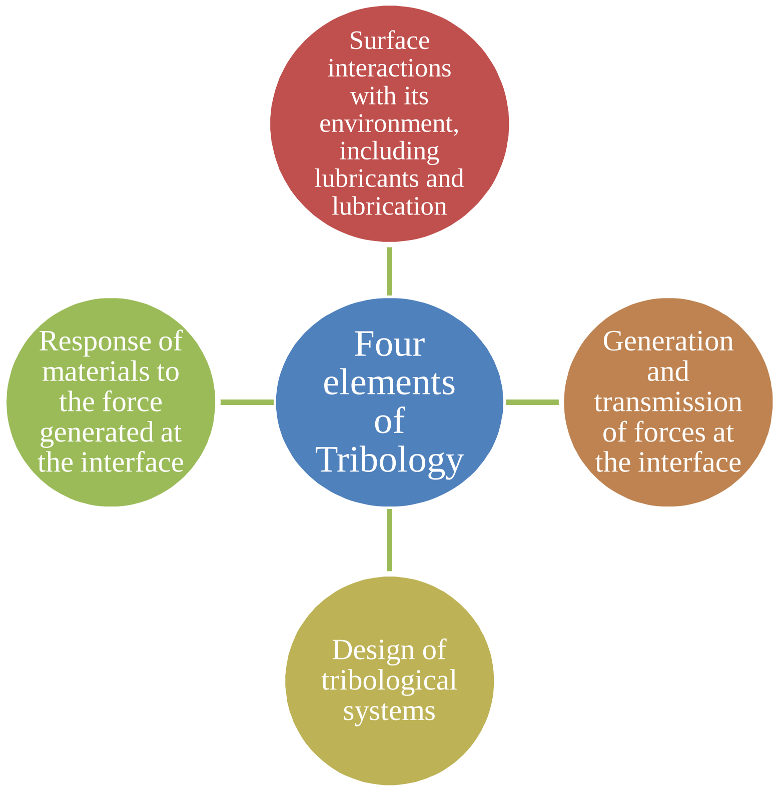


Figure 2.1 Showing the four elements of tribology

Thus, tribology has provided the scientists and engineers with a foundation for choosing lubricants in today's demanding environment and needs. The selection of lubricants for a particular application can be determined by taking into account the effects of tribological system parameters on lubricant chemistry [6]. A tribological system includes type of motion, speed, temperature, load and operating environment. A lubrication engineer identifies these system parameters and chooses the appropriate lubricant with suitable chemistries to optimize the performance of any tribological application. A tribological system comprises of the following:

Type of motion: Motions between two surfaces could be sliding, rolling, a combination of sliding and rolling, or oscillation. Depending on the type of motion, appropriate chemistries must be chosen to optimize the performance.

Speed is the second parameter of the tribological system. The optimum speed for the lubricated system can be estimated by the Stribeck curve that represents the relationship between coefficient of friction and the dimensionless number, $\eta n/P$, where η is the dynamic viscosity, n is the speed and P is the load per unit projected area. For instance, when the speed is very low, all the loading is carried by the asperities in the contact area, protected by the adsorbed lubricant molecules and/or a thin oxide layer, whereas at high speeds, the surface asperities are completely separated by a lubricant film. [7]

Temperature: Lubricants have a range of temperatures over which they are operational. Lubricants are chosen depending upon the application temperature, for example, aviation greases are expected to operate at the temperatures encountered by some of the high altitude military aircraft which range from -75℃ to +200℃. [8]

Load: At very light loading conditions, the effect from frictional torque sets in and a lubricant must be selected such that the fluid friction is minimized while still providing protection from solid friction. On the other hand, at high loading conditions, suitable additives must be used to protect the surfaces from pitting and extreme wear.

Operating environment: Depending on the environment (whether it contains moisture, vacuum, dust, chemicals or vapor)in which the tribological system operates, suitable lubricants must be chosen. For instance, if the environment includes moisture or water, the lubricant must provide good anti-corrosion properties and resistance to water contamination as well. [7]

Thus, proper selection of a lubricant for a given application calls for a thorough analysis of the tribological system. According to economists, in the U.S.A. it has been estimated that about 11% of total annual energy can be saved in the four major areas of transportation, turbo machinery, power generation and industrial processes through progress in tribology [8]. The purpose of tribology is either to find the appropriate film material for any given application or to predict the order of the events when a sliding/rolling/impacting contact is left to generate its own intervening film.

2.1.1 Friction

Friction is the resistance to motion between two solid bodies in direct or indirect surface contact when they are made to slide relative to one another. In machinery, friction converts part of the useful energy to heat and thus decreases the overall efficiency of the machine. Szeri [8] points out that about 30% of the power in an automobile is wasted through friction. Overcoming friction and mitigating the damage caused due to friction which may be wear or seizure of machine components or surface damage due to frictional heating are the challenges that need to be overcome by scientists and engineers.

2.1.1.1 Laws of friction

The two basic laws of friction are:

- Friction is proportional to the normal force between surfaces
- Friction is independent of the (apparent) area of contact

2.1.1.2 Adhesion theory of Friction

On a microscopic scale, the smoothest of the surfaces appear rough and show “peaks” and “valleys” on highly magnifying the surface. When two solid bodies are placed over each other only the tips of the “peaks” of the asperities come in contact. On increasing the normal load slowly, elastic deformation of the asperity riding on the flat surface occurs.

On increasing the load, the pressure at the contact point also increases till the elastic limit of one of the materials is reached and plastic flow starts. Thus, the asperities would undergo plastic deformation at significantly small loads till the area of contact is sufficient enough to support the load.

Since the tips of the asperities are points where the surfaces make contact, the pressures are very high. Such high pressures cause the asperities to weld. As the surfaces slide over each other, the welded junctions are sheared.

Let S be the shear strength of the material and A the area of real contact. The shear force can then be written as A*S. The coefficient of friction then can be written as:

$$f = \frac{F}{W} = \frac{AS}{AP} = \frac{S}{P} = \frac{\text{Shear strength}}{\text{Yield Pressure}}$$ [8]

The coefficient of friction is an empirical property of the contacting materials. For surfaces at rest relative to each other, frictional force is equal to the force that would be needed to prevent motion between two surfaces. The coefficient of friction is then called coefficient of static friction. For surfaces in relative motion, the frictional force on each surface is exerted in the direction opposite to its motion relative to the other surface. The coefficient of friction in this case is known as the coefficient of kinetic friction. Friction can manifest itself as rolling friction (as found in ball bearings, roller bearings), sliding friction where any two plain surfaces move relative to each other as in an internal combustion engine where the piston rings slide against the cylinder walls creating sliding friction. During sliding of two surfaces over one another, a phenomenon called "Stick-slip" also occurs. [9] To the naked eye, the motion of the sliding objects appears steady. In reality, this motion is intermittent or jerky as the two interacting surfaces slow down when the shearing of the asperities at the area of contact occurs after which they accelerate. This process is repetitive when the surfaces are in sliding motion relative to each other and the coefficient of kinetic friction is less than the coefficient of static friction. The surfaces stick till the sliding force reaches the value of the static friction and the surfaces will slip over one another with a small value of kinetic friction till the two surfaces stick again. [10] This process is responsible for the squeaking or chattering sometimes heard in machinery. This phenomenon can be observed between the bearing liner and the shaft at slow speeds or light loads where the interface wavers between static and kinetic coefficients of friction. [11]

2.1.2 Wear

Wear is usually associated with the loss of material from contacting bodies in relative motion. Wear occurring in engineering practice can be divided into four broad categories:

Adhesive Wear is the transfer of material from one interface to another and is associated with the formation of adhesive junctions at the interface. It occurs under conditions of high loads, temperatures or pressures causing the asperities on the contacting surfaces, in relative motion, to spot-weld together then immediately tear apart, shearing the material in small discrete areas. Normal break-in is a form of mild adhesive wear, scuffing refers to moderate adhesive wear whereas galling, smearing and seizing result from severe adhesion. Adhesion can be prevented by applying lower loads, avoiding shock-loading and using extreme-pressure (EP) and anti-wear (AW) additives, if needed, to reduce damage.

Abrasive wear is the most common type of wear occurring in lubricated machinery. It arises when two contacting surfaces are in direct physical contact, and one of them is significantly harder than the other. There are two modes of abrasive wear: Three-body abrasion occurs when the grits are free to roll and slide over the surface since they are not constrained, whereas in two-body abrasion, when the hard asperities or rigidly-held grits pass over the surface like a cutting tool.

Corrosive wear is caused by a chemical reaction between the worn material and a corroding medium which may be a chemical reagent, reactive lubricant or air. Initially, the surfaces in contact react with the environment, creating reaction products that are deposited on the surface, thus slowing down further corrosion. If crack formation and abrasion occurs, the reaction products are removed and promoting corrosive wear.

Fatigue wear: Load-carrying nonconforming contacts, called Hertzian contact, are sites of relative motion that consists of varying degrees of pure rolling and sliding. The failure is attributed to multiple reversals of contact stress field and thus classified as fatigue failure. Fatigue wear is usually associated with rolling contacts, as in bearings, because of the cyclic nature of the load. Sliding surfaces are more prone to adhesive wear and occurs sufficiently rapidly such that there is little time for fatigue wear to occur.

2.1.3 Lubrication

Reducing friction, wear, and the occurrence of seizure by providing a suitable lubricant between the two surfaces in relative motion is called Lubrication. Lubricants have been a part of everyday existence from the time humans first built and moved objects. As Da Vinci observed more than 400 years ago, “All things and everything whatsoever, however thin it be, when interposed in the middle between two objects that rub together lighten the difficulty of this friction"[8]. Archaeological records show that the early Egyptians, Greeks and Romans were aware of lubricants and used them in building programs and on vehicles. A mural painted on the wall of a grotto at El Bershek (ca.1900 B.C.) depicts a sledge, carrying the colossus, being lubricated by oil that is poured on its path. A chariot dating from about 1400 B.C was found with some of the original grease on its axle in the tomb of Yuca and Thuiu [3]. Leonardo Da Vinci commented on and developed some friction laws, but it was only in the 1700 that a rise in the interest in lubricants was seen as machinery began to be developed [3]. The naturally available fats, oils and waxes were used. In retrospect, the development of lubricants was caused by the industrial revolution, the automotive industry, World War II, the space race and most recently, the influence of federal regulations. Under these influences, lubricants progressed from natural fats and oils to petroleum, then to synthetics, then to solids and gases. This development has been almost exponential because the truly scientific understanding of lubricants and friction dates only from about 1940 [3].

2.1.3.1 Stribeck Curve

The friction and wear mechanisms discussed so far are based on the physical interactions between two surfaces moving relative to each other. A lubricant is used for reducing the friction and wear, providing smooth running surfaces and a satisfactory life for machine elements. The physical and chemical interactions between the lubricant and the lubricating surfaces must be understood in order to provide the machine elements with satisfactory life. The Stribeck curve was named after Richard Stribeck (1861-1950) and provides the frictional behavior of different lubrication regimes, depending on the geometry, the properties of the lubricant and the operating conditions.

- Hydrodynamic and elastohydrodynamic lubrication ($h \gg \sigma$)
- Mixed lubrication ($h \sim \sigma$)
- Boundary lubrication ($h \ll \sigma$)

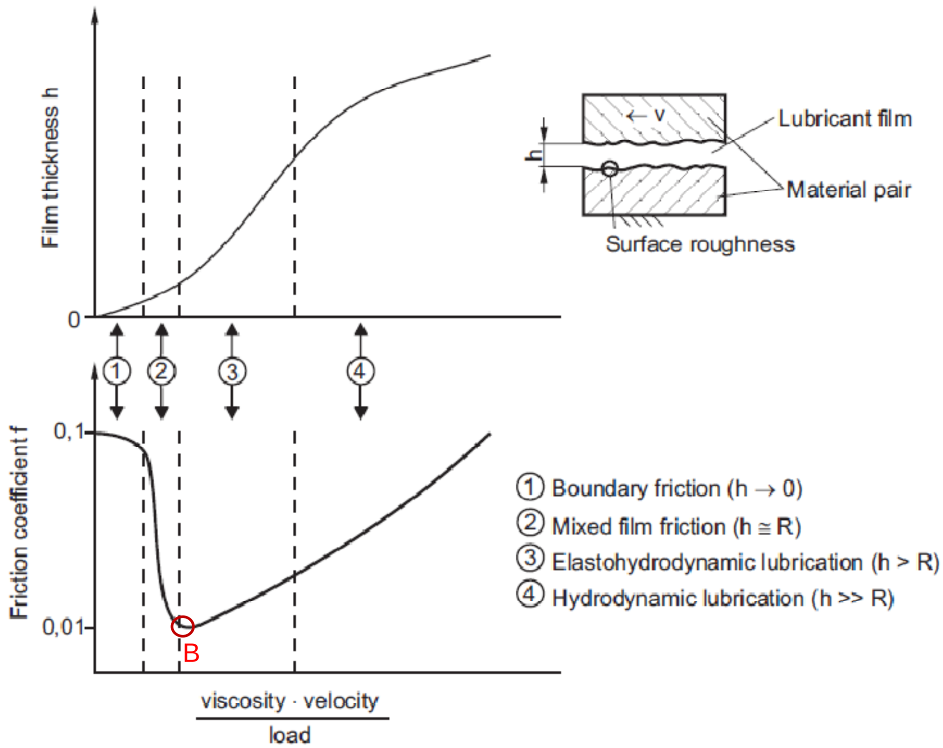


Figure 2.2 Stribeck curve

In the above expressions, h is the thickness of lubricant film, and σ is composite root mean square (rms) surface roughness of the mating surfaces, that is,

$\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$

where σ_1 and σ_2 are the surface roughness of the two mating surfaces respectively. Considering the lubricant film thickness in relation to the surface roughness, a relationship called specific film thickness λ is obtained, which is defined as

$\lambda = h_{min}\sigma^{-1}$

where h_{min} is the minimum film thickness. Typical values of h_{min}, λ and f are shown in the table. [12]

Table 2.1 Showing the properties of lubricant films under different lubrication regimes

Mechanisms of lubrication	Lubricant film properties		
	Lubricant film thickness, h_{min} (μm)	Specific film thickness, λ	Coefficient of friction, μ
Boundary Lubrication	0.005-0.1	<<1	0.03-1
Mixed lubrication	0.01-1	1-3	0.02-0.15
Elastohydrodynamic Lubrication	0.01-10	3-10	0.01-0.1
Hydrodynamic Lubrication	1-100	6-100	0.001-0.01

The differentiation of various lubrication modes is done through the Stribeck curve which illustrates the change in the coefficient of friction as a function of the lubrication parameter ηVP^{-1}, where η is the dynamic viscosity, V is the sliding speed, and P is the pressure.

The coefficient of friction varies with the operating conditions. The vertical axis indicates the coefficient of friction f=F/P and the horizontal axis, the bearing number ηVP^{-1}. The minimum value of f is very small and usually of the order of 0.001. There are three distinct zones in the graph, separated by the points A and B. At B, the frictional coefficient is at its minimum and the oil film is thick enough to ensure that there is no contact between asperities. In zone 3, to the right of B, the oil film thickness increases with increase in viscosity and speed and decrease in pressure. The different lubrication zones have an important influence on wear and are discussed separately as below.

2.1.3.2 Hydrodynamic Lubrication

Hydrodynamic lubrication is based on the formation of a sufficiently thick lubricant film between the two surfaces in relative motion, such that the two surfaces do not contact each other directly and wear hardly occurs (Figure 2.4). This type of lubrication is characterized by conformal surfaces. Conformal surfaces are those surfaces that fit snugly into each other with a high degree of geometrical conformity so that the load is carried over a relatively large area [13]. Lubricant film thickness depends on the speed of the surfaces is relative motion and the lubricant (oil) viscosity. The viscosity is the only property of the lubricant which is important in hydrodynamic lubrication. Thus, higher speed gives better lubrication and very low speed may cause lubrication failure.

Hydrodynamic lubrication is also referred to as “Ideal state of lubrication” in that friction is lower and wear hardly occur. The lubricant film thickness should be greater than the sum of asperity heights to ensure no contact between asperities of the two contacting surfaces. Although, technically, hydrodynamic lubrication refers to a type of lubrication by liquid, it can also be applied to lubrication by gases, provided that the load and speed conditions are suitable for the low viscosity of gases. However, elastohydrodynamic lubrication cannot be obtained with gases.

2.1.3.3 Elastohydrodynamic Lubrication

Elastohydrodynamic lubrication applies to hydrodynamic conditions where surface deformation is comparable with the hydrodynamic film thickness and surface deformation affects the hydrodynamic behavior of the interface. The fundamental characteristic of this type of lubrication is that heavy load causes deformation of the mating surfaces, which provides a coherent film and avoids asperity interaction. Under the high pressures generated, the lubricant properties are markedly different from those of the bulk. In particular, an enormous increase in viscosity may occur.

2.1.3.4 Boundary Lubrication

In boundary lubrication, the contacting solid surfaces move so close to each other that there is a considerable asperity interaction. A thin film of lubricant is adsorbed to the solid surface and the lubrication mechanisms are usually controlled by additives present in the lubricant. The operating principle of boundary lubrication can be illustrated by considering the coefficient of friction (f):

$f = F/W$

where F= frictional force and W = load applied normal to the surface. Since the contacting surfaces are covered by asperities, 'dry' contact is established between the individual asperities and the 'true' total contact area is the sum of the individual contact areas between the asperities. If we assume that friction is due to the adhesion between asperities, then

$F = A_t$

Where A_t is the true contact area [m^2] and τ is the effective shear stress of the material [Pa].

The applied load can then be expressed as:

$W= A_t P_y$

Where is the P_y plastic flow stress of the material (close to the indentation hardness value) [Pa].

Thus, $f = \tau/P_y$

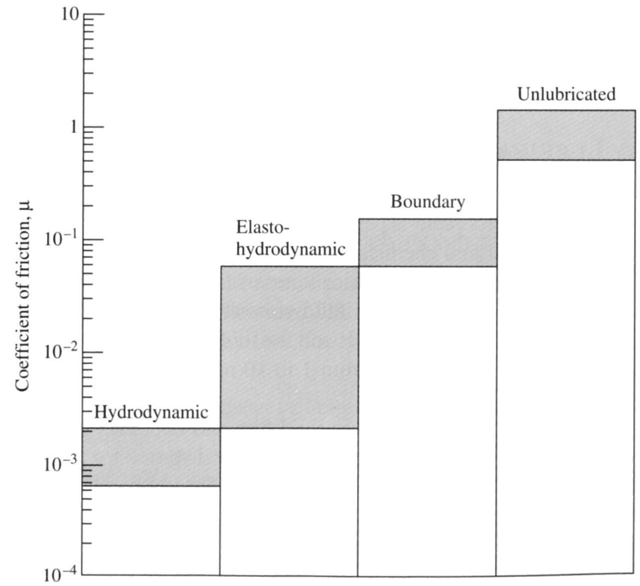


Figure 2.3 Bar-chart showing the values of coefficient of friction in the different lubrication regimes [7]

It is evident from the above equation that a low value of friction coefficient can be obtained if a material of low shear strength and high hardness is chosen, which seems to be an impossible proposition. However, if a low shear strength layer is formed on a hard substrate, low friction coefficient values can be achieved. Thus, the fundamental principles behind boundary lubrication involve the formation of low shear strength lubricating layers on hard substrates.

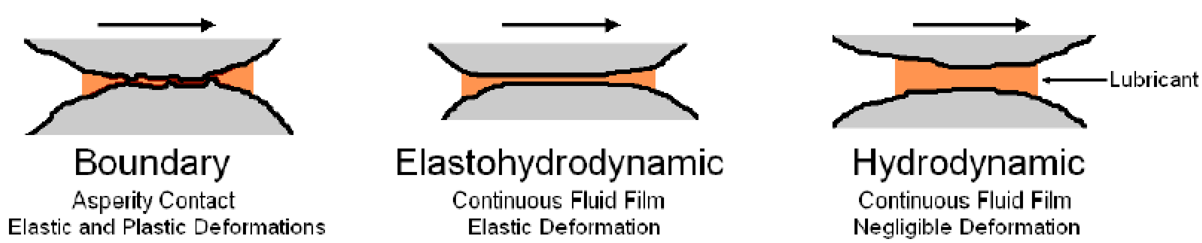


Figure 2.4 Schematic comparison of different lubrication regimes [2]

2.1.4 Lubricants

A lubricant is defined as a substance which reduces the friction when introduced between two surfaces. Apart from controlling wear and providing low frictional coefficient, a lubricant may perform some or all of the functions listed below:

1. It reduces the maintenance or running cost of the machine.
2. It reduces unsmooth relative motion of the moving surfaces.
3. It reduces the loss of energy in the form of heat, thus acting as a coolant.
4. It reduces waste of energy, so that the efficiency of the machine is increased.
5. It reduces surface deformation, as the direct contact between the moving surfaces is avoided.
6. It sometimes, acts as a seal, preventing the entry of dust and moisture between the moving surfaces.
7. It minimizes corrosion.

Lubricants are divided into four basic classes:

2.1.4.1 Oils: A general term to cover all liquid lubricants. Liquid lubricants reduce friction and wear between two moving surfaces by providing a continuous fluid film between the surfaces. They are further sub-classified as:

1. Animal and vegetable oils: These are glycosides of higher fatty acids. These have very good oiliness but are costly and oxidize easily.
2. Petroleum or mineral oils: They are obtained by fractional distillation of crude petroleum oils and have hydrocarbon chain length varying from C_{12} to C_{50}. They are the most commonly used lubricants. To improve the characteristics of oils, additives specific to the application of the machinery are added, thus giving the desired lubricating properties. There are three basic forms of mineral oil:

a. Paraffinic oil: As the name suggests, paraffinic implies straight chain hydrocarbons.
b. Naphthenic means cyclic carbon molecules with no unsaturated bonds.

c. Aromatic oils contain benzene type compounds.

3. Synthetic lubricants were developed to address severe operating conditions, such as those existing in aircraft engines. They are operable in temperature ranges of -50℃-+250℃; since mineral oils oxidize at high temperat ures while at low temperatures wax separation will occur. Examples of synthetic lubricants include polyglycol ethers, fluoro and chloro-hydrocarbons, organophosphates and silicones.

4. Greases: Grease is a semi-solid lubricant obtained by thickening liquid lubricating oil through the addition of a thickening agent (soap).

5. Solid lubricants: Solid lubricants are useful in conditions where conventional lubricants cannot be used. Graphite and molybdenum disulfide are the predominant materials used as solid lubricants. As dry powders, these materials make effective lubricant additives due to their lamellar structure, which orient themselves parallel to the surface in the direction of motion. Other materials that are used as solid lubricants are polytetrafluoroethylene (PTFE), talc, calcium fluoride and tungsten disulfide.

6. Gases: The gas usually used in gas bearings is air, but any gas which does not attack the bearings or itself decompose, can be used.

The broad properties of these four classes of lubricants are list in the table given below:

Table 2.2 Properties of basic lubricant types [2]

	Lubricant property	*Oil*	*Grease*	*Dry lubricant*	*Gas*
1.	Hydrodynamic lubrication	Excellent	Fair	Nil	Good
2.	Boundary lubrication	Poor to excellent	Good to excellent	Good to excellent	Usually poor
3.	Cooling	Very good	Poor	Nil	Fair
4.	Low friction	Fair to good	Fair	Poor to good	Excellent
5.	Ease of feed to bearing	Good	Fair	Poor	Good
6.	Ability to remain in bearing	Poor	Good	Very good	Very poor
7.	Ability to seal out contaminant	Poor	Very good	Fair to good	Very poor
8.	Protection against atmospheric corrosion	Fair to excellent	Good to excellent	Poor to fair	Poor to good
9.	Temperature range	Fair to excellent	Good	Good to excellent	Excellent
10.	Volatility	Very high to low	Generally low	Low	Very high
11.	Flammability	Very high to very low	Generally low	Generally low	Unlimited variation
12.	Compatibility	Very bad to good	Fair to good	Excellent	Generally good
13.	Cost of lubricant	Low to very high	Fairly high to very high	Fairly high	Generally very low
14.	Complexity of bearing design	Fairly low	Fairly low	Low to high	Very high
15.	Life determined by	Deterioration and contamination	Deterioration	Wear	Ability to maintain gas supply

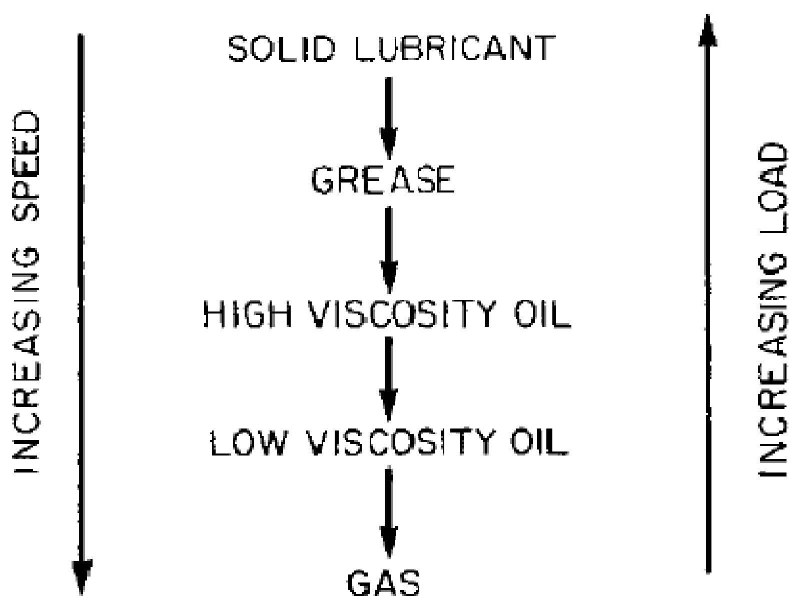


Figure 2.5 Effect of speed and load on choice of lubricant [5]

2.2 GREASES

After gaining an insight into the various aspects of lubrication and tribology, we now focus on the theories and principles of greases and the research conducted towards the development of a high-performance, universal grease with chemistries incorporating suitable additives.

The American Society for Testing of Materials defines a lubricating grease as follows:

“A solid to semi-fluid product of dispersion of a thickening agent in liquid lubricant. Other ingredients imparting special properties may be included” (ASTM D 288, Standard Definition of Terms relating to Petroleum). [14]

2.2.1 Components of grease

Greases always contain three basic active ingredients: a base mineral or synthetic oil, additives and thickener. It may be said that greases, in general, contain 65-95% w/w base oils, from 5-35% w/w thickeners and from 0-10% w/w additives. [15]

2.2.1.1 Base Oils

Mineral oils are most often used as the base stock in grease formulation. About 99% of the greases are made with mineral oils. The oil in a grease is constrained by minute thickener fibres. Since the oil is constrained and unable to flow it provides semi-permanent lubrication. Naphthenic oils are most popular since they maintain their liquid phase at low temperatures and easily combine with soaps. Paraffinic oils are poorer solvents for many additives used in greases. However, they are more stable than naphthenic oils and less likely to react during grease formulation. Synthetic oils are used for greases which are expected to operate under extreme conditions for applications like high performance aircrafts, missiles and in space. Vegetable oils are used in applications in food and pharmaceutical industries.

2.2.1.2 Thickener

The thickener used in greases determines the characteristics of greases. Depending on the fundamental types of thickeners, commercial greases can be categorized into two primary classes: soap and non-soap based. In soap-based greases, the principal thickeners used are metallic soaps which consist of long-chain fatty acid and alkali. The reaction between the fatty acid and alkali causes the metal to be incorporated in to the carbon chain, making the resultant molecule polar and a soft, fibrous matrix of interlocking particles results. This interlocking structure forms tiny pockets, entrapping the oil. Soap thickeners provide consistency to the grease, and influence the flow of greases, shape change and lifetime as the greases are mechanically worked and at extreme temperatures. Soaps such as calcium, sodium aluminum, lithium, clay are currently used. Soaps of other metals have not gained acceptance commercially due to cost, health and safety issues, environmental concerns, or performance problems. Complex grease is similar to a regular grease except that the thickener contains two dissimilar fatty acids, one of which is a complexing agent. This imparts good high temperature characteristics to the final product.

Non-soap type thickeners are used in certain greases to obtain some desirable properties. The thickeners exist as very fine powders that have enough porosity and surface area to absorb oil. The thickeners could be organic, inorganic or synthetic. The most commonly used are silica and bentonite clays.

2.2.2 Basic Performance Requirements of greases

As Boner [16] in his book suggests, “Greases are most often used instead of fluids where a lubricant is required to maintain its original position in a mechanism, especially where opportunities for frequent relubrication may be limited or economically unjustifiable. This requirement may be due to the physical configuration of the mechanism, the type of motion, the type of sealing, or to the need for the lubricant to perform all or part of any sealing function in the prevention of lubricant loss or the entrance of contaminants. Because of their essentially solid nature, greases do not perform the cleaning and cooling functions associated with the use of a fluid lubricant. With these exceptions, greases are expected to accomplish all other functions of fluid lubricants.”

Greases are expected to perform the following functions:

1. Reduce friction by providing adequate lubrication and preventing wear of contacting surfaces
2. Corrosion and rust protection
3. Act as a sealant to prevent entry of dirt and water
4. Resist leakage, dripping, or undesirable throw-off from the lubricated surfaces
5. Retain its consistency or structure when mechanically worked for prolonged duration
6. Not stiffen excessively to cause undue resistance to motion in cold environments
7. Be compatible with materials of construction in the lubricated portion of the mechanism
8. Tolerant to some level of contamination, without losing significant characteristics

The disadvantages associated with greases are as follows (as reported by McCarthy [17]):

1. Lack of stability in storage
2. Due to its consistency, grease cannot dissipate heat by convection like a circulating oil
3. Less oxidation resistant, either in storage or in use

2.2.3 Types of base greases

Animal fats and vegetable oils are esters, theoretically formed by reaction between glycerol and long-chain fatty acids. On heating them with alkali, they break-down to give free glycerol and a mixture of alkali metal salts of the various fatty acids present. This process of saponification (which simply means conversion into soap) involves the trading of the metal in the alkali with the acid hydrogen atom that is attached to an oxygen atom on the end carboxyl group. The soap thus formed supplies the fiber structure giving the grease its semi-solid consistency and it is found that non-soap thickeners, which are not fibrous in shape, must often be used at higher concentrations than soaps in order to give the same degree of thickening.

In the manufacture of soap-based greases, the fat or fatty acid is dispersed in a small quantity of hot base oil, and the alkali is added to saponify it. Thus saponification helps to disperse the resulting soap in the oil. After the addition of base oil and additives, the grease is subjected to milling operation to give a smoother consistency before packaging.

The factors influencing the characteristics of greases are as follows: [15]

1. Metal atom in the soap
2. Fats from which soap is made
3. Percentage of soap used
4. Physical characteristics of fluid phase
5. Manufacturing techniques
6. Chemical additives

Table 2.3 Performance of petroleum oil lubricating greases

Thickener	Maximum usable Temperature (°C)	Pumpability at 0°C	Water resistance	Worked stability	Service life
Soap base					
Aluminum	80	F	F	P	S
Barium	177	F	G	G	MD
Calcium	80	G-F	G	F	MD
Calcium complex	121	F	G	F	MD
Lithium	149	G-F	G	E-F	MD-LG
Sodium	121	G-P	P	E-P	MD-LG
Sodium-calcium	121	G-F	F-P	E-P	MD-LG
Non soap base					
Bentone	121	G-F	G-F	P	MD-S
Silica	121	G-F	G-F	P	MD
Organic	149	G-F	G	G	MD-LG

Ratings: E, excellent; G, good; M, medium; F, fair; P, poor; MD, moderate; S, short; L, low; H, high; and LG, long

A “complexing agent” made from a salt of the named metal is the additional ingredient in forming a complex grease. The dropping point of a complex grease is at least 38℃ higher than its normal soap-thickened counterpart, with maximum usable temperature around 177℃ (350℉). A complex soap is formed by the reaction of a fatty acid and alkali to form soap, and simultaneous reaction of the alkali with a short-chain organic (acetic or lactic acids) or inorganic acid (carbonates or chlorides) to form a metallic salt (complexing agent).

2.2.4 Characteristics of greases

1. Consistency: It is a measure of the relative hardness or softness and may indicate something of flow and dispensing properties. Consistency is measured in terms of penetration and is the resistance to deformation by an applied force. Higher penetrations are indicative of softer greases. The National Lubricating Grease Institute (NLGI) has standardized the numerical scale for classifying the consistency of greases. The NLGI grades and the corresponding penetrations are shown in the following table:

Table 2.4 NLGI Consistency Classification

NLGI Consistency Number	ASTM Worked Penetration at 25°C
0	445-475
0	400-430
0	355-385
1	310-340
2	265-295
3	220-250
4	175-205
5	130-160
6	085-115

2. Apparent viscosity: Newtonian fluids are defined as materials for which the shear rate (or flow rate) is proportional to the applied shear stress (or pressure) at any given temperature. In other words, the viscosity, defined as the ratio of shear stress to shear rate, is constant. Grease, on the other hand, is a non-newtonian material that does not flow till a shear stress exceeding a yield point is applied. The viscosity so observed is called apparent viscosity, and it varies both with temperature and shear rate.
3. Dropping point: It is the temperature at which a drop of material falls from the orifice of a test cup under prescribed test conditions. It indicates the upper temperature at which the grease can hold its structure and hence indicative of the heat resistance of grease.
4. Pumpability and slumpability: Pumpability is the ability of a grease to be pumped or pushed through a system, whereas slumpability, or feedability is its ability to be drawn or sucked into a pump.
5. Shearing: Slipping or sliding of one part of a substance relative to an adjacent part.
6. Shear stability: The ability of a lubricating grease to resist changes in the consistency during mechanical working. A grease that softens when it is worked is called thixotropic. Greases that harden when worked are called rheopectic.

2.2.5 Lithium-base greases

The National Lubricating Grease Institute (NLGI) Production Survey [16] gives the proportion of lithium-base greases manufactured in U.S. as about 50 per cent of the market. Most of these greases are lithium soaps of 12-hydroxy acid or glyceride either alone or in combination with other fatty acids or glycerides. Lithium-complex greases differ from lithium-soap greases in that the former is thermally more stable, having a dropping point of 260℃ (500℉). They are buttery in texture and can be used at temperatures of about 135℃ (275℉). It has good shear stability and a relatively low coefficient of friction, which permits higher machine operating speeds. Pumpability and resistance to oil separation are good to excellent. Anti-oxidants and extreme pressure additives are also responsive in lithium greases. These greases hold the highest value as true multipurpose grease at a reasonably inexpensive cost. They are extensively used as multi-purpose automotive greases and in major industrial applications. Probably the greatest value of this type of lubricant is that it permits simplification of lubrication in that a single grease may serve for every need of many manufacturing plants or construction projects. Also, a recent English article [18] states that: “Certainly the advent of lithium based greases has enabled the operating speeds of grease lubricated bearings to be increased in the last few years”. Thus, this type of lubricants, namely lithium base greases, with such desirable characteristics are truly modern, multipurpose greases.

2.2.6 Additives

Some additives influence the physical characteristics of the lubricant and with the others the action is of chemical nature. Kalil [16] tabulated seventeen different types of additives and the additives that are of most interest to grease compounders are tabulated as below:

Table 2.5 Functions of different additives [63]

Additive Type	Purpose	Typical Compounds	Functions
Antiwear and EP Agent	Reduce friction and wear and prevent scoring and seizure	Zinc dithiophosphates, organic phosphates, acid phosphates, organic sulfur and chlorine compounds, sulfurized fats, sulfides and disulfides	Chemical reaction with metal surface to form a film with lower shear strength than the metal, thereby preventing metal-to-metal contact
Corrosion and Rust Inhibitor	Prevent corrosion and rusting of metal parts in contact with the lubricant	Zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines	Preferential adsorption of polar constituent on metal surface to provide protective film, or neutralize corrosive acids
Detergent	Keep surfaces free of deposits	Metallo-organic compounds of sodium, calcium and magnesium phenolates, phosphonates and sulfonates	Chemical reaction with sludge and varnish precursors to neutralize them and keep them soluble
Dispersant	Keep insoluble contaminants dispersed in the lubricant	Alkylsuccinimides, alkylsuccinic esters, and mannich reaction products	Contaminants are bonded by polar attraction to dispersant molecules, prevented from agglomerating and kept in suspension due to solubility of dispersant
Antioxidant	Retard oxidative decomposition	Zinc dithiophosphates, hindered phenols, aromatic amines, sulfurized phenols	Decompose peroxides and terminate free-radical reactions
Friction Modifier	Alter coefficient of friction	Organic fatty acids and amides, lard oil, high molecular weight organic phosphorus and phosphoric acid esters	Preferential adsorption of surface-active materials

2.2.6.1 Choice of lubricating additives

1. From a commercial standpoint, those additives that are most economical and effective should be used.
2. Additives should be stable under the maximum conditions to which the lubricants, of which they are a part, may be subjected.

3. Additives should be compatible with other ingredients of the lubricant as well as with the materials with which the grease comes in contact
4. Grease additives which might be toxic or combinations which might lead to undesirable products when heated, should be eliminated.

Many grease manufacturers of lubricating greases aim to reach an optimum proportion of desirable additive agents to achieve a given purpose. As a general approach, 0.3 – 1percent of oxidation inhibitors, 1 to 3 percent rust inhibitors, 0.3 to 2 percent structure modifiers, 2 to 10 percent of load-carrying or anti-wear additives and 0.05 to 0.25 percent of copper corrosion inhibitors, may be added to the lubricating greases.

2.2.6.2 Antiwear (AW) and Extreme Pressure (EP) Additives

When two contacting parts of machinery start to move and the hydrodynamic lubrication has not yet been built up or in conditions of severe stress and strong forces the lubricating system runs in the regime of mixed friction. To prevent the welding or seizure of the moving parts and reduce wear, extreme pressure and antiwear additives are used. These additives have polar structure and by the process of chemisorption or adsorption form layers on the metal surface during conditions of mixed friction. In the event when the hydrodynamic lubricating film is not yet or no longer present, the increase in the temperature cause the AW and EP additives to react with the metal surface forming tribochemical layers (iron phosphides, sulfides, sulfates, oxides and carbides- depending on the additive chemistry), preventing direct contact between sliding metals. These reaction layers cause the asperities to plastically deform, thus smoothening the asperities on the metal surface. Wear that could occur due to microwelding is reduced and real welding of the moving parts under extreme conditions is avoided. AW additives are designed to reduce wear under moderate stress conditions whereas EP additives are much more reactive and are used under high stress conditions to prevent welding of moving parts.

The thin mono-molecular layers of physically adsorbed polar substances like fatty oils, fatty acids and other or tribochemical friction-reducing reaction layers exhibit only poor or moderate high pressure properties and exhibit lower friction behavior as compared to AW and EP additives. Such additives are called friction modifiers. They are generally regarded as mild AW or EP additives that work at moderate temperatures and loads in the area of starting mixed friction. [19]

2.2.6.3 Sulfur Carriers

Rossrucker and Fessenbecker [20] describe sulfur carriers as “A class of organic compounds where the sulfur atom is bound either to a hydrocarbon or to another sulfur atom; that do not contain other hetero atoms except oxygen and are produced by adding sulfur to all kinds of unsaturated, double-bond containing compounds such as olefins, natural esters and fatty acids”. Sulfur-containing additives are used to provide protection against high-pressure, metal-to-metal contacts in boundary lubrication. The magnitude of EP activity is dependent on the sulfur content in the additive, meaning that high sulfur-containing additives are more effective EP agents than the lower-sulfur containing ones. However, there is a limit to the amount of sulfur that an additive can contain and must be balanced against the requirements of thermal stability and noncorrosiveness towards copper-containing alloys. As general as it may seem, any compound that can breakdown and allow for a free sulfur valence to combine with iron can serve as an antiwear and EP additive. Sulfur additives are probably the earliest known and widely used EP compounds in lubricants.

The mechanism of sulfur carriers under EP conditions begins with physical adsorption followed by chemisorption and finally cleavage of sulfur and its reaction with the metal surface. This reaction occurs generally at 600℃ [19].

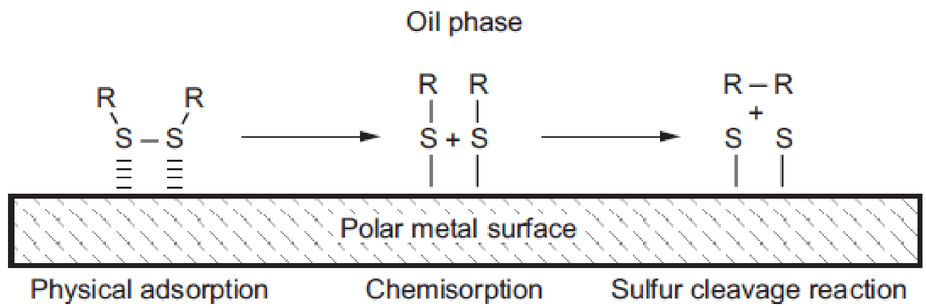


Figure 2.6 Mechanism of sulfur carriers under extreme pressure conditions [20]

The additive structure is dependent on the raw material and sulfurization method. In principle, any single or multi-double-bond-containing molecule may be sulfurized. The choice of the raw material depends on the price and performance benefits. The organic portion determines the polarity and hence the affinity of the product on the metal surface. EP performance improves with increasing polarity. Straight sulfurized olefins are unpolar and show relatively poor affinity to metal surfaces. The polarity increases in the order as:

Olefin< Ester < Triglyceride

The polarity and grade of polymerization determine the solubility of the sulfur carriers. As polarity increases, the solubility decreases from olefins to triglycerides. In general, sulfurized olefins have excellent solubility in solvents and all mineral oils. The viscosity of the additives increases as the degree of polymerization, hence molecular weight, increases. Sulfur carriers based on low-boiling olefins are applicable to closed lubricated systems due to the foul smell generated as a result of volatilization of the decomposition products.

There are two types of sulfur carriers: active and inactive. The inactive carriers with predominantly disulfide bridges possess relatively stable C-S bonds which react only at elevated temperatures. They need high temperatures to set the sulfur free and provide EP protection and to some extent antiwear properties. Inactive sulfurized additives are very stable and do not corrode copper. The active forms, on the other hand, contain 3 or 5 disulfide bridges and are much more reactive as the sulfur can be made available at relatively low temperatures from the labile polysulfide bridges. Being highly reactive with non-ferrous metals, they are not used for machining of the non-ferrous metals when they are used in an engine or other aggregates. "Active sulfur carriers prove to be excellent EP additives that prevent welding by a kind of controlled wear when the slideable reaction layers are removed continuously under severe loads" [19]. Active sulfur carriers also exhibit good antiwear properties.

2.2.6.4 Phosphorus Additives

Phosphorus-containing additives provide protection against moderate to high pressure, metal-to-metal contacts in boundary lubrication and Elastohydrodynamic lubrication. As against sulfur additives, phosphorus additives have good corrosion control. Phosphorus additives cannot replace the sulfur additives since the mechanism involved in the film formation rates and film strengths are different. The suggested mechanisms of action of phosphorus antiwear additives involve smoothing of rubbing surfaces, formation of thin, low friction layer and formation of a thick polymeric separating layer.

The principal types of phosphorus that find commercial use are the neutral and acid phosphates, phosphites, and phosphonates, and amine salts of the acids. There are also ashless compounds where sulfur or chlorine has been incorporated into the molecule as in thiophosphates and chlorinated phosphates.

Typically, phosphorus additives are extremely effective in applications with slow sliding speeds and high surface roughness.

2.2.6.5 Sulfur-Phosphorus additives

These additives provide protection against moderate to high-pressure, metal to metal contact under boundary lubrication and elasto-hydrodynamic lubrication. The common S/P additives available in the market are based on chemistries of dithiophosphates, thiophosphates, and phosphorothioates. S/P additives with metals, like Zinc Dithiophosphates (ZnDTP) are the most important antiwear/EP additives that find use in engine oils. The ashless classes are used less extensively.

1. Zinc DialkyldithioPhosphate (ZDDP)

ZDDP's have been in use for over 5 decades in the lubricant industry as low-cost, multifunctional additives in engine oils, transmission fluids, gear oils, greases and other lubricant applications. This compound functions both as an outstanding antiwear agent, a mild EP agent, and an effective oxidation and corrosion inhibitor, all at a cost lower than alternate chemistries available in the market. Companies like ExxonMobil Corporation, Chevron Corporation, Ethyl Corporation, Lubrizol Corporation, and others still manufacture ZDDP. [20] ZDDP serves as an anti-wear agent by decomposition into products that are adsorbed on the iron surface, and supplying antiwear function. Spedding and Watkins [23] suggest that the ultimate decomposition products formed as a result of decomposition of ZDDP, in terms of antiwear potency, are zinc phosphate and a mixture of alkyl sulfides (H_2S, RSH, RSSR, RSSSR).

The general formula of ZDDP is as below:[21]

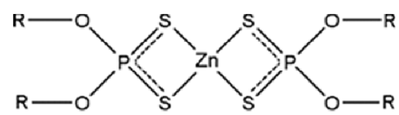


Figure 2.7 General structure of ZDDP

R in this figure represents the alkyl or the aryl groups. The types of alcohol used in the manufacture of ZDDP determine the R groups and the chain length of the molecule. The thermal stability and antiwear activity of ZDDP depends on the alkyl group structure; the increasing effectiveness of antiwear activity is as below:

Secondary alkyl>primary alkyl>aryl [22]

There are three structural forms of ZDDP that have been reported:

Monomeric $\{Zn[PS_2(OR)_2]_2\}$: Zinc atom is surrounded by four sulfur atoms arranged in a distorted tetrahedron and all Zn-S distances are equivalent. Two planar our-membered rings are formed between the sulfur atoms, zinc and two phosphorus atoms, which are perpendicular to each other.

Dimer/Neutral $\{[Zn_2(PS_2(OR)_2]_4\}$: Lawton and Kokotailo [23] suggested the dimeric form of ZDDP wherein each Zinc is bound to two di-thiophosphate groups; one bonded wholly to a Zinc and the other forms a bridge between two zinc dithiophosphate units. Neutral ZDDP can occur in two forms H-ZDDP or R-ZDDP; where the R generally is the n-butyl group that makes the ZDDP more stable with larger charge separation.

Basic: Basic ZDDP, with the formula $[(RO)_2PS_2]_6Zn_4O$ consists of a Zn_4O core with four zinc atoms in an almost perfect tetrahedral arrangement about a central oxygen atom. Yamaguchi et al. [24] suggest that at elevated temperatures, basic ZDDP converts into neutral ZDDP and ZnO.

2.2.6.6 Mechanism of Film formation

Till date, several mechanisms for the formation of ZDDP antiwear films have been postulated; the two most accepted mechanisms being the thermal decomposition of ZDDP and chemical reaction of the degradation products. [25] Willermet et al. have proposed a four-step process describing the reaction mechanism of ZDDP from solution under mild wear conditions. It proceeds as:

1. Adsorption of ZDDP on the metallic surfaces
2. Formation of phosphates and phosphorthionic species bound to the metallic surfaces by reaction of ZDDP and the metallic surfaces
3. Formation of precursors of phosphate film from antioxidant reactions of ZDDP
4. Condensation of phosphates and phosphothionates species and termination by zinc-containing compounds or other metals ions.

In contrast to Willermet et al., who suggest that short chain polyphosphates form first followed by polymerization to long-chain polyphosphates [25], Yin et al. [26] suggest that the long-chain polyphosphates are formed first, which then on extended rubbing form short-chain polyphosphates on interaction with metal ions.

2.2.7 Solid Lubricants

Solid lubricants are considered as any solid material that can reduce friction and mechanical interactions between surfaces in relative motion against the action of a load. They offer alternatives for conditions where traditional liquid additives cannot perform efficiently as under high temperature conditions where the decomposition and oxidation of a liquid lubricant is imminent and in conditions of high loads and contact stresses where lubricant starvation may occur as a result of the squeeze out of the liquid lubricant. Solid lubricants can be used as dry film or as additives in liquids or greases and thus are capable of providing enhanced lubrication in many applications. The two solid lubricants used as a part of this research work are as discussed below:

2.2.7.1 PTFE

PTFE or polytetrafluoroethylene has been used as a lubricant since the early1940s. It is most well-known under the DuPont brand name Teflon. The polymer structure consists of repeating chains of substituted ethylene with four fluorine atoms on each unit of ethylene, which gives the molecule long, straight chains. The structure is as shown below:

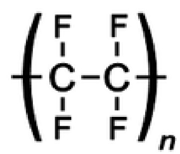


Figure 2.8 Structure of PTFE

PTFE exists as a white solid at room temperature and gains its properties from the aggregate effect of carbon-fluorine bonds. PTFE has an outstandingly low coefficient of friction; one of the smallest coefficients of static and dynamic friction than any other solid lubricant. Values as low as 0.04 for sliding conditions have been reported for various combinations of PTFE films on substrates [20]. It has high chemical stability and intermolecular bond strength. These molecules orient themselves in a manner that facilitates easy sliding and slip such that when the molecules slip along each other, rod-shaped macromolecules of PTFE result. It is chemically inert, thus useful in cryogenic to moderate temperatures and in a variety of atmospheres and environments. Due to the decomposition of the polymer, operating temperatures are limited to 260℃.

PTFE finds use in various bonded film lubrication at ambient temperatures, like fasteners, chain lubrication and engine oil treatments. It is widely used as an additive in lubricating greases and oils for industrial and commercial applications. It is non-toxic and thus finds use in pharmaceutical and food industries and as nonstick lubricant in domestic cooking utensils. [21]

2.2.7.2 MoS_2

MoS_2 consists of a hexagonal layered structure like graphite that consists of planes of Mo atoms alternating with the planes of S atoms. The forces holding the atoms together in each group of S:Mo:S layers are relatively strong covalent bonds whereas the forces between the adjacent planes of S atoms are relatively weak van der Waals types bond as a result of which the adjacent planes of S can slide over each other and this is regarded to be responsible for the low frictional resistance. At the same time, there exists resistance to penetration in a direction perpendicular to the crystallite lamellae. Such a structure of MoS_2 provides for the anisotropic shear properties with preferred planes for easy shear parallel to the basal plane of the crystallites. As Bhushan [12] points out that graphite proves to be a poorer lubricant than MoS_2 since the lubricating properties of graphite are dependent on the presence of water vapors and hydrocarbons to lower the friction. PTFE does not perform as well under high loading conditions because of its tendency to cold flow.

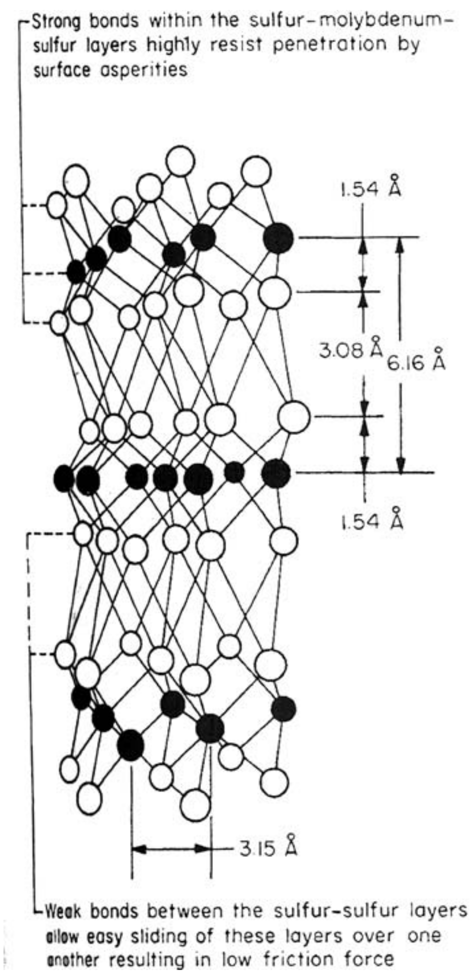


Figure 2.9 Lattice structure of molybdenum disulfide [20]

Incorporation of MoS_2 into greases is very common since oils and greases can be applied to various sliding surfaces and can be used in centralized lubrication systems. Greases typically contain 5 -10 percent MoS_2 and the concentration may go as high as 60 percent. Greases with 1 to 10 percent MoS_2 find use in automotive chassis lubrication. Trucks and buses use MoS_2 greases on steering joints, fifth wheels, universal joints, etc.

2.2.8 Synergistic/antagonistic additive effects

Often combinations of two or more additives demonstrate enhanced performance over that of the individual components and are used to tailor the properties of the lubricant to meet the demands. This widespread use of additives has developed rapidly since over the past 70 years in response to the increase in power/weight ratios and the reliabilities expected from modern engineering systems. Papcock et al. came out with simple definitions of ‘antagonism’ and ‘synergism’ [27]. According to them, “When the combined effect of two or more additives is higher than could be expected from simple additivity, the phenomenon is called ‘synergism’. The least active or inert component is called the ‘synergist’. The action opposite to synergism, when one additive suppresses the activity of another, is called ‘antagonism’”. Thus, interactions can occur between additives of the same class, as between two antiwear additives, or between additives of different classes like antiwear and EP additives.

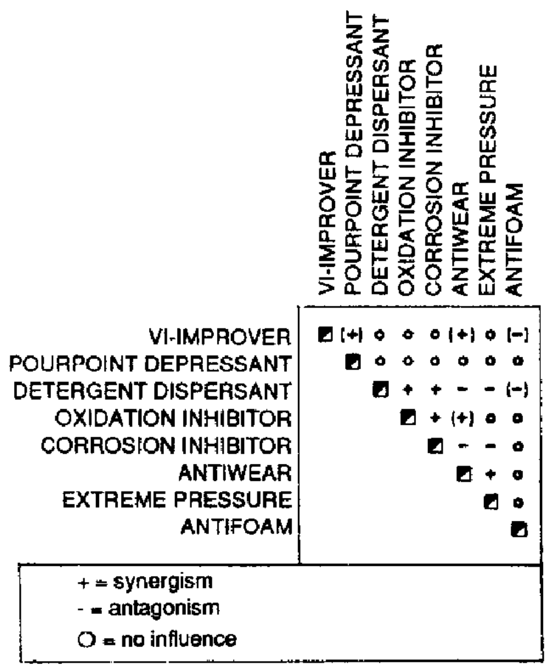


Figure 2.10 Direction of interaction between additives of different classes [28]

Spikes et al. [28] categorize the mechanism of interactions between lubricant additives in four classes:

2.2.8.1 Direct interactions in the liquid phase: These can be irreversible chemical reactions or reversible interactions. In few cases, chemical reactions can either result in the promotion of decomposition of one additive by another or inhibit the decomposition of one species by another.

2.2.8.2 Direct interactions on the surface: Additive molecules may react together directly at the metal surface or one additive may chemically react with the surface and the film formed may interact with another additive. Apart from chemical interactions, physical bonding or complex formation may also occur at surfaces.

2.2.8.3 Complementary and exclusory effects: These effects are not a result of direct bonding, unlike the previous two. The simplest case would be a surface-active additive reacting with the surface and masking it such that a second additive cannot react. Complementary, synergistic action occurs where a given function can be produced by two different mechanisms. Such synergy is seen in antiwear/EP additive mixtures, where a number of different protection mechanisms are possible.

2.2.8.4 Graded response: This is not a true additive interaction and states that a mixture, rather than a pure species, produces better performance as compared to concentrations of individual components. Since a mixture can react over a range of conditions, it provides more effective protection in most practical applications.

The interaction, its occurrence and magnitude, is very likely to be dependent on the base grease, including base oil and thickener. Silverstein and Rudnick [20] in their chapter on "Additives for Greases Application" show that when 3% MoS_2 is added to Lithium complex grease the 4-ball Weld Load is 500kg and 4-Ball wear scar diameter is 0.72; as opposed to Aluminum complex grease with 3%MoS_2 which gives a 4-Ball Weld Load of 400 kg and 4-Ball wear diameter as 0.90.

CHAPTER 3

PROCEDURAL PROTOCOL, EXPERIMENTAL SET-UP AND MATERIALS USED

The goal of the present study was to develop grease that exhibited superior antiwear and extreme pressure properties under standard and varying test conditions. New grease chemistry based on a synergistic interaction between a thiophosphate compound and fluoropolymer was developed as well all plausible interactions of various sulfur and sulfur carriers additives chemistries have been investigated. In this chapter, a review of the selected grease and the additives has been extensively addressed in order to gain an insight into the mechanism of antiwear and Extreme Pressure protection of metal surfaces in closed systems. It also discusses the tribometer used and the procedures followed to run wear and EP tests.

3.1 Standard Testing Methods for greases

All greases, before they are put to use, need to pass tests specific to the applications with minimum and/or maximum values of performance requirements. The National Lubricating Grease Institute (NLGI) has developed the ASTM (American Society for Testing of Materials) standard testing methods for greases to be tested for various characteristics. Continuous development is being carried out in understanding the real-time application conditions and simulation of such conditions in the test laboratories to produce results corresponding to the practical application conditions. The standard test for different grease characteristics are as given in the below table:

Table 3.1 ASTM Standards for grease testing [19]

ASTM NR.	Title
D-1743	*Test Method for Determining Corrosion Preventive Properties of Lubricating Greases*
D-2266	*Wear Preventive Characteristics of Lubricating Grease (Four Ball Method)*
D-2509	*Measurement of Load Carrying Capacity of Lubricating Grease (Timken)*
D-2596	*Measurement of Extreme Pressure Properties of Lubricating Grease (Four Ball Method)*
D-2619	*Hydrolytic Stability of Hydraulic Fluids (Beverage Bottle Method)*
D-2625	*Endurance (Wear) Life and Load Carrying Capacity of Solid Film Lubricants*
D-2670	*Method for Measuring Wear Properties of Fluid Lubricants (Falex Method)*
D-2714	*Calibration & Operation of the Falex Block-On-Ring Friction and Wear Testing*
D-2782	*Measurement of Extreme Pressure Properties of Lubricating Fluids (Timken)*
D-2783	*Measurement of Extreme Pressure Properties of Lubricating Fluids (Four Ball Method)*
D-2981	*Wear Life of Solid Film Lubricants in Oscillating Motion*
D-3233	*Measurement of Extreme Pressure Properties of Fluid Lubricants (Falex Pin & Vee Block Methods)*
D-3336	*Test Method for Life of Lubricating Greases in Ball Bearings at Elevated Temperatures*
D-3704	*Test Method for Wear Preventive Properties of Lubricating Greases using the (Falex) Block-On-Ring Machine in Oscillating Motion*
D-4170	*Test Method for Fretting Wear Protection by Lubricating Greases*
D-4172	*Test Method for Wear Preventive Characteristics of Lubricating Fluids (Four Ball Method)*
D-4871	*Guide for Universal Oxidation/Thermal Stability Test*
D-5183	*Coefficient of Friction Using a Four-Ball Wear Test*
D-5704	*Thermal Oxidation Stability Test*

3.2 Four-Ball Tester

The Four-ball geometry was developed in 1933 and is one of the most widely used test procedures. This instrument performs both wear preventive and Extreme Pressure analyses for measuring the wear and frictional properties of lubricants under sliding-on-steel conditions. The figure below shows the heart of the tester. Three ASTM standard designation D2266, chrome-plated steel balls (Bearing-quality

Aircraft Grade E52100 of 0.5 inch steel balls are rigidly clamped into a cup and covered with the test fluid. A fourth ball, in a chuck over the three bottom balls, makes point contact with each of the other three. The temperature of the lubricant was maintained at 75℃. During the test, a load (40kg or 392N) is applied between the top and bottom balls and the top ball is rotated at

1200 RPM and duration of test is 1 hour. These conditions are as specified by the ASTM D2266 Wear test. After initial motion starts, the point contact develops into a load bearing area contact. At the end of the test, the three balls are removed from the four-ball test machine and the width of the wear scar on each ball is measured using a microscope. Because of its high unit loading, the four-ball tester operates almost exclusively in the boundary lubrication regime. The ASTM D2266 standard allows for determination of wear-preventive characteristics of greases under the test conditions and if the test conditions are changed the relative ratings may be different. Lubricants are compared by using the average size of the scar diameters worn on the lower three clamped balls.

The Four-ball also allows for the determination of load-carrying properties of lubricating greases. With ASTM D2596, two determinations of Load Wear Index (an index of the ability of a lubricant to prevent wear at applied loads) and Weld Point (the lowest applied load at which sliding surfaces seize and then weld). For Weld Point determination, runs at consecutively higher test loads, as given in the below table, are conducted till welding occurs, at which point the balls are discarded. In event that welding does not occur, tests are repeated at next higher loads until welding is verified.

Table 3.2 Total of Compensation Line corrected Loads

Last Non-seizure Load, kgf	Weld Load, kgf										
	800	620	500	400	315	250	200	160	126	100	80
200	583	639	684	720	749	770					
160	410	466	511	547	576	597	615				
126	269.8	352.8	370.5	407	435	457	474	489			
100	159.7	215.8	260.5	296.7	325.3	346.9	364.4	378	390		
80	71.6	127.7	172.4	208.6	237.2	258.2	276.3	290	302	311	
63		56.1	100.8	137	165.6	187.1	204.7	218.8	230.4	239.3	246.7
50			44.7	80.9	109.5	131	148.6	162.7	174.3	183.2	190.6
40				36.2	64.8	86.4	103.9	118	129.6	138.6	145.9
32					28.6	50.2	67.7	81.8	93.4	102.4	109.7
24						21.6	39.1	53.2	64.8	73.8	81.1
20							17.6	31.6	43.2	52.2	59.5
16								14.1	25.7	34.6	42
13									11.6	20.6	27.9
10										9	16.3
8											7.4

Figure 3.1 Schematic of Plint Four-ball machine at UTA

The wear and EP tests performed in this research work were on the Plint Four-Ball tester (Model Number TE 92). This equipment consists of a bench-mounting test machine and control interface. The user's PC is installed with Phoenix Tribology COMPEND 2000 software. Below are given the basic machine specifications:

Rotational Speed: 60 to 3,000 rpm

Motor Power: 1.44 kW

Motor Torque: 3.9 Nm

The load range depends on the type of test being performed.

The Four-ball tests have several advantages. It presents a favorable geometry for boundary lubrication conditions. Test balls are relatively inexpensive, reproducible, and readily available. High pressures of up to 800,000 psi can be obtained. Geometry is well-defined. Small quantities of sample (15-20cc) are required for each test. A wide range of loads can be investigated since the relative behavior of lubricants under high loads may be different from that obtained at lower loads. The wear test results are reproducible.

3.3 Chemistries used

3.3.1 Base grease

Texaco Marfak Multipurpose 2 grease is used as the base grease in the present study. This grease is manufactured using highly refined base oils along with lithium 12-hydroxystearate thickener, and rust and oxidation inhibitors. It delivers value through good water resistance, corrosion protection, oxidation stability and simplified lubrication [29]. Few properties of this grease are given in the table below.

Table 3.3 Typical test data for Texaco Marfak Multipurpose 2 grease [29]

NLGI Grade	**2**
CPS Number	*220958*
MSDS Number	*8962*
Operating Temperature, °C(°F) Minimum[1] Maximum[2]	 -20(-29) 121(250)
Penetration, at 25°C(77°F) Worked Worked (10000X), %Change	 280 5
Dropping Point, °C(°F)	188(370)
Copper Corrosion	1B
Thickener, % Type	7.5 Lithium
Viscosity, Kinematic* cSt at 40°C cSt at 100°C	 220 18.1
Viscosity, Saybolt* SUS at 100°F SUS at 210°F	 1200 93
Flash Point, °C(°F)*	198(388)
Pour Point, °C(°F)*	-12(+10)
Texture	Buttery
Color	Brown

3.3.2 Additive

3.3.2.1 Sulfur carriers

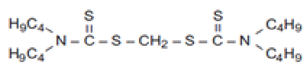
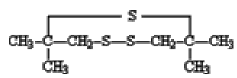
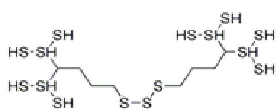
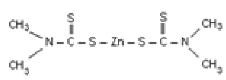
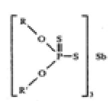
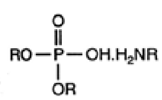
Vanlube SB, Vanlube 7723, Arkema VPS 15, Arkema TPS 20, Arkema TPS 44

3.3.2.2 Non-sulfur carriers

Zinc dialkyldithiophosphate, VanLube AZ, VanLube 622, VanLube 672

Listed below are some of the physical properties of the various additives from Vanderbilt that have been tested for antiwear/EP performance:

Table 3.4 Properties of various (sulfur and non-sulfur) additives

Additives	Formula	Chemical Composition	Mass % Sulfur	Physical State	Color	Flash Point °C	Viscosity @ 100°C cSt	Density @ 15.6 °C Mg/m^3
VL SB	Sulfurized Isobutylene	$-[S-C(CH_3)_2-CH_2-S-S-CH_2-C(CH_3)_2-S]_n-$	45-48	Liquid	Amber	79	10	1.14
VL 7723	Methylene bis(dibutyldithiocarbamate)		28.5-32	Liquid	Amber	177	15	1.06
VPS 15	Vegetable fatty acid esters		14.5-16	Clear liquid	Brown	>150	650 cSt (40°C)	
TPS 44	Ditertiarybutyl Polysulfide		42-46	Liquid	Clear	> 70	4.37 cP, (20 °C)	1007 kg/m^3
VL AZ	Zinc Dimethyldithiocarbamate		11.13.5	Liquid	Amber	136	9.8	1.02
VL 622	Antimony dialkylphosphorodithioate		16.5-22	Clear to slightly hazy liquid	Amber	150	5	1.2
VL 672	Ashless amine phosphate		0	Viscous liquid	Light Amber	113	250	1.02

3.3.2.3 Other (Solid Lubricants)

1. PTFE

Zonyl MP 1150 (from Dupont) is used as the fluoroadditive in this study. As is reported, when this additive is added to lubricants, it can enhance performance under severe conditions. Zonyl MP 1150 can be used at temperature from -190 to 250℃. The particle size is around 200 nanometers. This is a functionalized, irradiated PTFE containing short-chain PTFE molecules with carboxyl groups as the polar-end groups [30].

2. MoS_2

The two grades of MoS_2 used are the Technical Grade and Technical Fine grade with properties as given below. The typical MoS_2 content (calculated average) was 98% [31].

Table 3.5 Typical Particle Size and Bulk Density

Molysulfide® Grade	Fisher Number, μm	Particle Size Range by SEM, μm	Median Particle Size, μm**	Bulk Density (Scott)
Technical*	3 to 4	< 1 to 100	30	1.3 g/cm3
Technical Fine	0.65 to 0.8	< 0.5 to 20	6	0.4 g/cm3
Super Fine	0.4 to 0.45	< 0.5 to 8	1.5	0.3 g/cm3

3.3.3 Chemistries blended

3.3.3.1 Rationale behind the choice of various grease blends

Graphite and MoS_2 have been established as solid lubricants for a range of applications involving heavily-loaded surfaces. They are commonly used in greases for imparting high load-bearing capacity. To behave as successful solid lubricants, they should adhere sufficiently to the metal surface, orient in a direction of lowest shear and have the necessary shear strength. However, the low-friction of MoS_2 is an intrinsic property related to its crystal structure, whereas graphite requires the adsorption of water to behave as an effective solid lubricant. [20] Moreover, the non-polar structure of the graphite lamellae limits its adhesion to the metal surface, resulting in relatively low antiwear characteristics. On the other hand, Holinski et al. [32] assume that MoS_2 lamellae have a polarized surface, which explains the good adhesion of the lamellae on each other when brought in contact under pressure. Also, the polarized structure of MoS_2 is similar to that of iron oxide, hence good adhesion of the MoS_2 lamellae on the iron oxide. Considering all the above factors, it was thought worthwhile to choose MoS_2 over graphite as the inorganic solid lubricant in lithium grease.

The general treatment levels of such solid lubricants in greases are maintained at 1% and 5% (weight ratio). Antony et al. [33] have demonstrated that increasing the MoS_2 content from 0 to 5% in a lithium- base grease resulted in significant enhancement in weld loads and reduction in the wear scar diameter (in accordance with ASTM D 2266). A similar thought is shared by Mistry et al. [34] who, on the other hand, also suggest that with MoS_2 concentrations greater than 2% in calcium-base grease, there was noted a decrease in the weld load. The optimum load/wear performance appeared to be achieved when 5% of the additive was used in greases. With this background, the low and high concentrations of MoS_2 were set at 3 and 5 weight %.

PTFE (polytetrafluoroethylene) is another solid boundary lubricant that has been used to reduce wear and provide longer life for bearing surfaces. PTFE does not have a layered lattice structure and has the advantages of chemical stability and inertness over a wide range of temperatures-from cryogenic to approximately 250℃ with one of the smallest coefficients of static and dynamic friction that is attributed to the smooth molecular profile of the polymer chains, which orient such that easy sliding is promoted.

Another S-P containing lubricant, ZDDP (zinc diakyl dithiophosphate) has been used in the lubricant industry for more than five decades as a low-cost, multifunctional additive owing to its ability to function as an excellent antiwear agent, a mild EP additive, and an effective oxidation and corrosion inhibitor at costs very low compared to the alternate chemistries available in the market. Shaub et al. [35] suggest that it is extremely difficult to achieve both good anti-wear and EP characteristics in single grease, two properties that are required for greases. They also suggest that ZDDP and PTFE (functionalized and irradiated) alone do not provide significant extreme pressure protection. However, with the use of 2 % ZDDP and 2 % (by weight) to the grease doubled the weld load numbers as compared with grease comprising MoS_2 alone. The PTFE-ZDDP combination enhances the rate of decomposition of ZDDP and can form reaction products that can be used as high-performance lubricant additives. Therefore, two blends of the greases, Blend L (3% ZDDP and 2% PTFE) and Blend H (5% ZDDP and 4% PTFE) were formulated and the results compared with greases containing 3 and 5 weight % MoS_2. In an attempt to observe whether or not synergism occurs between MoS_2, ZDDP and PTFE, a mixture of 3% MoS_2 + Blend L is formulated. With the intent to understand the role played by sulfur and non-sulfur carriers when used with other additives like ZDDP, PTFE or a combination of ZDDP and PTFE, relevant chemistries have been formulated as are listed below.

1. 3% MoS_2 (Technical Grade and Technical Fine Grades) in Li-base grease
2. 5% MoS_2 (Technical Grade and Technical Fine Grades) in Li-base grease
3. Blend L (3% ZDDP and 2% PTFE)
4. Blend H (5% ZDDP and 4% PTFE)
5. 3% MoS_2 + Blend L
6. 3% Vanlube Additives (Sulfur and non-sulfur carriers) in Li-base grease
7. 3% Vanlube Additives (Sulfur and non-sulfur carriers) + 5% Blend L
8. 3% Vanlube Additives (Sulfur and non-sulfur carriers) + 2% PTFE
9. 3% Vanlube Additives (Sulfur and non-sulfur carriers) + 3% ZDDP

3.3.4 Protocol for running the Four-Ball Tests

The different grease chemistries were prepared following the methods as provided in the Appendix A and Appendix B.

3.3.5 Types of tests

The greases were tested for two types of tests on the Four-ball tester:

3.3.5.1 Wear Test

ASTM D 2266 specifies that the top ball be rotated at a speed of 1200rpm for 60 minutes and pressed with a force of 40 kgf. This test has been extensively used over the years to screen greases and other lubricants and compare the wear characteristics of these lubricants. However, applications are not limited to these conditions and frequently lower speeds, longer durations and higher loads are applied. Development of a model to predict the extent of wear under these varied conditions will be described in the following sections.

3.3.5.2 EP Test

This test is run according to ASTM D 2596-97 with one steel ball rotated against the other three stationary steel balls with a speed of 1770 +/- 60 rpm and the operating temperature is maintained at 27 +/- 8℃. A series of tests are con ducted of 10 second duration by increasing the load (as specified by the ASTM Standard) till the sliding surfaces seize and welding occurs.

3.3.6 Post-test Analysis Characterization Equipments

(1) Optical Microscope

Nikon SMZ 1500 Optical Microscope was used to perform primary low magnification studies of the wear track.

(2) SEM/EDS:

Scanning Electron Microscope was used to image the surfaces of the wear tracks formed as a result of the wear test performed on the 4-Ball tester. The images were taken both at low and high magnifications. The SEM in the facility used was a Hitachi S-3000N Variable Pressure SEM. Along with the SEM, Energy Dispersive Spectrometry was done to gain an elementary understanding into the chemical compositional analysis. Both spectral and elemental mapping was done to establish the presence of certain elements.

CHAPTER 4

EFFECT OF TEST PARAMETERS ON THE 4-BALL WEAR AND WELD PERFORMANCE OF GREASES WITH MOS_2 AND WITHOUT MOS_2 AS EP ADDITIVES

4.1 Introduction

Lithium based and lithium complex greases make up over 50% of the greases used in the industry today. While lithium based greases offer very good lubricating properties they do not provide either wear or load bearing capacity. In order to achieve both wear and load bearing capacity, different additives have been used over the years with varying degrees of success. The chief among these are MoS_2 [43, 40, 44] and graphite4 that have been used as extreme pressure (EP) additives in greases and poly tetrafluorethylene [46] (PTFE) that has been used to reduce friction and zinc dialkyl dithiophosphate [47] (ZDDP) that has been added to reduce wear. Many of these studies have examined the influence of additives one at a time to examine their effects on wear performance of the grease. In an effort to reduce the extent of wear ZDDP was added to Lithium 12 hydroxystearate grease and results indicated an improvement of wear properties. However, a NMR examination of the grease indicated an ion exchange with the Li in the grease yielding a lithium dialkyl dithiophosphate structure.

Molybdenum Disulfide (MoS_2) based greases have been in use for a very long time and have found application extensively in extreme pressure situations. The lamellar structure of MoS_2 provides very good weld protection by forming a layer that can be easily sheared under the application of extreme pressures. However, it has been found that at lower loads the MoS_2 sometime behaves as an abrasive and results in enhanced wear. In efforts to better understand the role of MoS_2 in grease performance several studies have been conducted. In one study it has been shown that MoS_2 forms a lubricating film on the metal surface and under extreme frictional conditions the MoS_2 reacts with the Fe on the surface forming FeS with Mo diffusing to the metal surface [43]. In a related study with MoS_2 it was shown that increasing the MoS_2 content in the grease resulted in improved load wear index and weld loads determined by four ball EP test[44]. In a study examining the role of graphite, it was shown that increasing the graphite content in a PAO grease improved wear performance under extreme load conditions and it was independent of the type of graphite used [45]. When graphite and MoS_2 were compared, it was shown that MoS_2 had superior load bearing capacity as well as anti-seize and anti-wear behavior at equivalent levels of additive2. In efforts to reduce the extent of friction in a wear test PTFE of different particle sizes was added. Results indicate that PTFE that was irradiated was superior to the un-irradiated PTFE and PTFE with smaller particle sizes yielded better frictional characteristics.

A more recent study examining the development of a low MoS_2 grease reported that in block on ring wear tests increasing the amount of MoS_2 in a grease at test loads of 15 and 30 kg resulted in increase in the size of the wear scar indicating at low loads that MoS_2 may actually behave as a pro-abrasive while under EP conditions it helps increase the weld load and load wear index. In an effort to develop MoS_2 free greases, new combinations of thiophosphate compounds and fluoropolymers were developed that offered very good combination of both antiwear and load bearing capacity. These chemistries were developed utilizing the synergistic interaction between the functionalized fluoropolymer and the thiophosphate compound [49]. The ASTM D 2266 test has been used extensively over the years to screen greases and other lubricants and compare the wear characteristics of these lubricants. While this method is very useful to compare several greases tested under fixed test conditions it is not always representative of conditions in the field where different speeds, duration and loads are applied. Applications are not limited to these conditions and frequently lower speeds are used, longer durations as well as higher loads are applied. Development of a model to predict the extent of wear under these varied conditions forms the basis of this chapter. In addition to using a MoS_2

based grease both for intermediate and extreme pressure loads we have developed a MoS_2 free grease based on using a functionalized fluoropolymer and an organophosphate and we compare the wear, weld and load wear index of this grease with a MoS_2 based grease. In addition, the role played by the base grease i.e. lithium stearate, organo lithium and poly urea on the wear, load wear index and weld behavior of these greases is explored.

The chapter will lead into development of a grease that exhibits both extreme pressure properties as well as good wear properties under a variety of conditions. A new grease based on a synergistic interaction between a proprietary thiophosphate compound and functionalized fluoropolymer was developed where the resulting grease had a favorable combination of wear behavior and weld and load wear index properties. Two compositions of this grease were developed to address both the intermediate and extreme load conditions of applications. The design of experiments approach is used to systematically vary the test conditions such as applied load, duration of the test and speed of the test to examine the outcome in the wear tests. We have used the DOE software to predict the extent of wear within these broad set of test conditions and determined the interaction between the test conditions and the extent of wear in both low and high MoS_2 based grease.

4.2 Design of Experiment

In an engineering environment, experiments are conducted to explore, estimate or confirm. We perform experiments to increase our knowledge and understanding of various processes. In manufacturing processes, it is crucial to explore the relationship between the key input process variables and the output performance characteristics.

One common methodology followed by engineers is the One-Variable-At-a-Time (OVAT) approach, where one variable is varied keeping the others fixed. This approach relies on guesswork, luck and intuition for its success and requires large resources to obtain limited information about the process. OVAT experiments are often unreliable, inefficient, time consuming and may give false optimum condition for the process.

When several variables influence a certain characteristics of the product, the best strategy is to design an experiment so that valid, logical and reliable conclusions can be drawn effectively and economically. It is important to note that some variables may have strong influences on the output performance, some may have medium and some have no influence at all. Thus, the objective is to understand the variables that affect the performance the most and determine the optimum levels for these variables to obtain satisfactory output functional performance.

The factorial design approach enables all variables to be varied simultaneously in a predetermined fashion. With this approach, it is possible to determine the influence of a factor on the outcome when two or more of the other variables are varied simultaneously. A factorial design first identifies the variables that need to be studied and their value ranges. These variables can either be numerical or categorical, depending on whether they are quantifiable or not. [43]

Design of Experiments refers to the process of planning, designing and analyzing the experiment so that valid and objective conclusions can be drawn. The three principles of experimental design such as replication, randomization and blocking can be utilized in industrial experiments to improve the efficiency. Randomization allows for the minimization of external variables, as operator error, test environment, machine variability, and the errors in the outcome and model. Replication is a process of repeating the entire or a portion of the experiment. Replication allows the experimenter to obtain an estimate of the experimental error and any bias or experimental errors can be evenly distributed across the experimental runs or trials. Blocking is a method of eliminating the effects of extraneous variation due to noise factors and thus improves efficiency of the experimental design. Generally, a block is a set of relatively homogeneous experimental conditions.

The outcomes of any design can be evaluated by various methods. The least square method gives quantitative information about the effect of a variable with respect to the other variables or the interactions between them. With this information, a list of the main effects and interactions can be estimated and can be ranked based on the relative importance. The Half-Normal Probability plot is the graphical counterpart that gives information about the relative importance of one, two or multifactor interactions. This plot does not apprise the user of the beneficial or detrimental effects of the variables and the interactions between them. After identifying the variables, the interactions between them can be graphically plotted using Response Surface Method (RSM). This method derives importance in situations where a curvilinear response is expected. Both contour and wireframe plots are used to show the dependence of the outcome on the variables. In a contour plot, the response surface is viewed as a two-dimensional plane where all points having the same response are connected to produce contour lines of constant responses. A wireframe plot displays the three-dimensional view of the interactions between two variables and provides a graphical method to view the response surface and provides physical explanation of the interaction between the variables. Both contour and wireframe plots help experimenters to understand the nature of the relationship between the two factors and the response.

4.3 Design software

Stat-Ease Version 7.1 of Design Expert software was used for the design of experiments (DOE). It provides the following statistical tools:

1. Two-level factorial screening designs identify the vital factors that affect the process or product
2. Response surface methods (RSM) for finding the optimal process settings to achieve peak performance
3. Mixture design techniques help discover the ideal recipe for product formulation

The design is selected depending on the application, whether process, screening, and experimentation. Experiments are performed in the order as specified by the design. After the response data has been fed in the design, the response or responses are analyzed individually. After the analysis, the responses are optimized as per the desired conditions.

4.4 Test Method

Four ball wears tests were performed using the Plint Four-ball Wear Tester (Model number TE92). ASTM standard designation D2266, chrome-plated steel balls (Bearing-quality Aircraft Grade E52100), three in number, of ½ inch diameter were clamped together and covered with the grease to be tested. The fourth ball was clamped in a ball chuck and the load was applied using a pneumatic loading system. The temperature of the lubricant was maintained at 75℃. The diameter of the wear scar produced on the three stationary balls was measured using an optical microscope.

Table 4.1 summarizes the tests conducted under various conditions of load, RPM and duration. Five chemistries, 280L, 280H, 3% MoS_2, 5% MoS_2 and 280L + 3% MoS_2 grease were studied and for each of these chemistries the test matrix listed below were conducted. A full factorial of tests was conducted in each case.

Table 4.1 Details of Test Conditions in Four-Ball Wear Design Matrix for 4 Ball Wear Test

Test Load (Kgs.)	RPM	Duration of Test (Hours)
40	600	1
40	600	2
40	1200	1
40	1200	2
80	600	1
80	600	2
80	1200	1
80	1200	2

Table 4.2 Chemistry of Base Grease and Antiwear Additives and Test Conditions of Wear and Weld Tests

Base Grease	Antiwear Additives	Tests Conducted
NLGI 2 Lithium 12 Hydroxy Stearate	280 H and 280 L	4 Ball Wear (40 and 80 Kg) Weld
NLGI 2 Lithium 12 Hydroxy Stearate	3% MoS_2 or 5% MoS_2	4 Ball Wear (40 and 80 Kg) Weld

The Plint Four-ball Wear test was carried out at University of Texas at Arlington, Texas. In conformance with the ASTM Designation D2596-97, one steel ball was rotated against the other three stationary steel balls with a speed of 1770+/-60 rpm and the operating temperature was maintained at 27+/-8℃. A series of tests each of 10-second duration were conducted with increasing loads until the weld point. The Weld Test, on the other hand, ascertains the lowest applied load at which the sliding surfaces seize and weld together.

4.5 Four Ball Wear Tests

Four ball wear tests were conducted for the five compositions listed in the experimental section and test conditions detailed in Table 4.1. The images of wear scars were also recorded in each case and representative wear scars are shown in the results.

4.5.1 3% MoS_2 Grease

Figure 4.1(a,c) is the response surface diagram for wear scar in a four ball wear test of the 3% MoS_2 grease as a function of time of test and RPM for loads of 40 and 80 kg respectively, superimposed are the actual data for the test conditions. Figures 4.1(b,d) are predictions of the test conditions for a specific wear scar diameter. Figures 4.1(a,c) indicate that MoS_2 behaves as a physical lubricant as well as a abrasive, increasing the test duration at either 40 Kg or 80 Kg always results in an increase in wear .

The total amount of wear at the end of a test conducted at 600 rpm for 2 hours and a test conducted at 1200 rpm for 1 hour, both of which have the same number of rotations is approximately the same with the test conducted at 1200 rpm having a slightly larger wear scar. The wear scar diameter for the standard ASTM 2266 test condition is approximately 0.6 mm while longer duration test result in an increase in wear scar diameter to 0.9 mm indicating that a protective film is not formed. In addition, increasing the load of the test to 80 Kg results in a significant increase in wear scar diameter with the test conducted at 80 Kg for 2 hours at 1200 rpm having a wear scar diameter of 1.28 mm. In all cases the wear scar indicated that abrasive wear is the mechanism of material removal and evidenced by the deep scratch marks on the wear scar. The predictions for the wear scar indicate an approximate -45° slope in the relation between test duration and rpm of the test indicating that number of cycles in a test is the primary factor that determine the extent of wear, again indicative of abrasive wear as the primary mechanism of material removal.

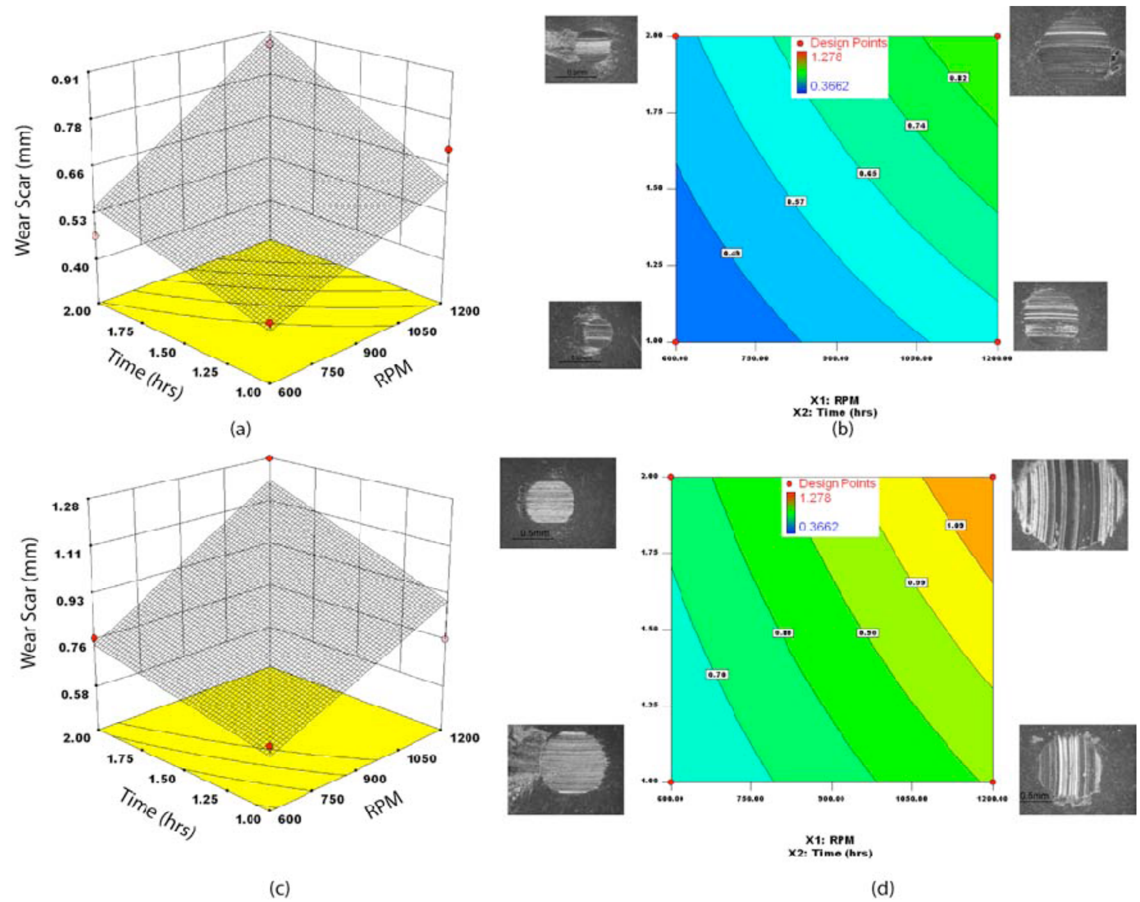


Figure 4.1 (a,c) Response surface diagram of a 3% MoS_2 grease tested at a load of 40 and 80 Kg respectively showing the role played by test duration and RPM on wear scar diameter. (b,d) shows the predicted wear scar diameter for various combinations of RPM and test time for the same test combinations. Superimposed are optical micrographs of the wear scars measured at the four extremes of test duration and rpm of test.

MoS_2 has been added as an EP additive extensively in greases. MoS_2 has a layered hexagonal structure where strong covalent bonding hold the Mo and S together, the hexagonal layers are held together with weak Vanderwaals bonding and the layers can be sheared easily along the S-S bond providing physical lubrication. The particles of MoS_2 are sheared and thus prevent the contacting layers from seizing together. However, at low loads it is quite possible that the MoS_2 layers are not sheared and the hard and rough surfaces of the MoS_2 can potentially act as an abrasive. It has been shown that at lower temperatures MoS_2 does not interact with the metal surface and behaves as a physical lubricant. In a study on the role of environment on the lubrication properties of MoS_2 it was shown that the presence of moisture in the test environment resulted in poor wear properties while an Ar or dry air environment resulted in better wear behavior. In a mechanistic study of the role of moisture on wear characteristics of MoS_2 in sliding conditions it was shown that in the presence of moisture there is a softening of the MoS_2 resulting with a thinner contact film formed. The thinner films formed in presence of moisture was attributed to the poor wear performance. The poor performance of the 3% MoS_2 grease may be attributed to the combination of irregular particle size of the Techfine MoS_2 (Figure 4.2) and the possible influence of moisture during the test on the wear behavior.

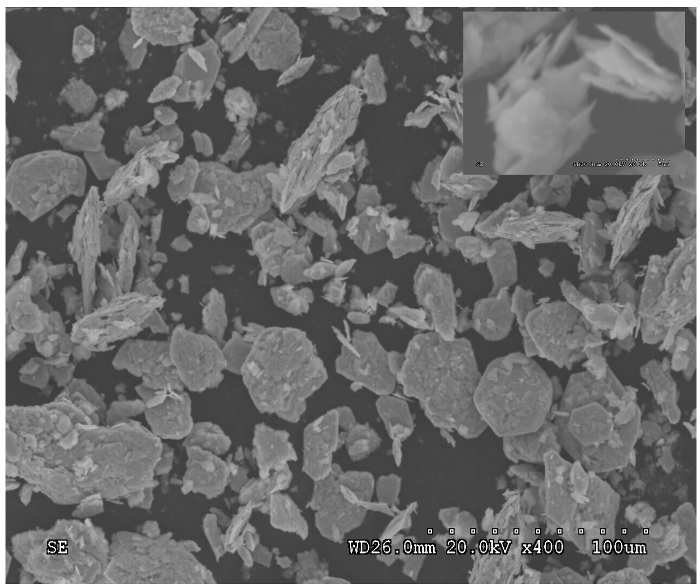


Figure 4.2 SEM image of MoS_2 particles at magnification of 400X

4.5.2 5% MoS_2 Grease

In order to develop grease for EP conditions, 5 wt. % MoS_2 was added. Figure 4.2(a,c) is the response surface diagram for wear scar in a four ball wear test of the 5% MoS_2 grease as a function of time of test and RPM for loads of 40 and 80 kg respectively, superimposed are the actual data for the test conditions. Figure 4.2(b,d) are predictions of the test conditions for a specific wear scar diameter.

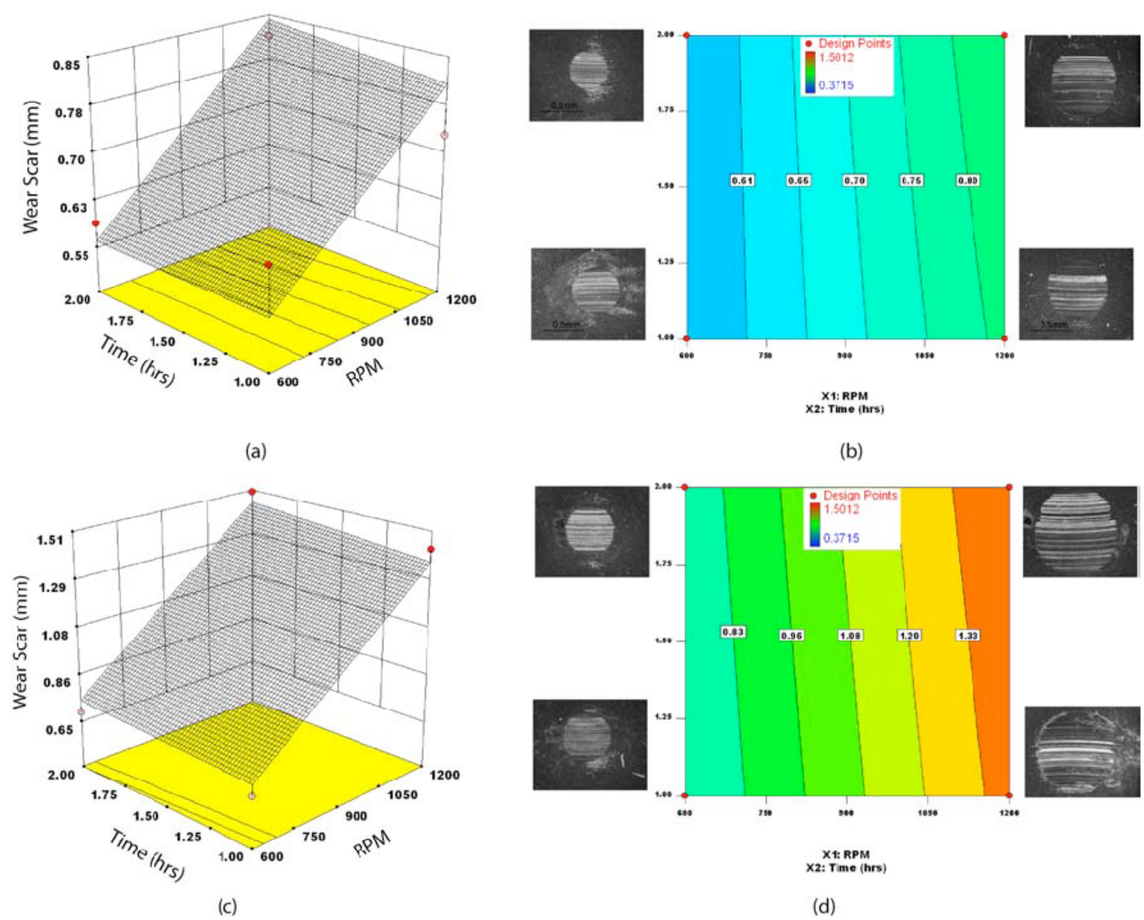


Figure 4.3 (a,c) Response surface diagram of a 5% MoS_2 grease tested at a load of 40 and 80 Kg respectively showing the role played by test duration and RPM on wear scar diameter. (b,d) shows the predicted wear scar diameter for various combinations of RPM and test time for the same test combinations. Superimposed are optical micrographs of the wear scars measured at the four extremes of test duration and rpm of test.

Comparison of Figure 4.1(a,c) with figure 4.2(a,c) indicates that increasing the amount of MoS_2 increase the extent of wear for all test conditions. However, an important difference between the 3% MoS_2 and 5% MoS_2 is the strong dependence on duration of the test on the wear scar diameter in the composition with 3% MoS_2 while in the composition with 5% MoS_2 the extent of wear while larger than the composition with 3% MoS_2, it does not show the same dependence. The wear surfaces in this case also exhibit extensive amount of abrasive wear. The predictions of wear scar diameter as a function of test duration and rpm also indicate that for a given rpm the duration of the test does not increase the wear scar diameter. However, increasing rpm of the test does result in an increase in the extent of wear.

4.5.3 280 L Grease

280 L is a mixture of organo phosphate and functionalized fluoropolymer used at a 5% treat rate and meant as a replacement of the 3% MoS_2 grease. Figure 4.3 (a,c) is the response surface diagram for wear scar in a four ball wear test of the 280L grease as a function of time of test and RPM for loads of 40 and 80 kg respectively, superimposed are the actual data for the test conditions. Figure 4.3 (b,d) are predictions of the test conditions for a specific wear scar diameter.

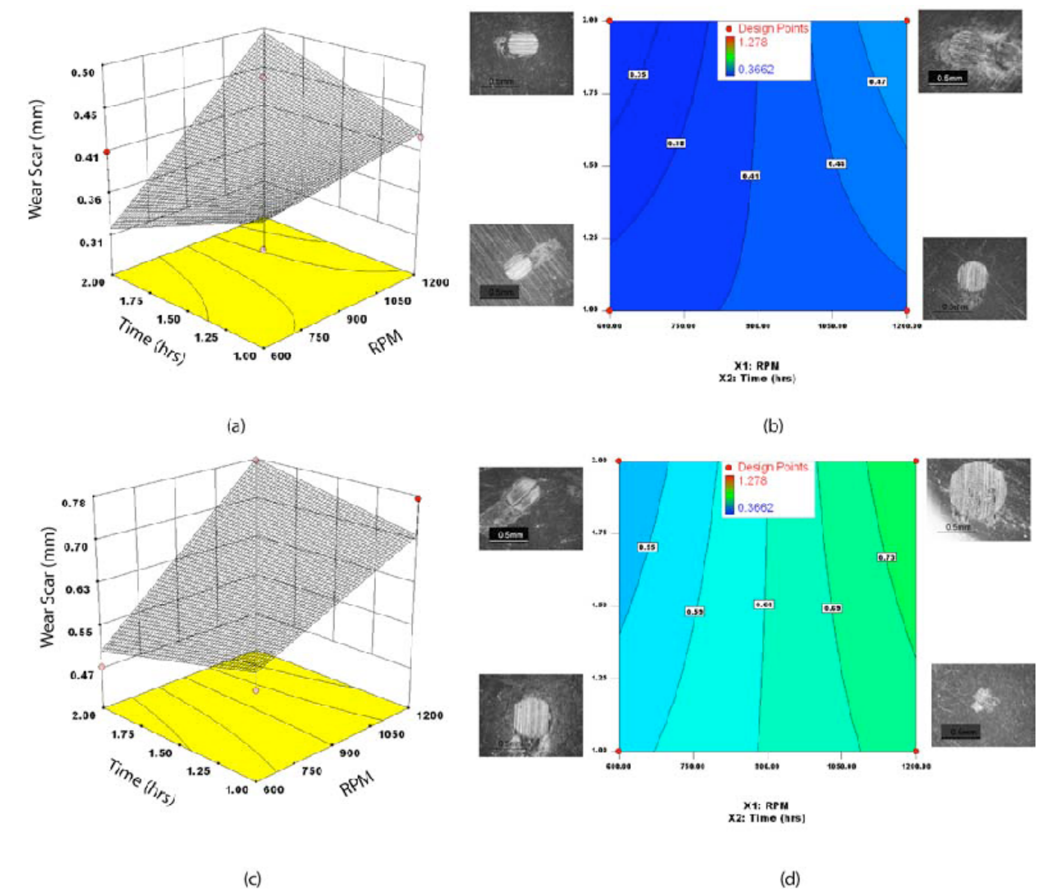


Figure 4.4 (a,c) Response surface diagram of a 280 L grease tested at a load of 40 and 80 Kg respectivelyshowing the role played by test duration and RPM on wear scar diameter. (b,d) shows the predicted wear scar diameter for various combinations of RPM and test time for the same test combinations. Superimposed are optical micrographs of the wear scars measured at the four extremes of test duration and rpm of test.

Comparison of Figure 4.1(a,c) with Figure 4.3(a,c) it is evident that greases with 280L as the antiwear additive exhibit significantly lower levels of wear for test conditions in 4 ball wear. In addition, for all test conditions including 2 hrs at 1200 rpm at 40 Kg load the extent of wear is below 0.5 mm. Even at 80 Kg load the maximum wear scar diameter is 0.78 mm. It is also evident that increasing the duration of the test at a fixed rpm either at 40 Kg or 80 Kg does not significantly increase the extent of wear indicating that a tribofilm forming on the surface is responsible for the reduced levels of wear. The functionalized fluoropolymer has carboxylic acid functional groups surrounding it making it much more active and it interacts with the organothiophosphate.

Organo thiophosphate compounds such as Zinc dialkyl dithiophosphate have been used extensively as anti-wear additives in applications ranging from engine oils [44,45] to greases [43] and gear oils and help protect the surface by forming a protective glassy tribofilm made up of short and long chain poly phosphates of Fe and Zn together with sulfides of Zn and Fe. These glassy films are formed by a thermochemical breakdown of the organothiophosphate compounds and their subsequent reaction with the substrate to form the tribofilms.

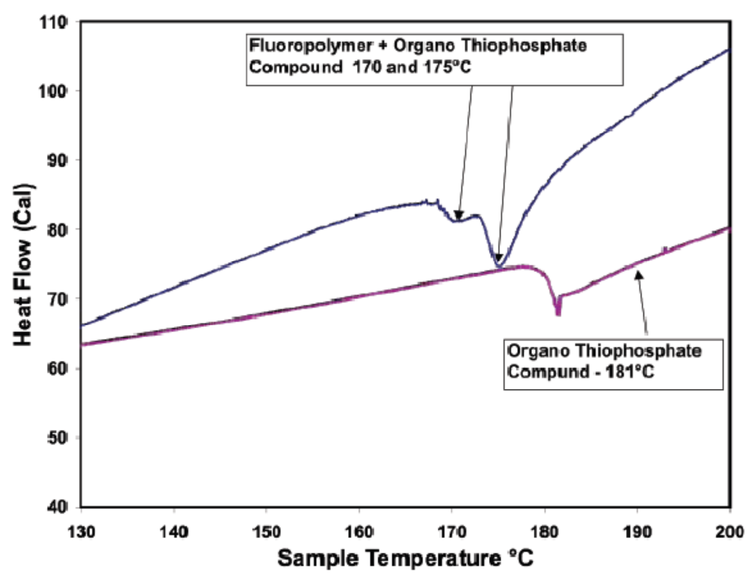


Figure 4.5 Differential scanning calorimeter scans of the organothiophosphate compound and a mixture of fluoropolymer with the organothiophosphate compound.

Figure 4.4 is a Differential scanning calorimeter plot of the organothiophosphate and a mixture of the organo thiophosphate and functionalized fluoropolymer heated from room temperature to 200℃, for clarity the data from 130 to 200℃ is shown. The figure indicates that the organothiophosphate decomposes at a lower temperature in the presence of the fluoropolymer; in addition, an extra endotherm present at 170℃ suggests the formation of a new reaction product in the presence of the fluoropolymer. In an earlier study with ZDDP and FeF_3 it was shown that compounds that are fluorinating agents are able react with ZDDP yielding a fluorinated version of ZDDP that is more reactive and effective as an antiwear agent [46]. It is likely in the current case the functionalized fluoropolymer being very reactive, forms a complex with the organophosphate making it more likely to deposit on the tribological surface reducing the extent of wear.

4.5.4 280 H Grease

280 H is grease with a larger concentration of both the fluoropolymer and thiophosphate compound and is used at a 9 % treat rate. Comparison of Figure 4.3 and Figure 4.5 for the 280L and 280H indicate that the extent of wear in both cases is very similar. 280 H is developed as an alternate to the 5% MoS_2 grease and a comparison of Figure 4.2 and Figure 4.5 indicates that the 280 H exhibits superior wear performance for all test conditions in 4 ball wear in comparison to a 5% MoS_2 grease. The mechanism elucidated for the 280 L is equally valid in this case. It is anticipated that having a larger concentration of both the organothiophosphate and fluoropolymer may yield better load bearing capacity compared to a 280 L and the MoS_2 based grease.

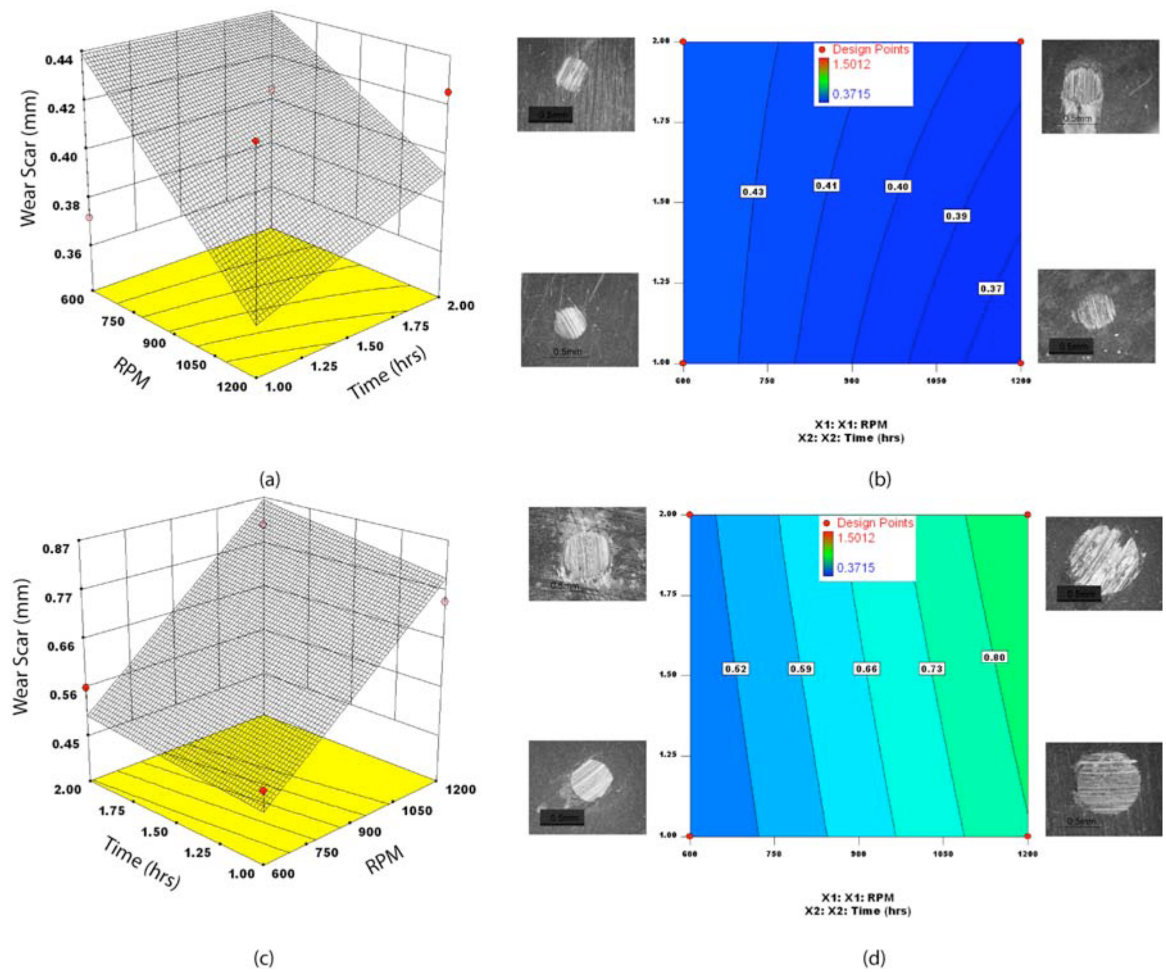


Figure 4.6 (a,c) Response surface diagram of a 280 H grease tested at a load of 40 and 80 Kg respectively showing the role played by test duration and RPM on wear scar diameter. (b,d) shows the predicted wear scar diameter for various combinations of RPM and test time for the same test combinations. Superimposed are optical micrographs of the wear scars measured at the four extremes of test duration and rpm of test.

4.5.5 280L + 3% MoS_2 Grease

The 3% MoS_2 grease exhibited very high levels of wear both with the 40 and 80 Kg loads as shown in Figure 4.1. 280 L on the other hand exhibited very good 4 ball wear resistance both at 40 and 80 Kg. A blend of 280 L and 3% MoS_2 grease was prepared to examine if there was any synergistic interaction between the mixture of fluoropolymer and organothiophosphate and the MoS_2. Figure 4.6 (a,c) is the response surface diagram showing the wear scar diameter as a function of test duration and rpm in four ball wear at both 40 and 80 Kg respectively. Comparison of figure 4.6(a,c) with figure 4.1(a,c) and Figure 4.3(a,c) indicate some similarities and important differences. It is evident that addition of the 280 L to the 3% MoS_2 grease significantly improved its wear properties and brings the wear scar diameter more in line with the 280 L. However, the dependence of the wear scar diameter on the duration and rpm of the test indicate that the mechanism is similar to the 3 % MoS_2 grease as shown from a comparison of figures 4.1(b,d), 4.3(b,d) and Figure 4.7(b,d). This indicates that the combination of the fluoropolymer and the organophosphate mitigate the abrasive nature of the MoS_2 but does not completely eliminate it.

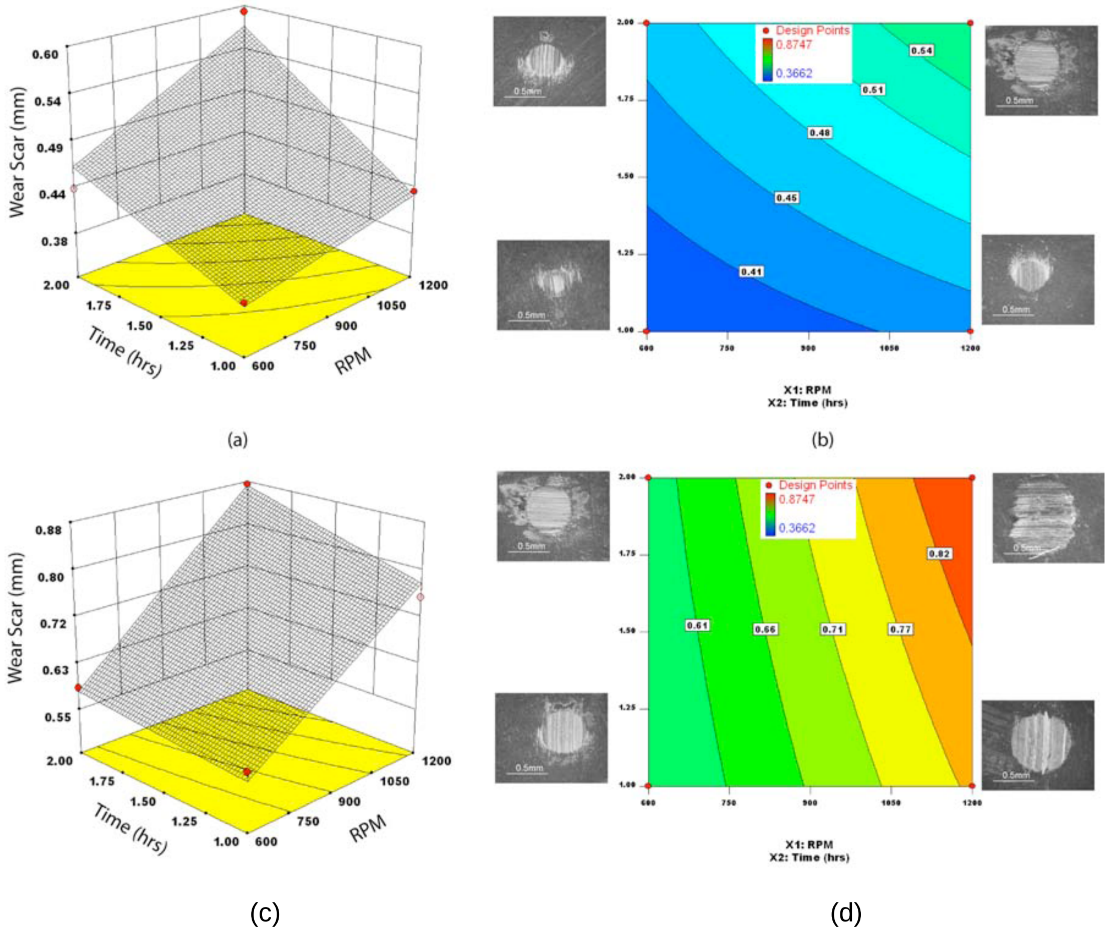


Figure 4.7 (a,c) Response surface diagram of a 280 L + 3% MoS_2 grease tested at a load of 40 and 80 Kg respectively showing the role played by test duration and RPM on wear scar diameter. (b,d) shows the predicted wear scar diameter for various combinations of RPM and test time for the same test combinations. Superimposed are optical micrographs of the wear scars measured at the four extremes of test duration and rpm of test.

4.6 Weld Load

Weld load tests were conducted in accordance with ASTM D 2596 -2002.

Figure 4.8 shows the weld load for the different EP additives in different base grease formulations. It is immediately apparent from the figure that the additive 280H offers extremely good load carrying capacity with weld loads as high as 800 Kg in a lithium-base grease. The synergistic interaction between the functionalized fluoropolymer and the organothiophosphate are responsible for the improved performance. In addition, it is also evident that having a larger concentration of the EP additive plays an important role in determining the weld load when 280H (9% treat rate) is compared to 280L (5% treat rate). 280L as a weld load comparable to a 3% MoS_2 grease while the 280H far exceeds the performance characteristics of a 5% MoS_2 grease.

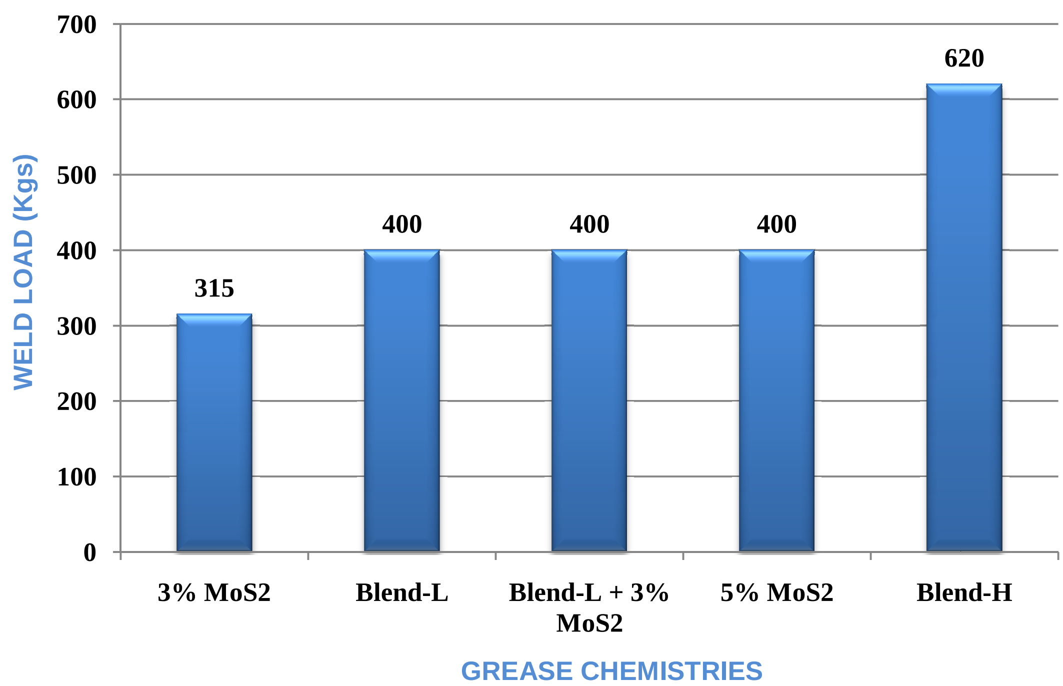


Figure 4.8 Four-Ball EP weld test performed based on ASTM D2596-2002 standard

4.7 Morphological Analysis of films formed by MoS_2

The response surface diagrams and the optical micrographs for the different grease chemistries, subjected to various conditions of load, RPM and duration on the Four-ball Wear Test, suggest that the Blend-H and Blend-L offer excellent combination of wear, load wear index and weld load. Solid lubricants may also be used as additives to enhance the performance of the greases under boundary conditions. MoS_2 has long since been used as an EP additive in greases, but experimental results suggest that Blend-L and Blend-H outperform 3% MoS_2 and 5% MoS_2 respectively, on the wear and weld performance. The mechanism of lubricating action has further been studied by Scanning Electron Microscopy and EDS analysis.

The lubricating behavior of MoS_2 is based on its ability to form a film on the metal surface by many-fold displacement of the MoS_2 layers. Further displacement of the MoS_2 lamellae does not occur once the film has been formed. MoS_2, however, becomes abrasive if the MoS_2 lamellae are not arranged parallel to the contact point or the particles are irregularly-shaped and have hard edges. The SEM images (Figure 4.9 (a) through (d)) for 3% MoS_2 and 5% MoS_2 suggest that MoS_2 particles act as an abrasive by ripping the surface. The presence of plowing grooves parallel to the direction of sliding, wear debris and few cavities on the wear tracks are indicative of occurrence of abrasive wear.

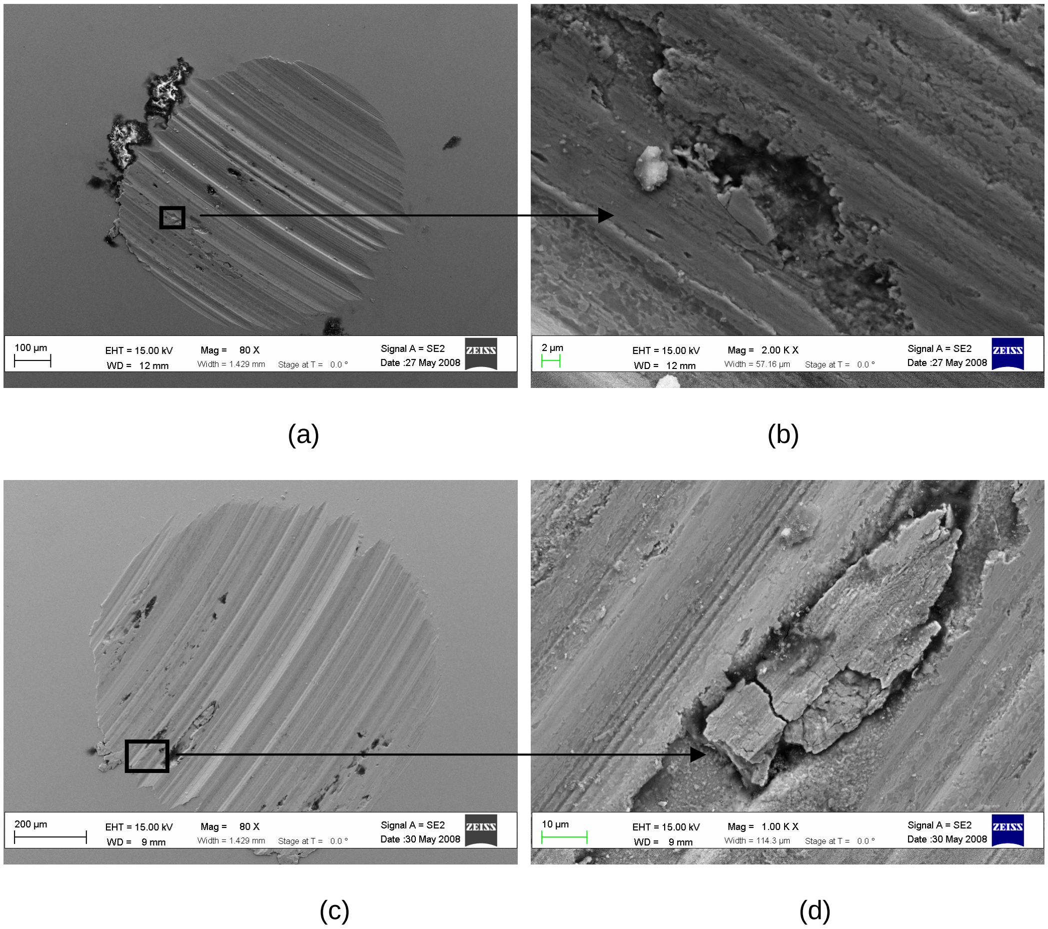


Figure 4.9 SEM micrographs showing the wear tracks observed at 80kg/1200rpm/1hour test condition. (a,b) For 3% MoS_2 at 80X and 2000X magnifications respectively, and (c,d) For 5% MoS_2 at 80X and 1000X magnifications respectively.

The wear track (Figure 4.10) for the grease containing 3% MoS_2 shows distinct grooves and wear debris indicating that abrasive wear has occurred. This is in conformance with the fact that the hard and rough edges of the MoS_2 are abrasive and rip the film off the surface. Also, unless the shear planes enter parallel in the contact point, protection by MoS_2 is not provided. There appears some microcracking in a direction perpendicular to the direction of sliding suggesting the brittle nature of the tribofilm.

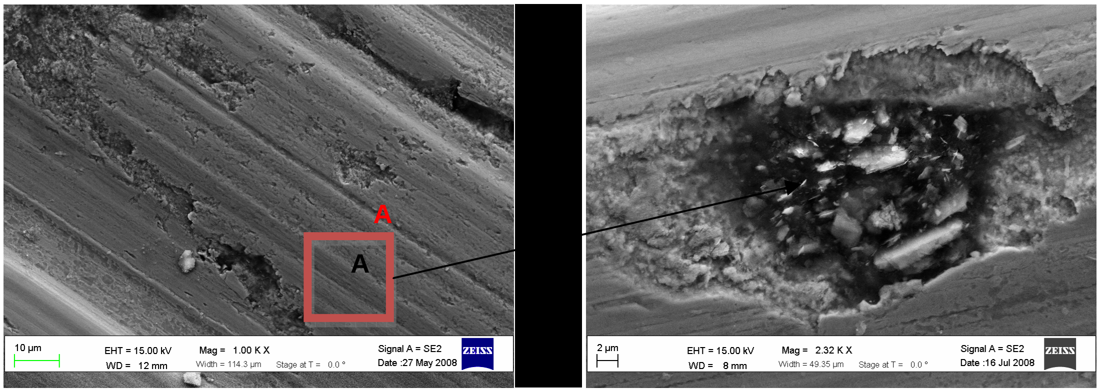


Figure 4.10 SEM images on the wear track of a 3% MoS2 grease 80kg/1200RPM/1hour conditions(left) and enlarged image of the area ‘A’ (right)

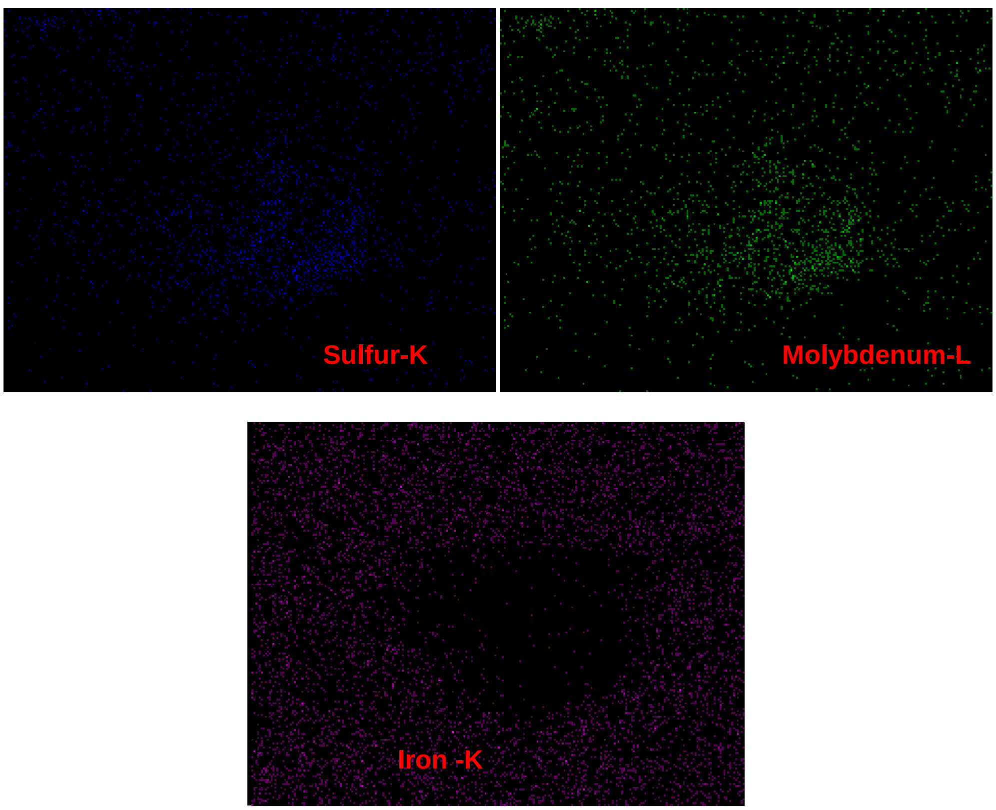


Figure 4.11 Elemental mapping of the area ‘A’ on 3%MoS_2 grease run at 80kg/1200RPM/1hour

The elemental mapping performed on the region A (as shown in Figure 4.11) suggests the presence of Mo and S in the area A and large concentrations of Fe in the surrounding area.

The MoS_2 particles have abraded the surface and the wear debris in the area of interest have deposited on the wear tracks.

CHAPTER 5

ROLE OF SULFUR AND NON-SULFUR CARRIERS ON THE WEAR AND EP PERFORMANCE OF GREASES

5.1 Overview

This chapter discusses the effect of various sulfur carriers on the wear and extreme pressure properties of greases. The wear and EP tests are conducted on the Four-ball wear test, with methodology as specified in Chapter 3 and the results studied through response surface plots obtained through the Design of Experiment Stat-Ease software.

There are two main types of AW and EP additives, active and non-active. The active additives usually react chemically with the metal surface to form a sacrificial film on it. The non-reactive species form films by deposition of themselves or their by-products. Examples of non-active types include boron, silicon, aluminum and lead compounds. In this work, only the active species are dealt with. Papay [47] in his paper on antiwear and extreme-pressure additives in lubricants quotes that only elements that can form iron compounds can be used in EP/AW additives which make compounds of sulfur, phosphorus and chlorine the preferential options. With sulfur, any compound that can break under the energy input stress, as heat, and allow for a free sulfur to combine with iron could do well as an EP/ AW additive [48]. Such compounds include dialkyl mono,di, or polysulfides, sulfurized olefins, sulfurized fats, and dithiocarbamates. Sulfur, alone or with other materials and in different chemical combinations, is one of the most important elements in various lubrication applications. Of all the elements, sulfur probably gives the best synergistic results in combination with other elements and organic compounds [49].

5.2 Selection of the design

The variables used in the formation of the design were the concentrations of ZDDP, PTFE, and the various sulfur and non-sulfur-carrier chemistries in the lithium base grease. Full-factorial designs were used since it allows studying the main effects and desired interaction effects in minimum number of trials or experimental runs. They are most widely and commonly used types of design in the industry. For each of the factor that is studied, there is a low and high level associated, thus the selection of two-level half-factorial design.

The high and low level of the additives was based on the fact that the commercially available lithium greases generally contain 10% the total concentration of the additives. To obtain maximum performance at optimum cost, the level of the sulfur carriers was kept at 0 and 3%, ZDDP 0 and 3%, PTFE (Irradiated) 0 and 2%.

5.3 Design and design evaluation

The design type chosen is the full factorial with two levels. The design model is 2-FI and no blocks were included in the design.

Table 5.1 Design matrix for the evaluation of interactions between ZDDP,PTFE and sulfur and non-sulfur carriers in Li-base greases

S.No.	Run Order	Concentration of ZDDP (%)	Concentration of PTFE (%)	Concentration of Sulfur and Non-sulfur additives (%)	Response 1: Wear Scar Diameter (WSD) mm	Response 2: Weld Load (kgs)
1	5	0	0	0		
2	2	3	0	0		
3	6	0	2	0		
4	9	3	2	0		
5	1	0	0	3		
6	3	3	0	3		
7	4	0	2	3		
8	7	0	2	3		
9	8	3	2	3		

After obtaining the test results, the values are entered in the response columns and the responses are analyzed using the Stat-Ease Version 7.1 Design of Experiment software.

5.4 Wear and Weld results

The wear (Figure 5.1 and Figure 5.2) and weld tests (Figure 5.3 and Figure 5.4) and were run on the Four-Ball tester under ASTM Standard D 2266 and D 2596 test conditions respectively. The results obtained are as given in the following graphs and the interactions are studied and discussed using the Design of Experiments and the wear surfaces are analyzed using SEM/EDS (Chapter 6).

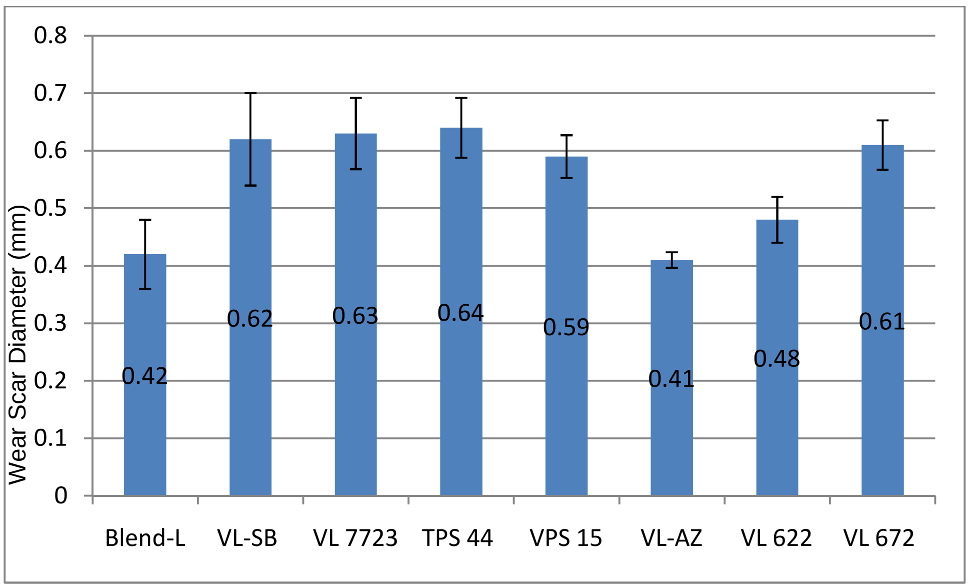


Figure 5.1 Chart showing the WSD values for different grease formulations with 3% VL additives in Li-base grease

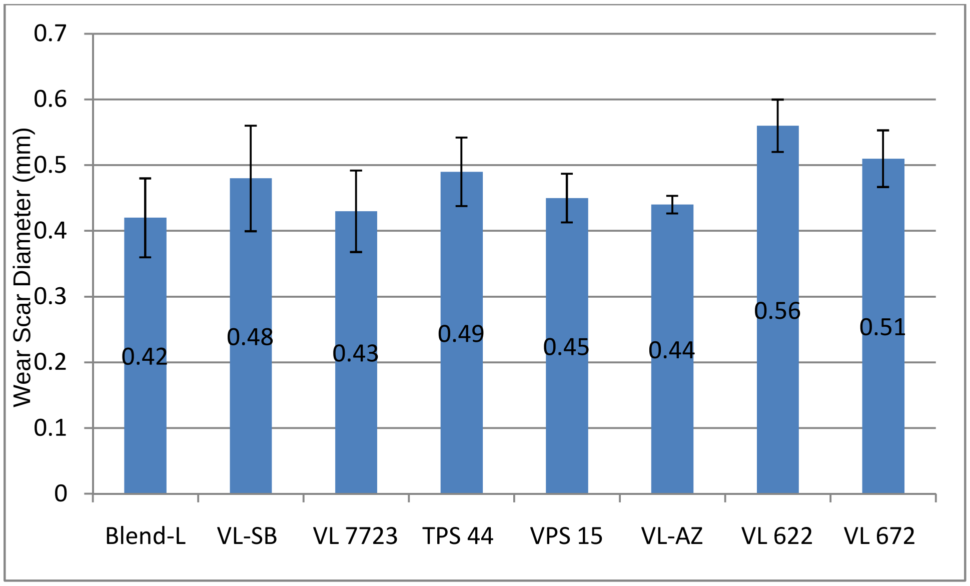


Figure 5.2 Chart showing the WSD values for different grease formulations with combination of 3% VL additives and Blend-L in Li-base grease

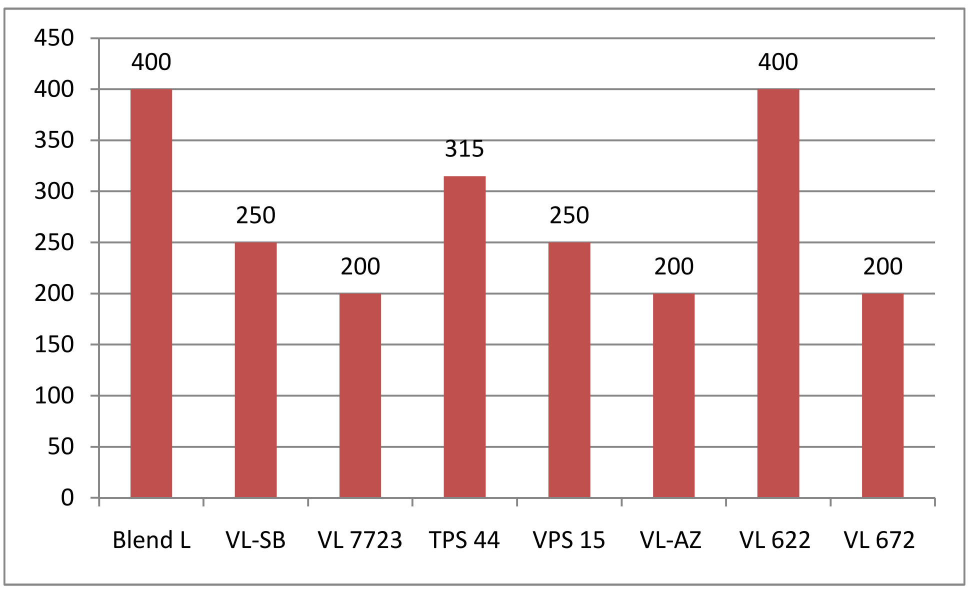


Figure 5.3 Chart showing the weld loads values for different grease formulations with 3% VL additives in Li-base grease

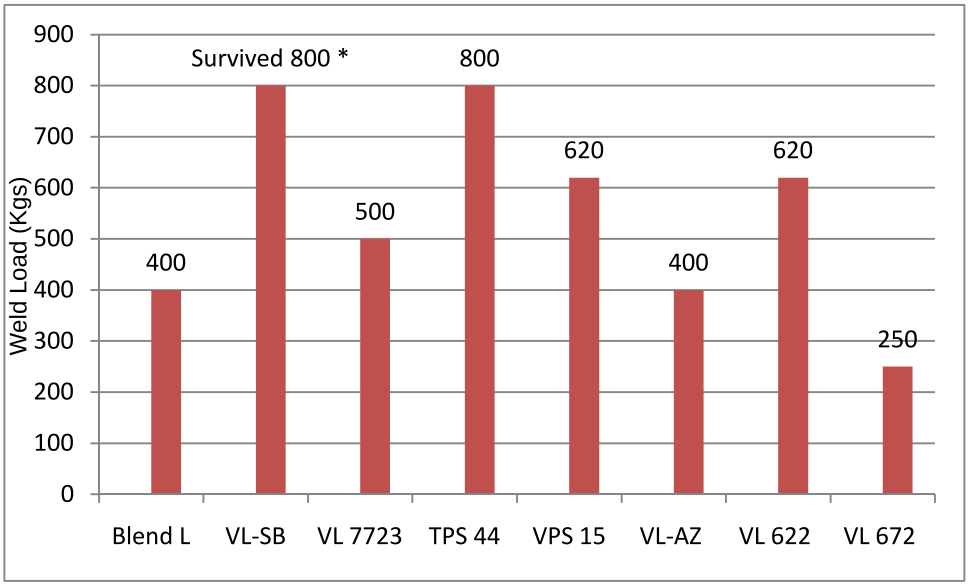


Figure 5.4 Chart showing the weld load values for different grease formulations with combination of 3% VL additives and Blend-L in Li-base grease

5.5 Study of interactions between ZDDP and PTFE in Li-base grease

5.5.1 ZDDP +PTFE

5.5.1.1 Design Analysis- Wear Behavior

The surface response plots (Figure 5.5) highlight the contributions of ZDDP+PTFE on the wear performance of the grease under standard conditions of 40 Kg/ 1200 rpm/ 1 hour (ASTM D 2266). As is evident from the Figure 5.5, increasing the amount of only PTFE increases the wear numbers from 0.70mm to 0.80mm. Stolarski et al [50] suggest that the adhesion of the PTFE transfer film to the counter surface plays an important role in reducing the wear rate of PTFE. However, PTFE shows high wear and suffers from cold-flow under prolonged loads. Ballester et al. [51] propose that the PTFE particles improve lubrication by modifying the surface of moving parts coming in contact under boundary lubrication conditions. The particle size of PTFE is a crucial factor in the functionality of PTFE and its degradation impacts the physical and chemical properties of the fluoropolymer. Irradiation causes the reduction in the molecular weight making PTFE more brittle and to be easily fractured. Ion irradiation helps create electron acceptor groups on the PTFE particle surface, enhancing the adhesion of PTFE on the metal surface. Irradiated PTFE particles melt flow under the presence of heat and pressure, such as that existing in a four-ball test, and may serve as a highly lubricious temporary coating. However, the high wear numbers obtained with 2% PTFE could be attributed to the insufficiently irradiated, large particles of PTFE that would have hindered the lubrication process and not shearing enough to form a coating over the metallic surface.

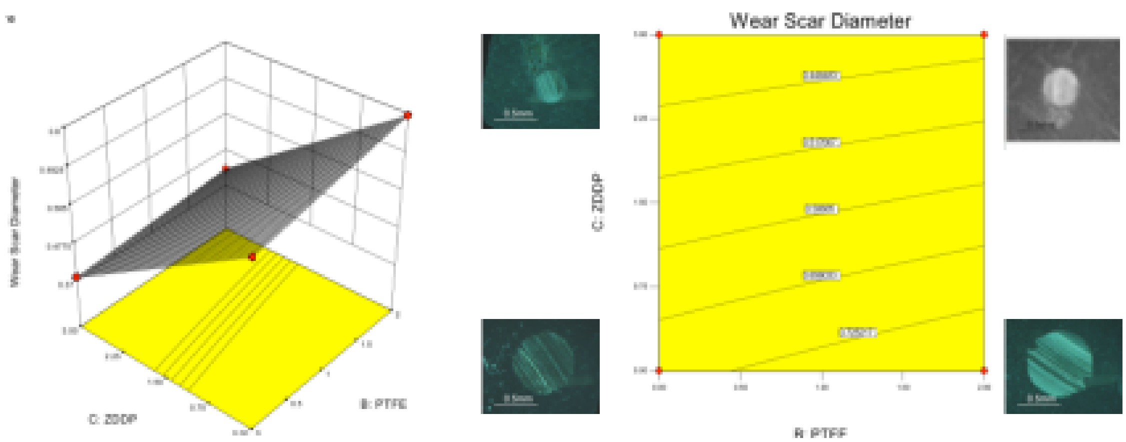


Figure 5.5 Wireframe plot showing the wear behavior for lithium- base grease with ZDDP+ PTFE on a Four-ball Tester (ASTM D2266); Contour plots with the optical micrographs of the corresponding grease chemistries

The reason that lithium-base grease offers considerable wear numbers is because the soap-thickened greases have load-carrying lubricants superior to base oils from which they are derived. It has also been noted that lithium grease performs better on the wear and EP than oil in a Four-ball test. This is attributed to the anticorrosive nature of the Li-soap [50]. Yamamoto et al [52] suggest that (for point contact) greases, in general, exhibit superior frictional performance as compared to base oils at low sliding speeds where the soap fibers are capable of supporting the applied load. At high sliding speeds where a hydrodynamic action is effective and the supply of lubricant is critical, the base oil of high fluidity is superior in frictional performance to grease. In the present work, the wear scar diameter obtained for lithium-base grease is 0.7056mm under ASTM Standard D2266.

When ZDDP alone is added in the lithium-base grease, low wear numbers of 0.38mm are obtained. A lot of research has been on the mechanism of film formation of ZDDP in oils to establish it as an antiwear, extreme pressure and antioxidant agent. Spedding and Watkins [53] suggest that it is not the ZDDP that is substantially chemisorbed on iron substrate, but it's the decomposition products. Simply said the decomposition of ZDDP produces zinc polyphosphates and mixed alkyl sulfides. These zinc phosphates are rapidly transformed into a film at locations subject to highest loads, thus inhibiting wear at these locations [54]. More on the morphology of films formed by ZDDP are discussed in the next chapter. However, to obtain the best combination of antiwear and extreme pressure behavior, ZDDP and PTFE act in synergism as was discussed in the previous chapter.

5.5.1.2 Design Analysis- Weld Load

From the response surface plots (Figure 5.6) with no VL SB, it is palpable that both ZDDP and PTFE individually have a similar effect on the EP properties of lithium base grease, increasing it from 160 kgs (for base grease) to 250 kgs. However, the best weld loads of 400 kgs are obtained through the synergistic interaction between ZDDP and PTFE when they are added to the base grease.

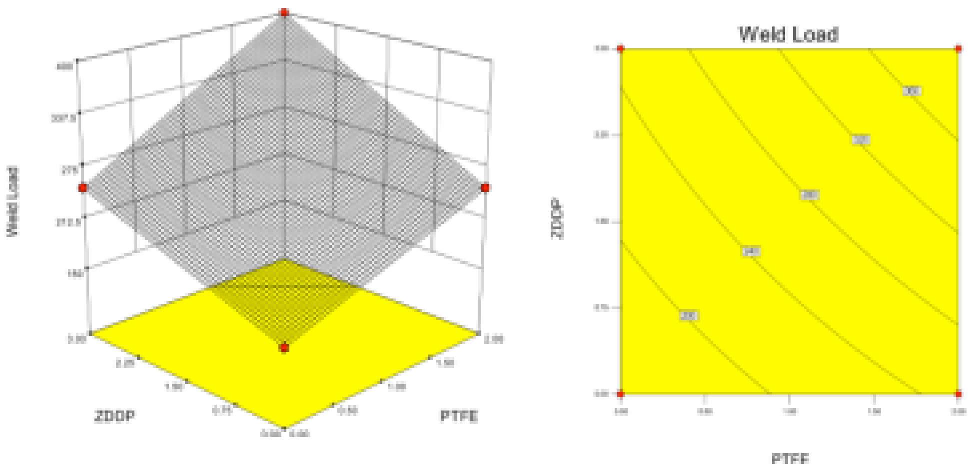


Figure 5.6 Wireframe (left) and contour (right) response surfaces for the weld load behavior of Li-base grease containing ZDDP and PTFE (at 5% treat rate)

5.6 Study of interaction of various additives (sulfur and non-sulfur) with ZDDP and PTFE in Li-base grease

5.6.1 VL SB

VL SB is a sulfurized olefin containing 45-48% S. Sulfurized olefins are of two types, one based on long-chain olefin and containing 10-20% S, and the other based on a shorter olefin, such as isobutylene (45% S), or a dicyclopentadiene or a dipentene (~35% S). Rossrucker and Fessenbecker [20] suggest that active sulfur has a significant influence on the antiwear performance. With higher sulfur content comes higher expected incidence of S-S bonds in the molecule and higher reactivity and EP potency. Thus, sulfurized isobutylene is a strong EP additive.

5.6.1.1 Design Analysis- Wear Behavior

Analysis is the first phase (design) of DOE; one of the three main features offered by the Design-Expert software. In the design, no transformations were included suggesting that the results are analyzed as obtained. On analyzing the contribution of the different factors on the wear widths, the software predicts a mathematical equation for the wear scar diameter.

Final Equation in Terms of Actual Factors:

Wear Scar Diameter = +0.70560-0.031433 * VL Additives + 0.044400* PTFE - 0.10877 * ZDDP - 0.014067 * VL Additives * PTFE + 0.030867 * VL Additives * ZDDP-7.70000E-003 * PTFE * ZDDP-2.51667E-003 * VL Additives * PTFE * ZDDP

In this equation, ‘VL additives’ refers to the concentration of the sulfurized olefin in weight %;’PTFE’ refers to the concentration of polytetrafluoroethylene in weight % and concentration of ZDDP (in weight % of concentrate where concentration of ZDDP is 68% of the concentrate). This equation gives an overall idea of the additive interactions in the grease and can be used to optimize the formulation of the lithium grease. The factors with positive coefficient would contribute to increased WDS values and the negative factors to lower WSD value. Thus, the amount of the additives should be chosen (considering the contribution from various combinations of additives) such that the wear scar is minimized. It is clear from this equation that the most important positive contribution as a single factor is the sulfurized olefin and the most negative single factor is PTFE. The other negative interaction is between the two-factor interaction between the sulfurized olefin and ZDDP. More details of these interactions can be understood by examining the response surface plots.

Figure 5.7 shows the response surface diagrams (contour and wireframe) for 3% VL SB in grease containing 0 and 3 % ZDDP and 0 and 2% PTFE. Plots containing 3% VL SB show that there exists interaction between ZDDP and PTFE and VL SB. The wireframe plot shows the dip in the WSD value when 3% ZDDP and 2% PTFE are used in conjunction with VL SB. When VL SB is used alone in the base grease, WSD of 0.61mm is obtained. The wear behavior is better than the base grease suggesting the adsorption of the additive on the surface. The addition of PTFE to the grease containing 3% VL SB does not contribute towards the betterment of wear performance of the additive since PTFE is more of a friction-reducing agent rather than antiwear. The addition of 3% ZDDP to the grease containing 3% VL SB, does not significantly improve the wear numbers (3%ZDDP + 3% VL SB has WSD of 0.56mm as against 3% VL SB with WSD of 0.61mm).

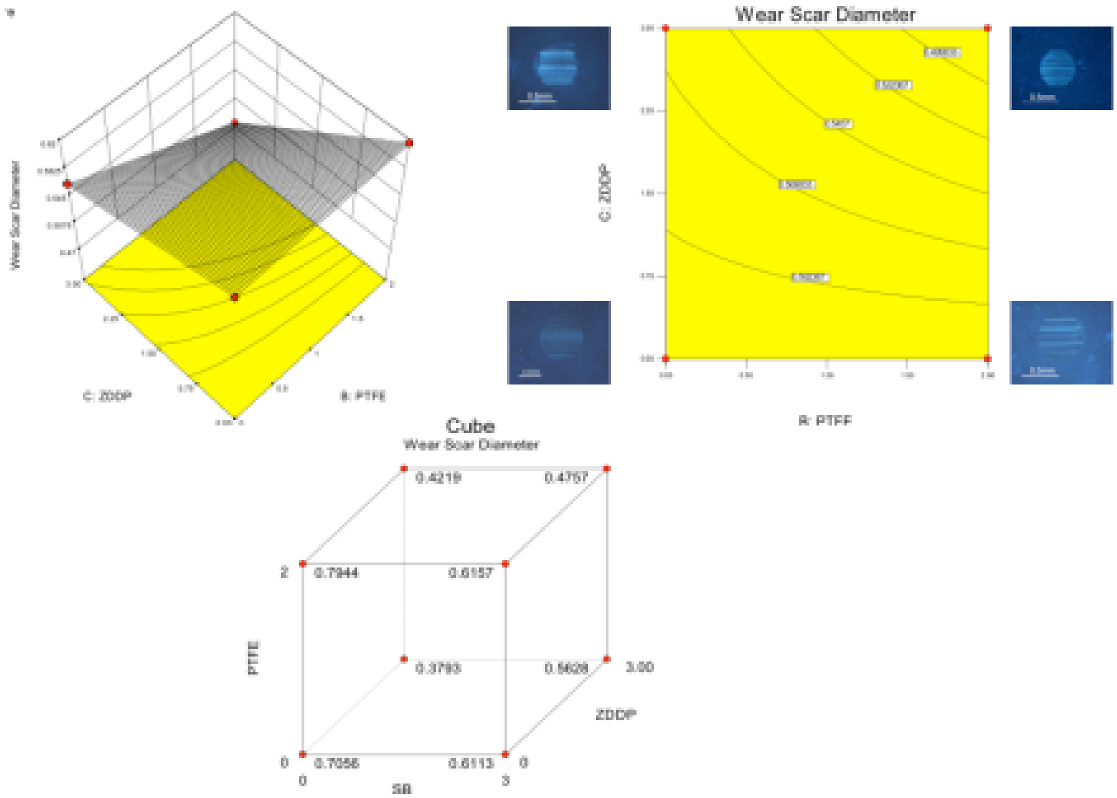


Figure 5.7 Wireframe plot showing the wear behavior for lithium- base grease with 3%VL SB+ 3% ZDDP+ 2% PTFE on a Four-ball Tester (ASTM D2266); Contour plots with the optical micrographs of the corresponding grease chemistries; Cube plot showing the wear outcome of different chemistries at low and high levels.

These results show that had competition for the surface were the dominant mechanism, a gradual transition of the wear scar diameter (WSD) value from VL SB (no ZDDP) to something approaching that for ZDDP alone would be expected as the concentration of ZDDP was increased in the base grease. The initial effect of adding ZDDP was to nullify the effect of VL SB resulting in a WSD value comparative to that of base grease alone, even though the ZDDP concentration present would be sufficient to significantly lower the WSD if added alone to the base grease (no VL SB). It can be speculated that VL SB cancels the effect of ZDDP by forming compounds like sulfides making both the additives unavailable for forming an effective surface coating. Alternatively, Since the antiwear nature of ZDDP comes from its decomposition and adsorption of the decomposition products on the surface, it is likely that in the absence of PTFE (which has been shown to lower the decomposition temperature of ZDDP) ZDDP has not decomposed. Since both ZDDP and VL SB are polar molecules, the competition of surface could have caused VL SB to be preferentially adsorbed on the surface (being highly active) rather than ZDDP and thus, the wear numbers obtained with VL SB+ ZDDP are closer to those obtained from VL SB alone in Li-base grease. With the addition of PTFE to the grease containing VL SB additive and ZDDP, the decomposition of ZDDP might be favored and the synergistic interaction of PTFE and ZDDP produces WSD value of 0.4757mm (with 3% VL SB), lying in the same ballpark (WSD=0.4218mm) of the grease containing ZDDP and PTFE (no VL SB).

5.6.1.2 Design Analysis- Weld Load

The ASTM D 2596 standard on the Four-ball tester describes a method to ascertain the load-carrying ability of lubricants. The load at which the balls weld together is referred to as the Weld Load.

From the response surface plots (Figure 5.8), it is evident that PTFE and ZDDP individually have a strong effect on the load bearing behavior of VL SB. When PTFE, ZDDP and VL SB are added to the grease, it survives even 800 kgs load. The Four-ball machine can test for weld loads up to 800 kgs; it is not suitable for testing chemistries with weld loads above 800 kgs as in (PTFE+ZDDP+VL SB).

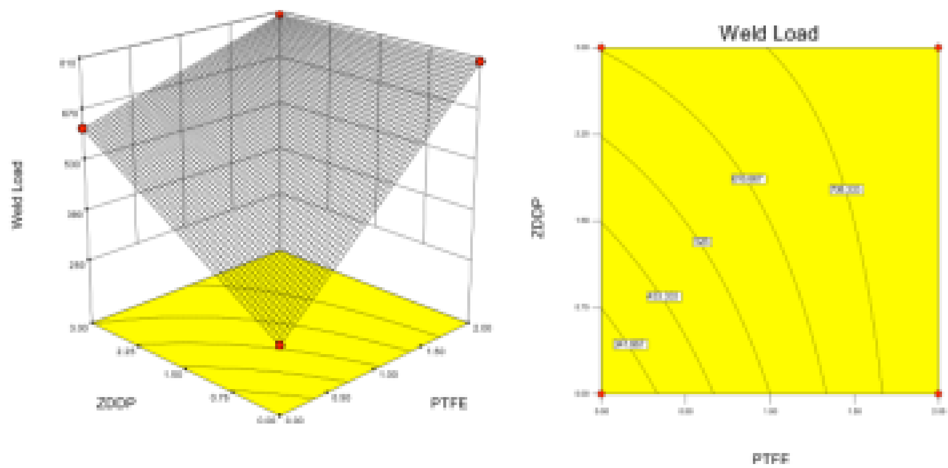


Figure 5.8 Wireframe (left) and contour (right) response surfaces for the weld load behavior of Li-base grease containing 3% VL SB with ZDDP and PTFE (at 5% treat rate)

These results suggest strong synergistic interactions between ZDDP, PTFE and VL SB. Interactions are expected with all polar molecules as they would sooner or later meet at the metal surface. This chemistry acts as an excellent antiwear additive (with WSD= 0.48mm) and EP agent (survived 800 kg load) in lithium-base greases.

5.6.2 VL 7723

VL 7723 is a methylene bis-dimethyldithiocarbamate with 28.5 – 32 % S. Dithiocarbamates are known to have strong metal-binding properties and are effective antiwear/EP agents. They also serve as good antioxidants [22].

VL 7723 has the following structure (Figure 5.9):

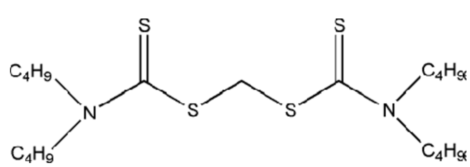


Figure 5.9 Structure of VL 7723

5.6.2.1 Design Analysis-Wear Behavior

The response surface plots (Figure 5.10) with grease chemistry containing 3% ZDDP, 2% PTFE and 3% VL 7723 are as given below.

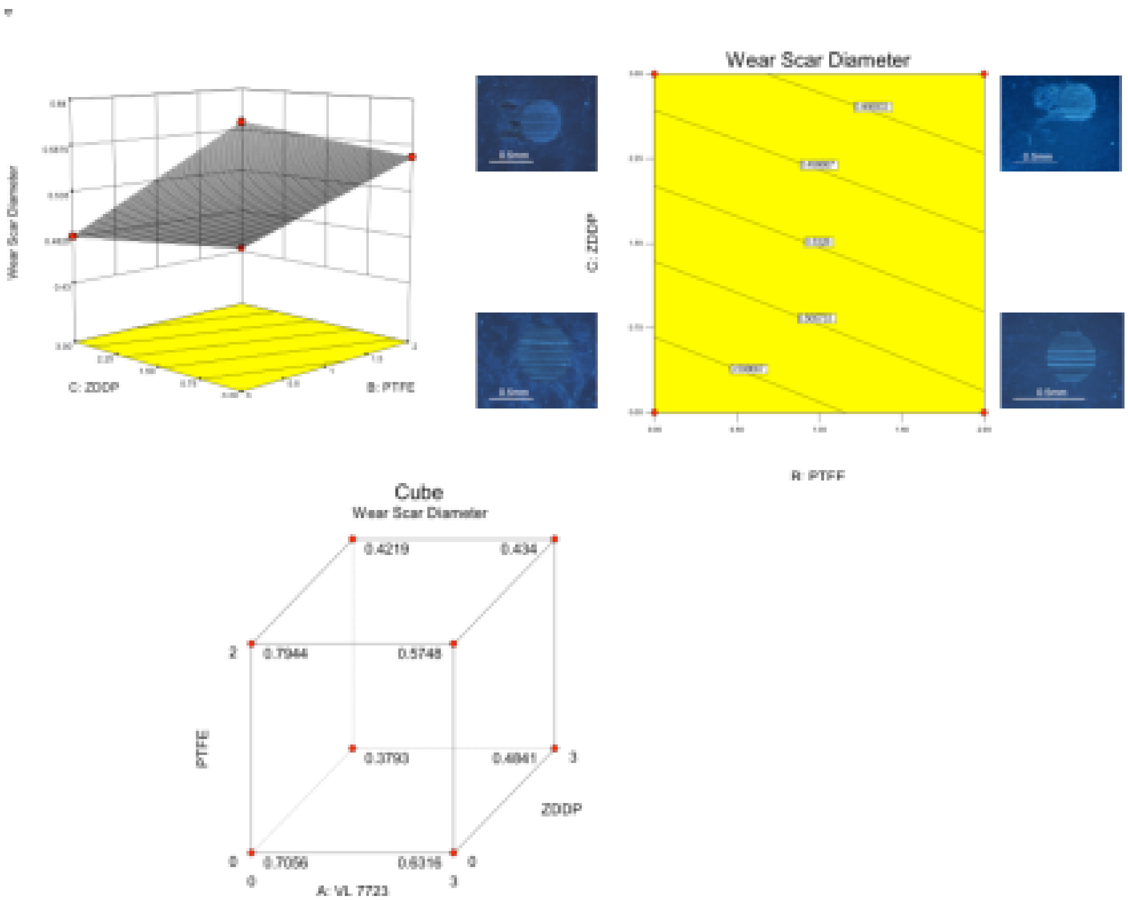


Figure 5.10 Clockwise: Wireframe plot showing the wear behavior for lithium- base grease with 3% VL 7723 and ZDDP+ PTFE (at 5% treat rate) on a Four-ball Tester (ASTM D2266); Contour plots with the optical micrographs of the corresponding grease chemistries; Cube plot showing the wear outcome of different chemistries at low and high levels.

Assessment of the above response surface plots (Figure 5.10) suggests that VL 7723 behaves quite like VL SB in that when the additive is added in combination with ZDDP, the WSD reduces significantly from 0.6316mm (no ZDDP) to 0.4841mm (with ZDDP). The WSD is further reduced to 0.434mm when 3% ZDDP and 2% PTFE is added along with 3% VL 7723 to the lithium-base grease suggesting the synergism between the three additives. The contour map of the chemistry with ZDDP, PTFE and VL 7723 shows that the contour lines become more linear and even-spaced than in VL SB. The almost -45℃ slope hints that there synergism between the three additives to give low wear numbers.

The final equation for the WSD as determined by the software is as below:

Wear Scar Diameter =+0.70560-0.024667*VL7723+0.044400*PTFE-0.10877*ZDDP-0.024267*VL7723*PTFE+0.019867*VL7723*ZDDP-7.70000E-003*PTFE* ZDDP+2.93889E-003 * VL 7723 * PTFE * ZDDP

5.6.2.2 Design Analysis- Weld Load

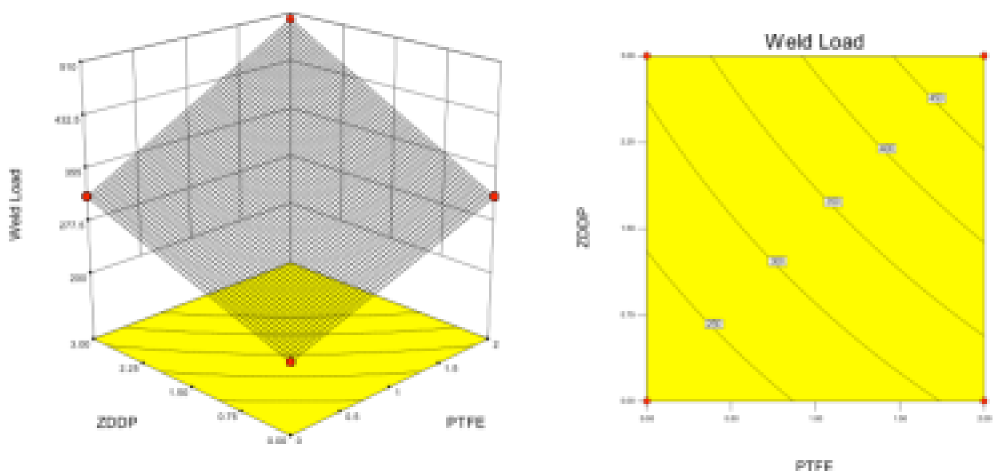


Figure 5.11 Wireframe (left) and contour (right) response surfaces for the weld load behavior of Li-base grease containing 3% VL 7723 with ZDDP and PTFE (at 5% treat rate)

The Figure 5.11 shows the wireframe plot for the weld loads obtained with grease chemistries containing 3% VL 7723. Some interaction is seen between the three additives as the weld load obtained is 500 kgs, one notch higher than what is obtained with ZDDP and PTFE (no VL 7723). But the results are not as significant as obtained with VL SB. Since the intermediate film of iron sulfide, responsible for preventing metal seizure under extreme pressure conditions, is not sufficiently formed, thus the weld loads are not as superior.

The maximum weld load obtained with ZDDP, PTFE and VL 7723 is 500 kgs, lower than that obtained with VL SB which survived 800kgs load. McFadden et al. [55] suggest that the effectiveness of organic sulfides depends on the bond dissociation energy of R-S bond (R=S,C) and the load carrying capacity of sulfur compounds has been shown to be directly related to their reactivity with nascent steel surfaces. However, there are sulfur compounds that react comparatively slowly with nascent steel surfaces and the molecular adsorption of the additive occurs without scission of the S-S bond. This bond does not break until a critical temperature is reached, when the R groups are released, leaving behind an iron sulfide film.

5.6.3 VPS 15

VPS 15 is a polysulfide derived from vegetable fatty acid esters containing 14.5 – 16% S. This is produced from renewable vegetable raw materials and fall under the class of inactive sulfur additives. Inactive sulfur carriers are very stable and do not corrode copper [56].

5.6.3.1 Design Analysis- Wear Behavior

Below is shown the wireframe plot of lithium base grease containing ZDDP, PTFE and VPS 15 (Figure 5.12).

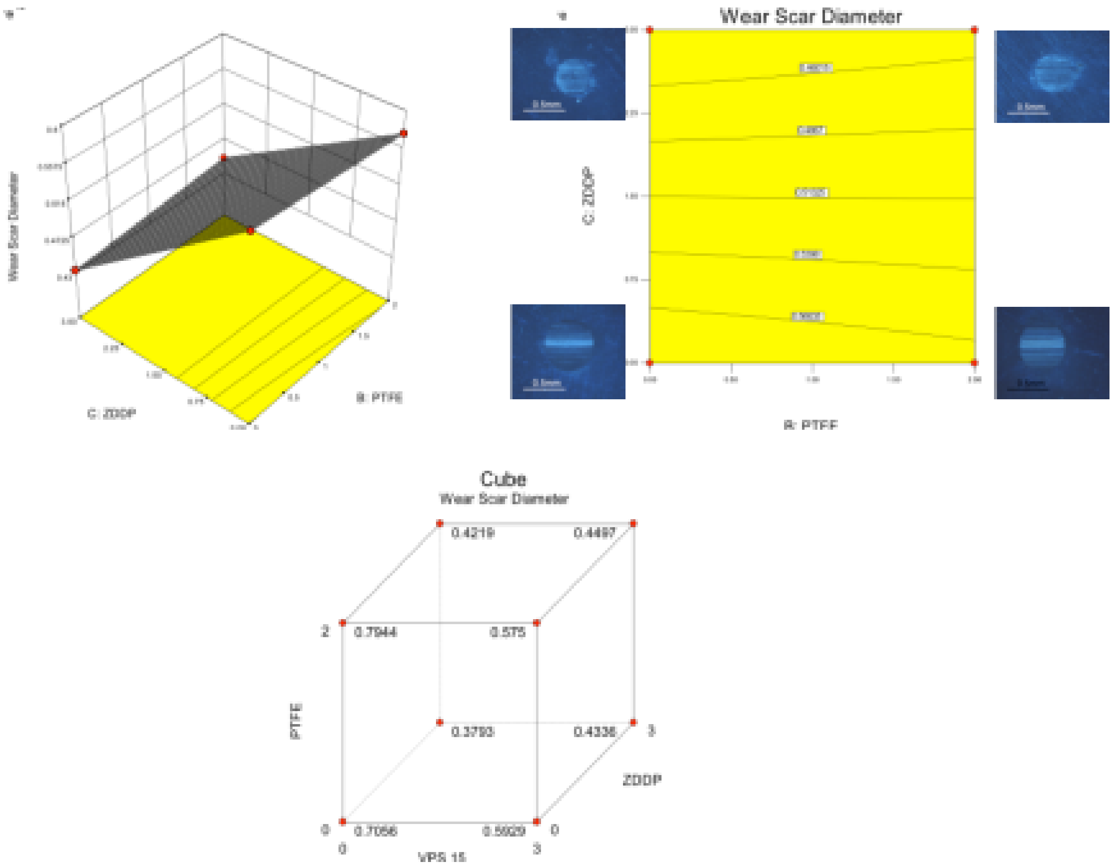


Figure 5.12 Clockwise: Wireframe plot showing the wear behavior for lithium- base grease with 3% VL 7723 and ZDDP+ PTFE (at 5% treat rate) on a Four-ball Tester (ASTM D2266); Contour plots with the optical micrographs of the corresponding grease chemistries; Cube plot showing the wear outcome of different chemistries at low and high levels.

Inspection of the Figure 5.12 suggests that the antiwear behavior of VPS 15 is not dependent on the PTFE content; the WSD value with only VPS 15 in the grease is 0.59mm whereas with PTFE, it is 0.58mm. However, ZDDP has significant influence on the antiwear properties of VPS 15. The WSD reduces by 0.16mm when ZDDP is added to grease with VPS 15. The contour plot interaction of ZDDP, PTFE and VPS 15 showing contour lines connecting the points of same response. The lines are almost parallel to the horizontal suggesting that the WSD is dependent on ZDDP to a greater extent than on PTFE. This behavior can be accounted for owing to the polar nature of PTFE and VPS 15 which compete for the surface. VPS 15 is known to be highly polar in nature [57] and quite likely to be preferentially adsorbed on the metal substrate.

The interactions between the additives can be summarized in the form as an equation as below:

Wear Scar Diameter = +0.70560-0.037567 * VPS 15+0.044400 * PTFE-0.10877 * ZDDP-0.017783 * VPS 15 * PTFE+0.018556 * VPS 15 * ZDDP-7.70000E-003 * PTFE * ZDDP+4.45556E-003 * VPS 15 * PTFE * ZDDP

5.6.3.2 Design Analysis- Weld Load

The response surface plots (

Figure 5.13) of the weld load suggest that PTFE does not play a role in enhancing the load-bearing properties of the additive. ZDDP too does not have a very significant effect role in that it increases the weld load from 250 kgs (with no ZDDP) to 315 kgs. However, when ZDDP, PTFE and VPS 15 are used together in the grease, considerable increase in the weld load numbers are obtained (of 620 kgs). This can be attributed to the presence of iron sulfide (formed under condition of very high loading that could damage the lubricating film) and zinc phosphide layers. Sulfide and phosphide films shear more easily than the metal itself; consequently less frictional heat is generated and the potential for severe welding is reduced [58].

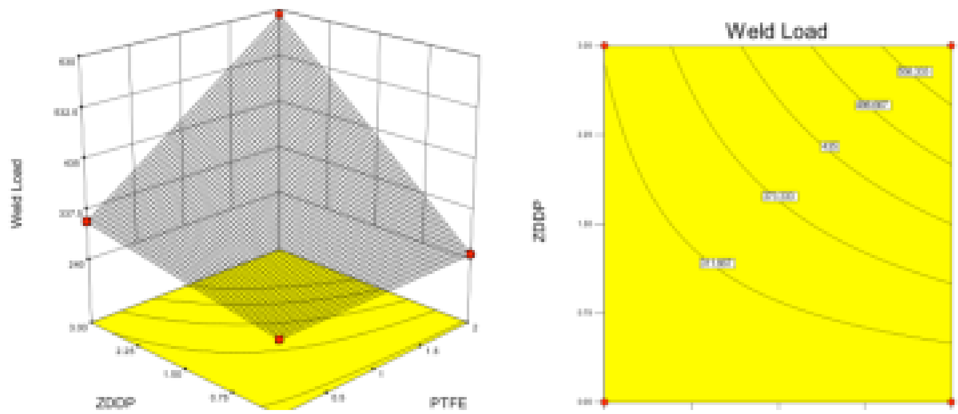


Figure 5.13 Wireframe (left) and contour (right) response surfaces for the weld load behavior of Li-base grease containing 3% VPS 15 with ZDDP and PTFE (at 5% treat rate)

5.6.4 TPS 44

This active sulfurized (dialkyl trisulfide) additive reacts at low temperatures and is high on sulfur (42-46% S).

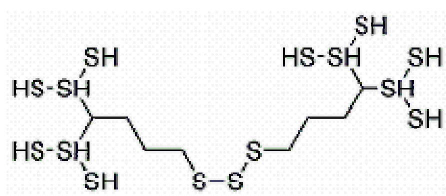


Figure 5.14 General structure of a sulfurized olefin

5.6.4.1 Design Analysis- Wear Behavior

The 3D response surface of TPS 44 showing its interaction with ZDDP and PTFE is as below:

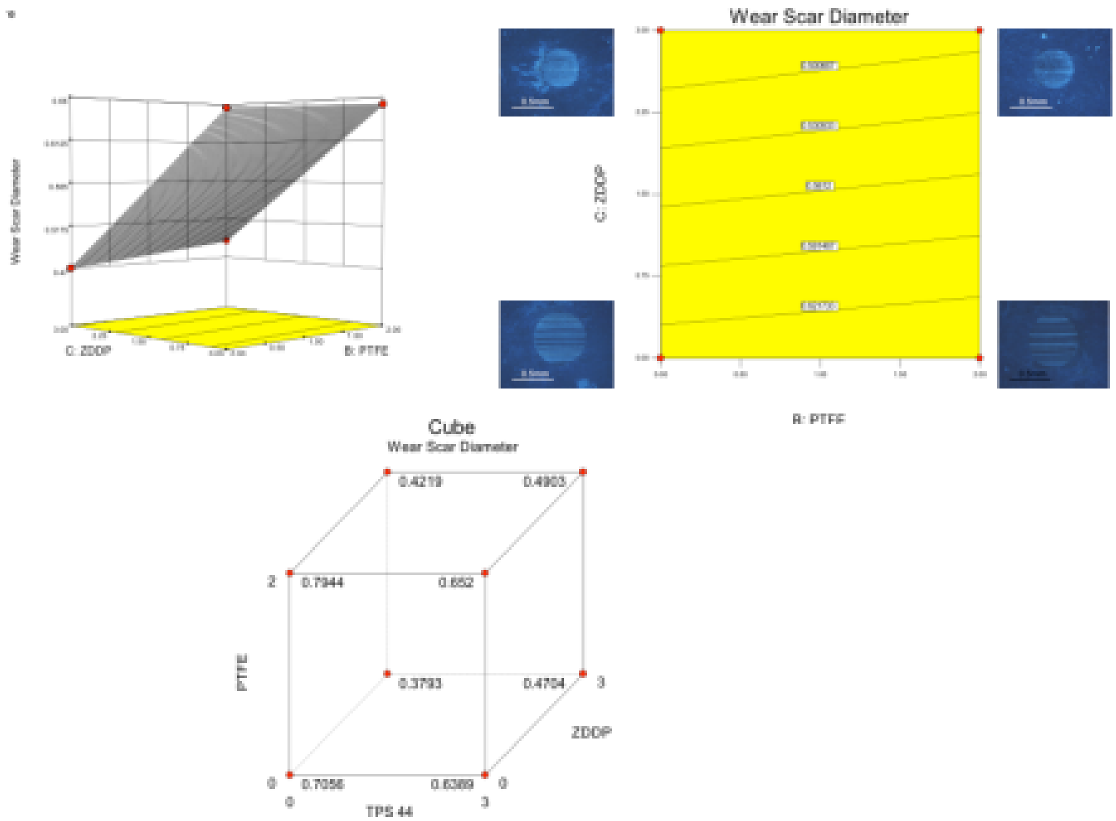


Figure 5.15 Clockwise: Wireframe plot showing the wear behavior for lithium- base grease with 3% TPS 44 and ZDDP+ PTFE (at 5% treat rate) on a Four-ball Tester (ASTM D2266); Contour plots with the optical micrographs of the corresponding grease chemistries; Cube plot showing the wear outcome of different chemistries at low and high levels.

From the response surface plots (Figure 5.15), it can be deduced that there is no interaction between PTFE and TPS 44. 0.639mm is the WSD value obtained when only 3% TPS 44 is used in lithium-base grease and 0.652mm when TPS 44 and PTFE are used. Synergistic interaction is observed between ZDDP and TPS 44; the WSD value in this case is 0.470 mm. The contour plot gives a better picture of the dependence of WSD on ZDDP and on ZDDP+ PTFE indicated by the slope of the lines. To obtain lower WSD numbers, the presence of ZDDP is essential. Going up the contour lines, the WSD values reduce.

There is some synergism observed between ZDDP, PTFE and TPS 44, but it is not stronger than the interaction between ZDDP and TPS 44. The result can be shown in the form of an equation as:

Wear Scar Diameter =+0.70560-0.022233*TPS44+0.04440*PTFE-0.10877*ZDDP-0.012617*TPS44*PTFE +0.017533*TPS44*ZDDP-7.70000E-003 *PTFE*ZDDP+2.94444E-003*TPS44*PTFE*ZDDP

5.6.4.2 Design Analysis- Weld Load

Synergism between ZDDP, PTFE and TPS 44 is observed as the weld loads obtained are as high as 800 kgs(Figure 5.16). This could be attributed to the high sulfur contents with increased loads and temperature under EP conditions as well as formation of zinc phosphate patches. The combined use of these additives results in a considerably superior performance over that of sulfur compounds alone.

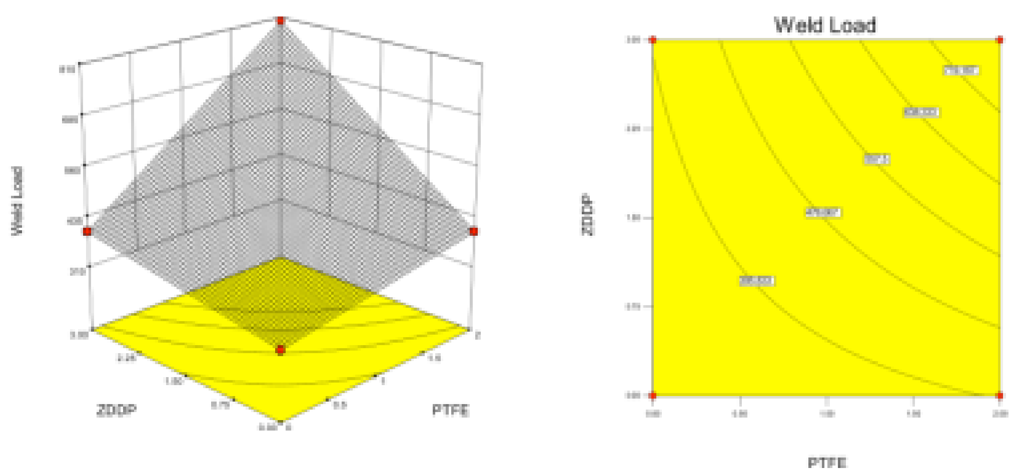


Figure 5.16 Wireframe (left) and contour (right) response surfaces for the weld load behavior of Li-base grease containing 3% TPS 44 with ZDDP and PTFE (at 5% treat rate)

5.6.5 VL AZ

This phosphorus-free additive is a zinc diamyldithiocarbamate containing 11- 13.5 mass percent sulfur and has the following structure (Figure 5.17):

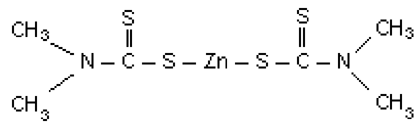


Figure 5.17 Structure of a zinc diamyldithiocarbamate

5.6.5.1 Design Analysis- Wear Behavior

The different response surfaces are as shown in the Figure 5.17. As can be observed, VL AZ gives good wear numbers when used alone in the lithium-base grease (0.41mm). When used in conjunction with PTFE, PTFE + ZDDP, and ZDDP, the WSD values increase gradually (in the same order). However, they are known to be good oxidation and corrosion inhibitors with some antiwear properties. The contour map (Figure 5.18) suggests that for obtaining lower values of WSD, the ZDDP content should be contained within 1.50 weight percent. When the PTFE content is lower than 1 percent, the contours are almost linear. On increasing the PTFE content beyond 1 percent, the contour lines become curvilinear, suggesting the predominance of one factor over the other in a three-factor interaction system.

The equation showing the interaction between the additives can be quantitatively written as:

Wear Scar Diameter =+0.70560-0.097900 * VL AZ+0.044400 * PTFE-0.10877 * ZDDP-0.012467*VLAZ*PTFE+0.040189 * VL AZ * ZDDP-7.70000E-003 * PTFE * ZDDP+1.21111E-003*VLAZ*PTFE*ZDDP

From the equation, to obtain lower WSD values, it is reasonable to use either ZDDP or VL AZ alone in the lithium-base grease. With two-factor-additive-interaction, VL AZ+PTFE respond better than VL AZ+ZDDP. Three factor additive-interactions do not have a profound effect on the WSD values.

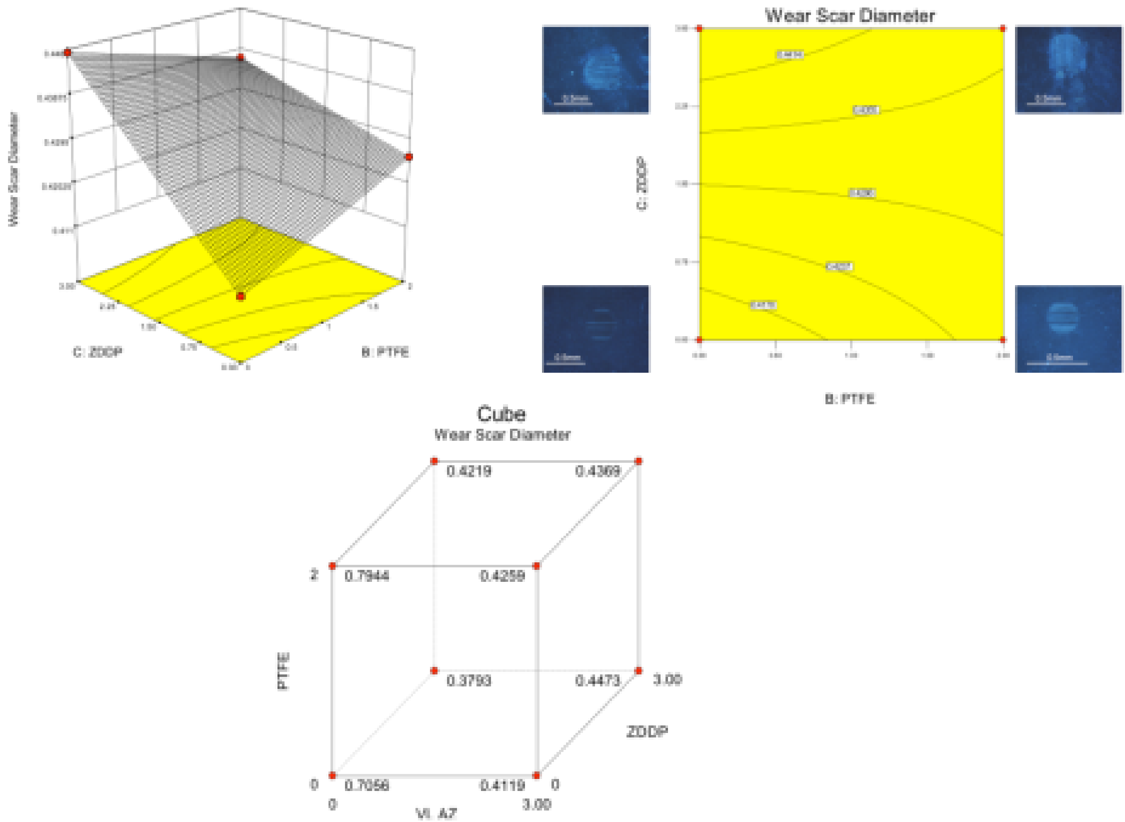


Figure 5.18 Clockwise: Wireframe plot showing the wear behavior for lithium- base grease with VL AZ+ ZDDP+ PTFE on a Four-ball Tester (ASTM D2266); Contour plots with the optical micrographs of the corresponding grease chemistries; Cube plot showing the wear outcome of different chemistries at low and high levels.

5.6.5.2 Design Analysis- Weld Load

The weld load of VL AZ+ZDDP+PTFE is almost in line with the weld loads obtained for ZDDP+PTFE (Figure 5.19). There is significant interaction occurring between the three additives under EP action. The -45°C indicates the dependence of weld load performance on the ZDDP and PTFE compositions, in the presence of 3% VL AZ. The spacing between contour lines increases with the decrease in the ZDDP and PTFE content and become closer and steeper with increase in the ZDDP and PTFE content, indicating the action of combination of ZDDP and PTFE (with the VL AZ additive) in increasing the weld load capacity of the grease.

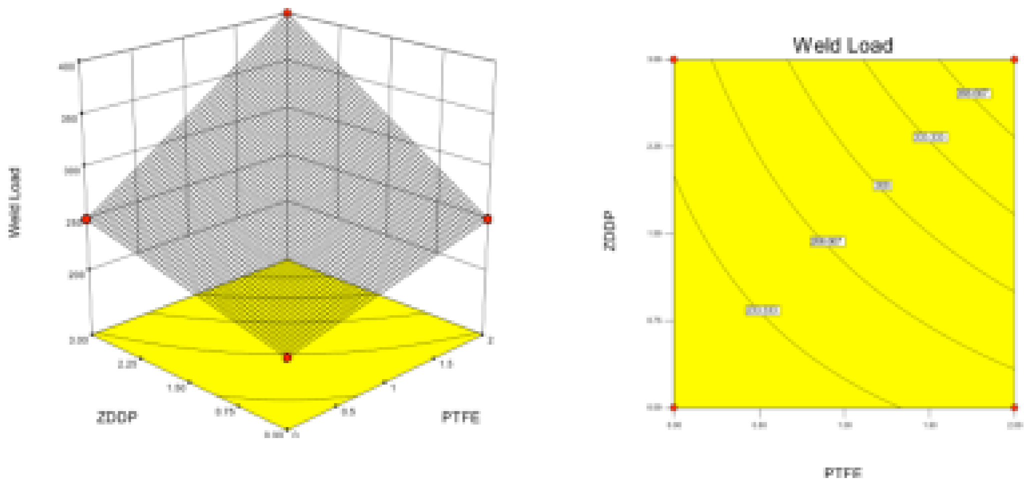


Figure 5.19 Wireframe (left) and contour (right) response surfaces for the weld load behavior of Li-base grease containing 3% VL AZ with ZDDP and PTFE (at 5% treat rate)

5.6.6 VL 622

This is an antimony dialkylphosphorodithioate, containing 16.5-22% sulfur and 10.5-12.5% Sb, with the following structure (Figure 5.20).

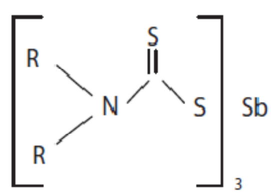


Figure 5.20 Structure of antimony dialkylphosphorodithioate

Phosphorodithioate and dithiocarbamate complexes of Mo, Zn, Sb, Ti, Cu, and other transition metals are two such classes of additives, that have found extensive use as AW, antifriction, antioxidant, and EP additives in lubricants for various applications.

5.6.6.1 Design Analysis- Wear Behavior

VL 622 gives good wear numbers when used by itself in the lithium-base grease (0.48mm). However, the WSD values increase to 0.61mm when ZDDP + VL 662 are used (Figure

5.21). This suggests the antagonistic interaction between the two additives. PTFE does not increase the WSD values, when used with VL 622, but serves to decrease the wear values to 0.56mm when a mixture of VL 622+ZDDP + PTFE is used.

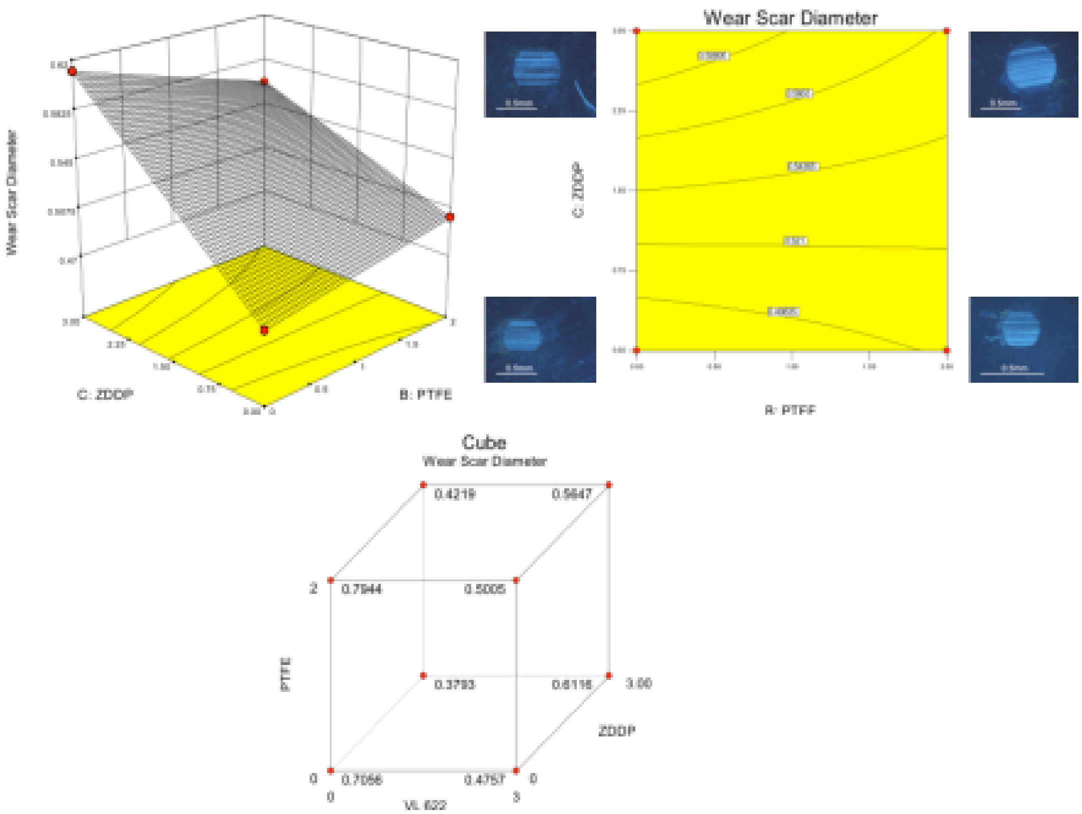


Figure 5.21 Clockwise: Wireframe plot showing the wear behavior for lithium- base grease with VL 622+ ZDDP+ PTFE on a Four-ball Tester (ASTM D2266); Contour plots with the optical micrographs of the corresponding grease chemistries; Cube plot showing the wear outcome of different chemistries at low and high levels.

The governing equation predicting the WSD as a function of the concentration of the variables in weight percent is given by:

$$\text{Wear Scar Diameter} = +0.70560 - 0.076633 * \text{VL622} + 0.044400 * \text{PTFE} - 0.10877 * \text{ZDDP} - 0.010667 * \text{VL 622} * \text{PTFE} + 0.051356 * \text{VL 622} * \text{ZDDP} - 7.70000\text{E-}003 * \text{PTFE} * \text{ZDDP} - 1.41667\text{E-}003 * \text{VL 622} * \text{PTFE} * \text{ZDDP}$$

In this equation, positive terms result in higher WSD values and negative terms result in lower WSD values. The ingredients, VL 622 and ZDDP, when viewed singly offer improvement in WSD values whereas PTFE would gives higher values of WSD. However, on considering the two-factor interactions, synergism can be observed between VL 622 and PTFE and PTFE and ZDDP. The three-factor interaction, although synergistic, is not as significant.

5.6.6.2 Design Analysis- Weld Load

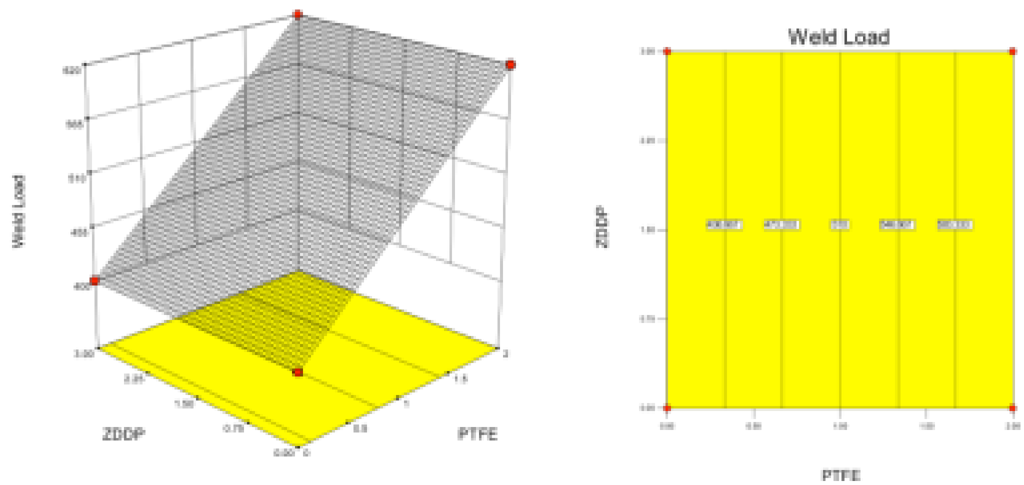


Figure 5.22 Wireframe (left) and contour (right) response surfaces for the weld loads for VL 622+ZDDP+ PTFE on the Four-ball Wear/EP tester (ASTM D 2596)

The response surface plots (Figure 5.22) of the weld loads obtained for the grease chemistry with ZDDP+PTFE+VL 622 strongly suggest the synergistic interaction between PTFE and VL 622. The weld load behavior of VL 622 is independent of the ZDDP content. The high weld load numbers could be attributed to the possible formation of antimony thioantimonate, which has been proven as a solid-lubricant additive in greases, exhibiting superior extreme-pressure and anti-wear properties as displayed by the Four-ball weld points and load-wear indices on AISI-52100 and AISI-440C steels. It has been shown to be compatible with all types of base greases and King et. al consider antimony thioantimonate to be a potential solid-lubricant additive for use under extremely high loading conditions where conventional solid lubricants are found to be inadequate. [57]

5.6.7 VL 672

This additive is an amine phosphate with no sulfur content. The general structure of this additive is as given below (Figure 5.23):

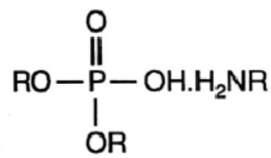


Figure 5.23 General structure of an amine phosphate

Amine phosphate salts have been proven as a load-carrying additive to provide lubricant compositions having balanced antiwear/extreme pressure and stability properties. However, such behavior has been observed in industrial oils such as gear oils. Testing the effectiveness of the additive as an antiwear/EP agent, shows the incompetence of the additive in lithium-base greases, when used by itself or in conjunction with ZDDP, PTFE or both.

5.6.7.1 Design Analysis- Wear Behavior

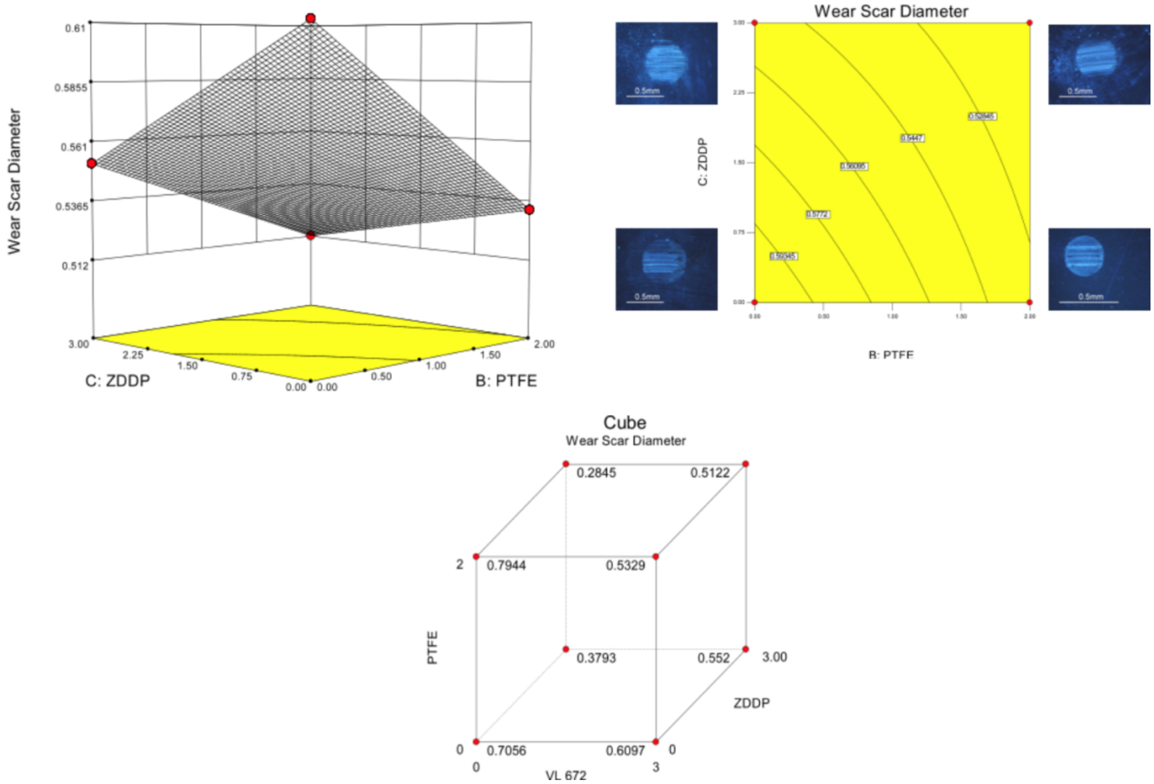


Figure 5.24 Wireframe plot showing the wear behavior for lithium- base grease with VL 672+ ZDDP+ PTFE on a Four-ball Tester (ASTM D2266); Contour plots with the optical micrographs of the corresponding grease chemistries; Cube plot showing the wear outcome of different chemistries at low and high levels.

The response surfaces showing the dependence of the wear behavior on the additive chemistries is shown in Figure 5.24. From these plots, it can be deduced that the amine phosphate serves as a moderate antiwear agent. There is some synergism seen between ZDDP, PTFE and VL 672, as can be seen in the contour plots with contour lines sloping at -45℃.These contour lines are helpful in that when a specific outcome is desired, it is possible to determine the combination of variables that would give the desired result. Thus, when the same wear numbers are desired, one or more ingredients can be substituted.

5.6.7.2 Design Analysis- Weld Load

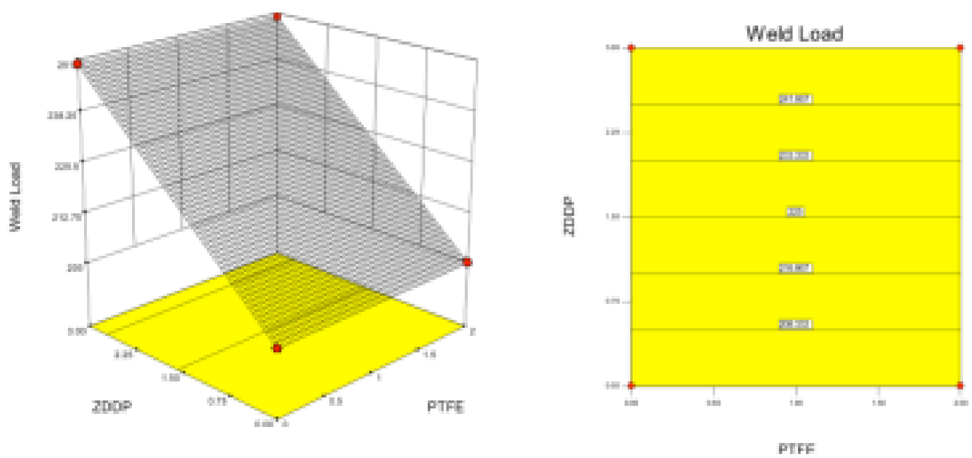


Figure 5.25 Wireframe (left) and contour (right) response surfaces for the weld loads for VL 672+ZDDP+ PTFE on the Four-ball Wear/EP tester (ASTM D 2596)

The wireframe and contour plots (Figure 5.25) for the weld load suggests that the weld load of VL 672 is independent of the PTFE content. As is apparent from the plots, the additive shows dependence on ZDDP that serves to raise the weld load of the additive from 200kg to 250kg. However, these two weld loads may be in the error range of the Four-ball tester. The low weld load numbers could be attributed to the formation of phosphate pads and sulfides in insufficient amounts.

CHAPTER 6

MORPHOLOGICAL AND COMPOSITIONAL ANALYSIS OF TRIBOFILMS

6.1 Introduction

The study of the wear processes is a part of the discipline of tribology. Wear is, by and large, an undesirable flow of material from a surface. The durability of machines and structures is often controlled by surface-related phenomena such as wear. There are two major types of wear found in a majority of engineering applications, namely, adhesive and abrasive wear. Adhesive wear can be best described as the adhesion that occurs when the pressure and heat generated during sliding cause small areas of one of the surfaces to chemically bond to the other surface. The particles transferred may remain adhered to the other surface or may separate to become loose debris. Adhesive wear can occur via surface plastic flow, scraping off soft surface films, breaking-up or removal of oxide layers. The breaking of junctions formed by adhesion between opposing surface asperities is accepted as being largely responsible for the wear observed under conditions of thin film lubrication. If it is not controlled, adhesion between surfaces can lead to galling and eventually to machine failure. Abrasive wear, on the other hand, involves the removal of particles from the mating surfaces by asperity shearing due to asperity collision or collision with loose debris passing between sliding surfaces. In plowing (a form of abrasive wear), the material is displaced to one side, away from the wear particles, resulting in the formation of grooves. Ridges are formed adjacent to the grooves that may be removed by subsequent passage by abrasive particles.

Lubricated wear, by definition, is wear under lubricated conditions. Within lubricated wear, most wear occurs under boundary lubrication conditions and refers to the conditions when the load is either partially or totally supported by the asperity contacts and the surfaces interact chemically with the lubricants to form a boundary lubricating film [58]. When antiwear additives are present, a reaction film adherent to the sliding surfaces is formed at contact positions by complex chemical reactions involving the additive incorporated in the lubricant base [61]. As a function of load or speed, the wear goes through a transition from a mild wear regime to a more severe wear regime. Mechanistically, this is usually due to (a) the introduction of third-body wear at the interface, (b) the asperity flash temperature reaching a critical temperature that the lubricating film cannot support or (c) the onset of a different wear mechanism such as corrosion or fretting as load and speed or their combination reaches a critical value [58].

The four-ball wear tester is the predominant wear tester used to study the chemical interactions occurring at wearing contacts. There are various reasons for this. One is the availability of low-cost high precision wear samples in the form of bearing balls. The contact geometry ensures self-alignment. The rotating axis maintains high trueness in rotation. There are three separate and distinct worn samples per test which allows some statistical averaging to account for the material uniformity. It also provides multiple samples for surface analysis. The small differences from different lubricants can be measured with precision.

The primary measurement made with four-ball wear tester is wear. ‘Run-in’ is a term that has been used to describe the early stages of operation of practical engineering systems such as automotive engines, gears and bearings and has a strong influence on the convetional four-ball tests, which are commonly run at a high rate of change in the wear scar during the early stage of the test. The contact pressure at the beginning of the test under boundary lubrication conditions is very high, of the order of 1-3 GPa. At this high pressure, rapid wear and considerable amount of surface damage occurs through adhesion, abrasion and a variety of other wear mechanisms. Because of the rapid wear process, the temperature of the wear contacts, the contact pressure and the lubricant film thickness vary significantly with time. As wear progresses to a nearly steady-state operation, the temperature and pressure of the contacts gradually approach their mean distribution values. The lubricant-film remains relatively constant throughout this process [58].

In this chapter, the morphological and compositional of the wear tracks is performed through SEM/EDS and the nature of films formed by combination of ZDDP+PTFE is compared with the formulations containing the different additives (sulfur and non-sulfur carriers) in combination with Blend-L (3% ZDDP + 2% PTFE).

6.1.1 Analysis of tribofilm of ZDDP and PTFE

6.1.1.1 3%ZDDP+2% PTFE

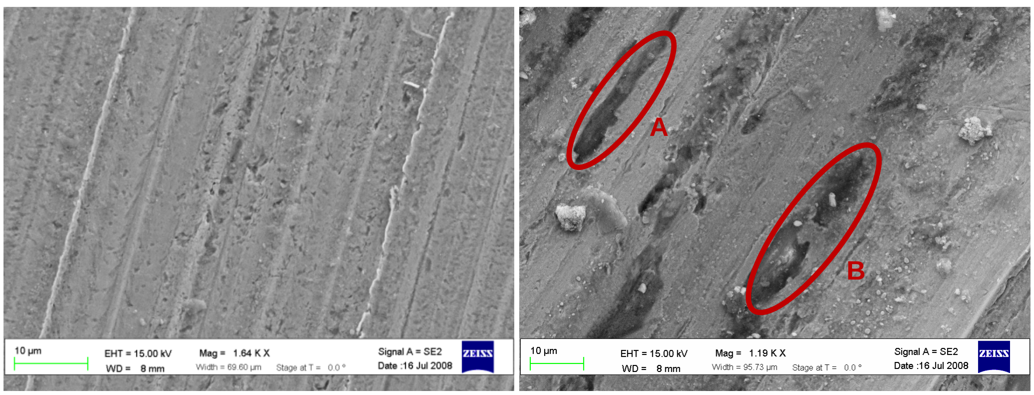


Figure 6.1 SEM images of the wear track formed on the ball samples from a ZDDP+PTFE-containing Li-base grease

The SEM images (Figure 7.1)suggest that the tribofilm formed from 3%ZDDP+2% PTFE (in Li-base grease) consists of numerous plowing grooves parallel to the direction of sliding, plastic flow and fine wear debris, all indicating the occurrence of abrasive wear. Such characteristics are seen in tribofilms formed from P-containing additives. The pull-out of the tribofilm (area A and B) suggests adhesive wear and these areas could be regions where the tribofilm was formed insufficiently or was weakly adherent to the metal surface. The combination of abrasive wear and mild adhesive wear is suggestive of the presence of phosphate and sulfide phases in the tribofilm.

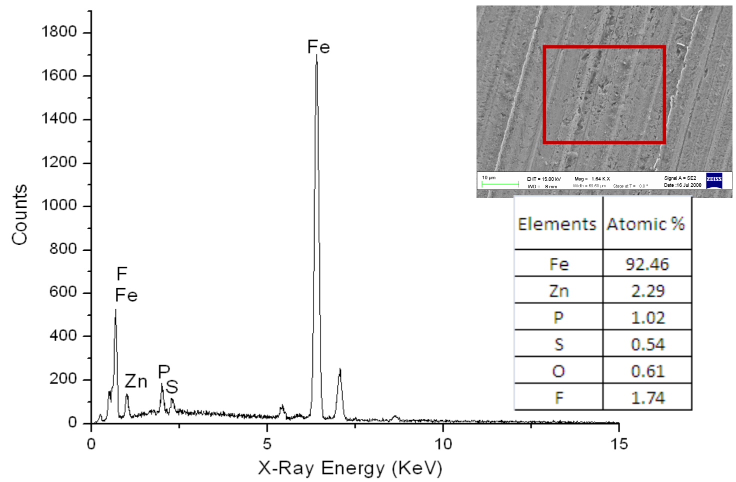


Figure 6.2 EDS spectrum performed on the wear track with grease chemistry 3% ZDDP+2% PTFE (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.2) done on the wear track of one of the three stationary balls after running the ASTM D2266 on the Four-ball wear tester for the grease chemistry containing 3%ZDDP, 2% PTFE reveals the presence of Zn, P, S. O.

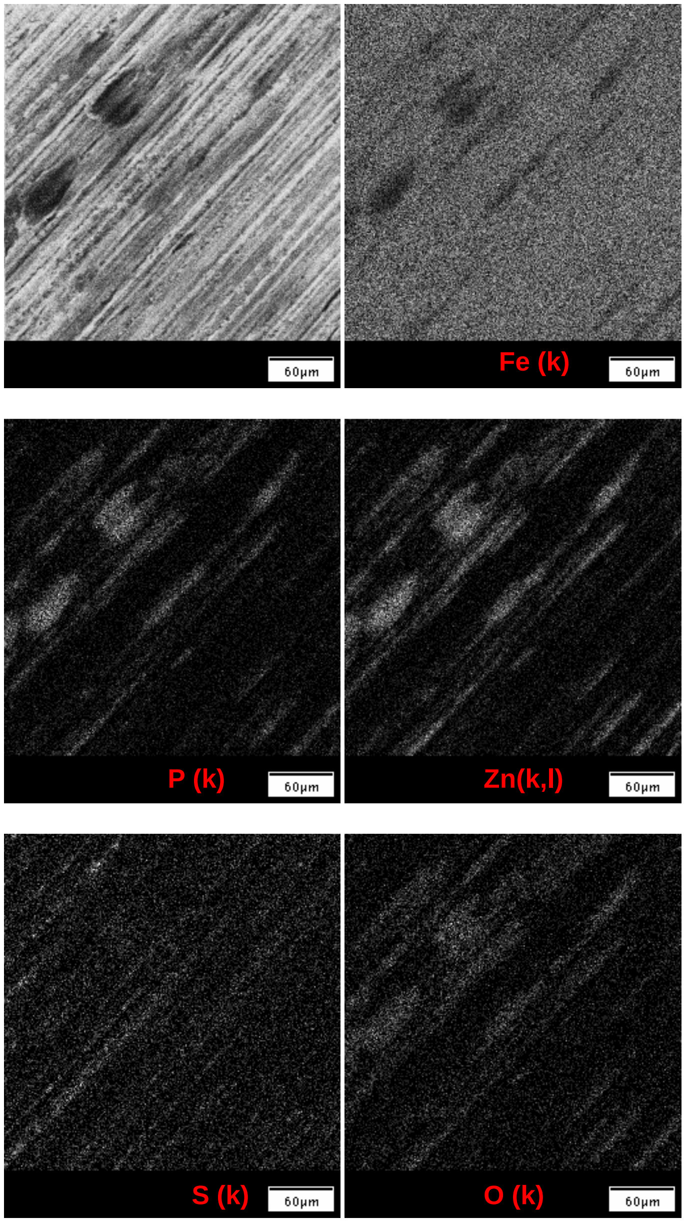


Figure 6.3 Elemental maps of the various elements found on the wear track formed from a ZDDP+PTFE-containing (Blend-L) Li-base grease

The elemental maps of ZDDP + PTFE (

Figure 6.3) strongly suggest the formation of zinc phosphates and iron sulfides. ZDDP needs both adsorption and thermal decomposition for antiwear/EP action. The first step involves the adsorption of the additive on to the metal surface, usually the metal oxide. The presence of polar compounds decreases the adsorption of the AW/EP additive via natural competition. Higher polarity and longer chain length increase the adsorption, leading to heavy build-up of molecules on the metal surface. The additive then breaks up and reacts with the metal surface. The frictional heat produced by the collision of opposing asperities causes the oxides formed on the metal surface to be scraped off and the reaction products (formed by the break-down of the additives), react with the metal surface to form an “Antiwear or EP” film. These films are more easily sheared than the underlying metal, yield more readily during sliding than the substrate, remaining between the metal surfaces and serving as effective solid lubricants under high contact loading conditions. [59] In the present work, PTFE used is irradiated and has reactive functional groups which form complexes with ZDDP and help it get adsorbed on the metal surface.

The AW/EP action of ZDDP comes from the zinc polyphosphates and iron sulfides in the tribofilms. Komvopoulos et al. [59] report that iron sulfide acts as an excellent solid lubricant because of its high melting point (1100℃), relativ ely low hardness and shear strength, and good adhesion to iron and steel surface. The sulfide film typically consists of FeS with a layered hexagonal lattice and some amount of FeS_2 and exhibits good solid lubrication behavior. The zinc phosphate pads, on the other hand, correspond to experience highest pressure during sliding and the pads of zinc phosphates act as load-bearing points. This accounts for the good wear and EP properties of the grease chemistry with ZDDP+PTFE.

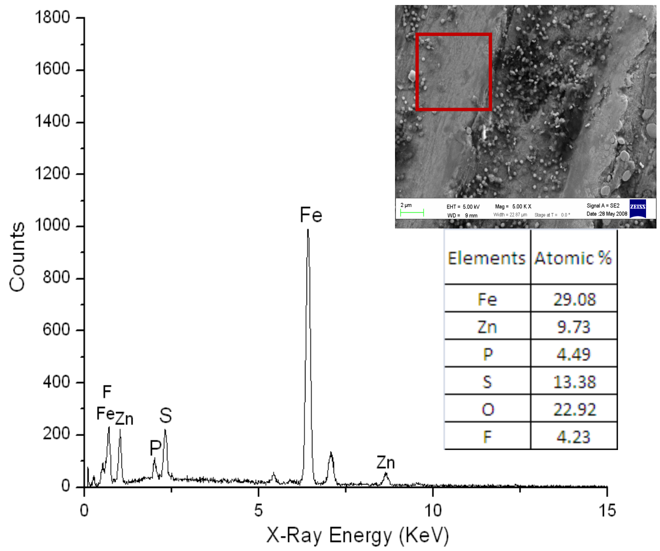


Figure 6.4 EDS spectrum performed on the wear track with grease chemistry 5% ZDDP+4% PTFE (Inset: SEM image of the wear track)

On increasing the content of ZDDP and PTFE to 5 and 4 % respectively in the Li-base grease, the amount of Zn,P, S and O increase relative to the Blend-L grease suggesting that a thicker film might have been formed with the Blend-H grease as compared with Blend-L. The S:P ratio is higher in the case of Blend-H as compared to Blend-L, suggesting the increased formation of sulfides which is responsible for better wear performance. There is also a higher amount of P and O present in the Blend-H grease, implying that there could be higher phosphates formed and thus high weld load numbers of 620kgs as compared with Blend-L.

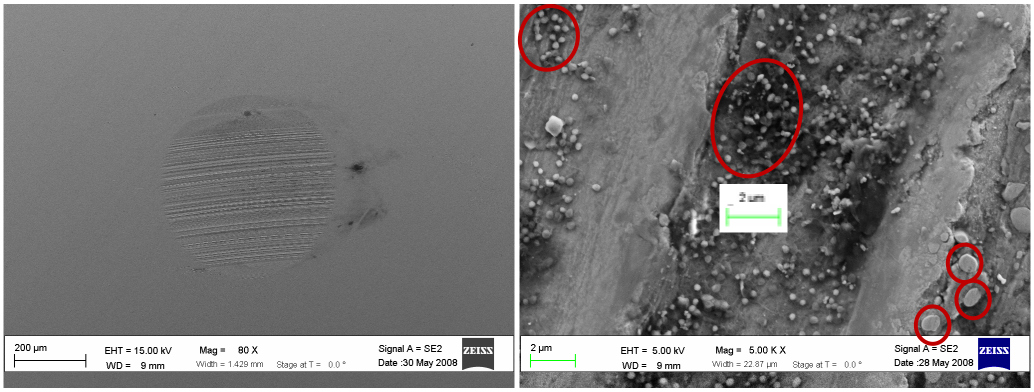


Figure 6.5 Elemental maps of the various elements found on the wear track formed from ZDDP + PTFE-containing (Blend-H) Li-base grease

A closer examination of the SEM image (Figure 6.5) of the wear track created by the Blend-H grease shows smooth plateaus, suggestive of sulfide films. The round particles noticeable on the wear track (area marked as B) appear much smaller than 2µm and could be suggestive of PTFE particles since the particle size of PTFE used in this study was around 200nm. Spikes et al. [62] quote in their paper that "PTFE particles may play a role in filling the irregularities in the metal counterface and providing a smooth, low-friction surface between the moving parts". This behavior has been observed in engine oil applications. However, PTFE has been used in high concentrations in greases and pastes. They also suggest that PTFE particles are ineffective in high pressure contacts such as in the four-ball tests. But these experiments were carried out in mineral oils and not in greases. Running wear tests with PTFE and ZDDP in base grease does produce significant reduction in wear scar diameter (only 3% ZDDP gives WSD of 0.42mm; whereas Blend-L under the same ASTM D-2266 conditions gives WSD of 0.38mm). It could be hypothesized that PTFE particles could be rejected from high-speed contacts. They may also appear to penetrate slow speed, mixed rolling/sliding contacts where they help reduce friction in the thin film regime [62]. With the present results in greases, PTFE particles seem to have penetrated the sliding contacts and apart from synergistically interacting with ZDDP, could also support a part of the applied load. In addition, the load could also be supported by the wear debris produced on the wear track (indicated by the regions A). The particles are spherical in shape and thus do not negatively impact the tribofilm, unlike MoS_2 particles which, due to their hard, irregular and rough edges rip the film formed on the steel surface producing higher wear numbers.

6.1.2 Analysis of tribofilms of VL Additives

6.1.2.1 VL SB

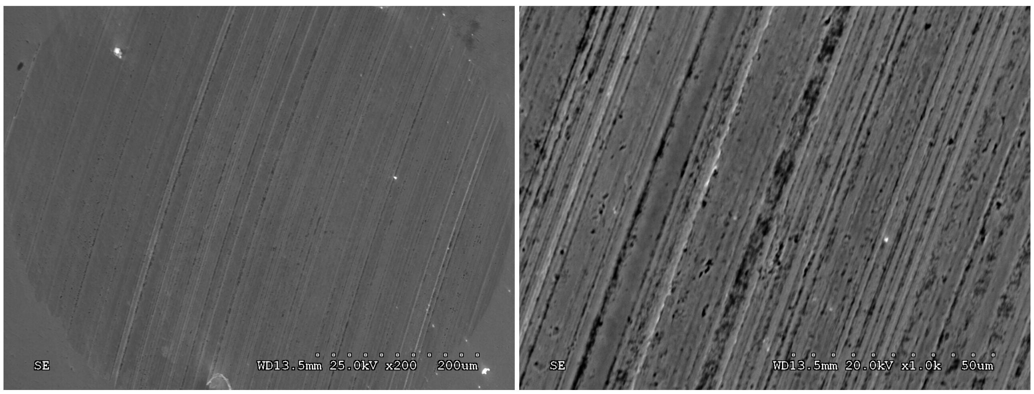


Figure 6.6 SEM images of the wear track formed through a Four-ball wear test (ASTM D 2266) from a Li-base grease containing 3%VL SB

The presence of wear grooves and cavities on the track (Figure 6.6) indicates abrasive type of wear. At higher magnifications, smooth plateaus can be observed, presumably of a sulfide tribofilm (iron sulfide) as was suggested by the elemental mapping of sulfur on a portion of the wear track (Figure 6.7). The EDS spectrum shows the presence of sulfur on the surface (Figure 6.8).

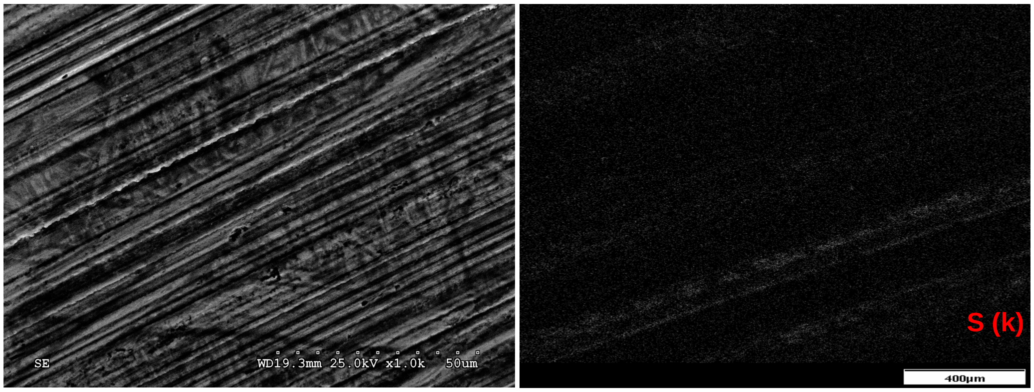


Figure 6.7 Elemental map of sulfur as found on the wear track formed from VL SB -containing Li-base grease

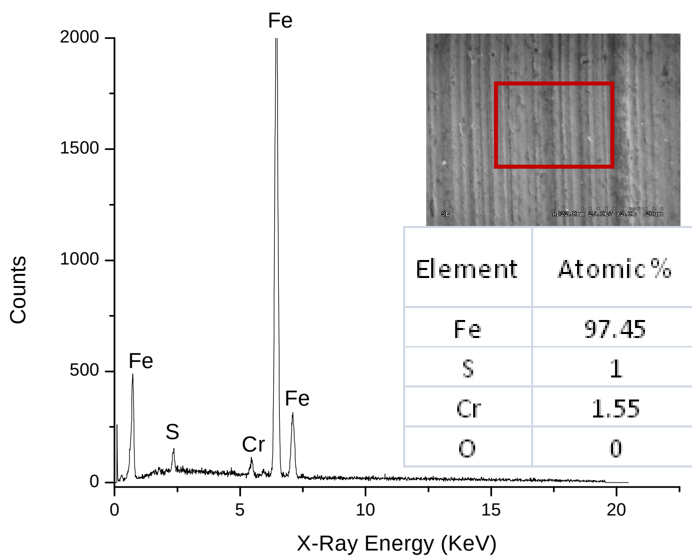


Figure 6.8 EDS spectrum performed on the wear track with grease chemistry VL SB (Inset: SEM image of the wear track)

6.1.2.2 VL SB+ PTFE+ ZDDP

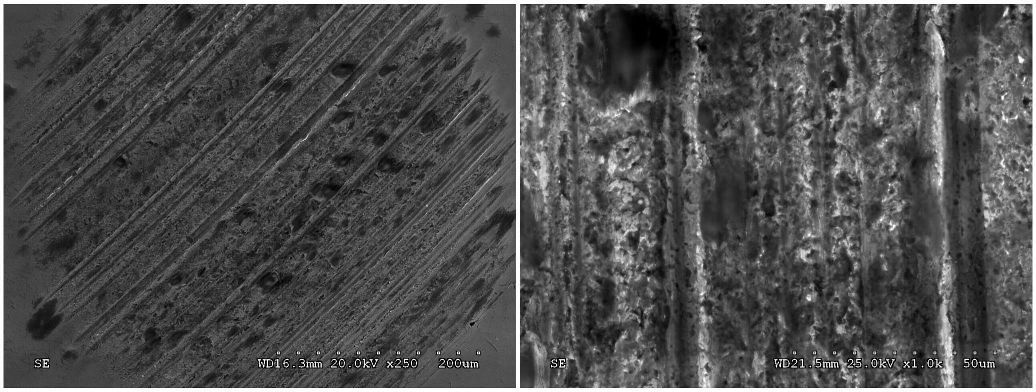
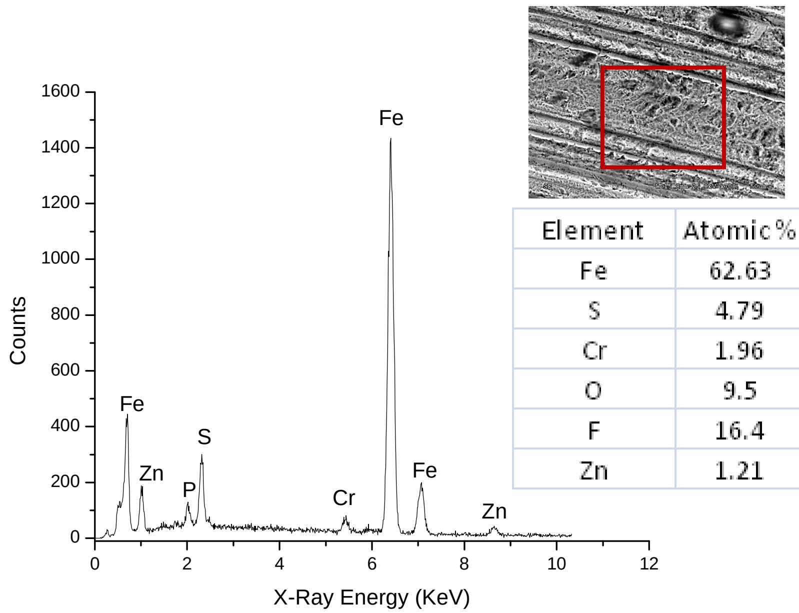


Figure 6.9 SEM images of the wear track formed through a Four-ball wear test (ASTM D 2266) from a Li-base grease containing VL SB+ PTFE+ ZDDP

Inspection of the SEM image (Figure 6.9) for the grease containing VL SB+PTFE+ ZDDP shows the presence of linear grooves on a metallic surface, indicative of two-body abrasion. The tribofilm appears patchy and contains few cavities, indicative of abrasive wear and the presence of sulfide film. The appearance of the film is also indicative of adhesive wear.

The wear track generated on the test steel balls with grease chemistry containing 3% ZDDP, 2% PTFE and 3% VL SB was analyzed through a Hitachi S-3000N Scanning Electron Microscope attached with an EDS system for compositional analysis and elemental mapping. The mapping of the track was done for distribution of sulfur, phosphorus, zinc, iron, oxygen and fluorine on the wear track. Through the data obtained, the plausible composition of the tribofilm can be speculated.



Element	Atomic %
Fe	62.63
S	4.79
Cr	1.96
O	9.5
F	16.4
Zn	1.21

Figure 6.10 EDS spectrum performed on the wear track with grease chemistry VL SB+ ZDDP+PTFE (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.10) above shows the presence of the elements responsible for tribofilm formation. To gain an insight into the spatial distribution of elements in the tribofilm, elements maps are acquired for the important elements for showing the compositional zonation.

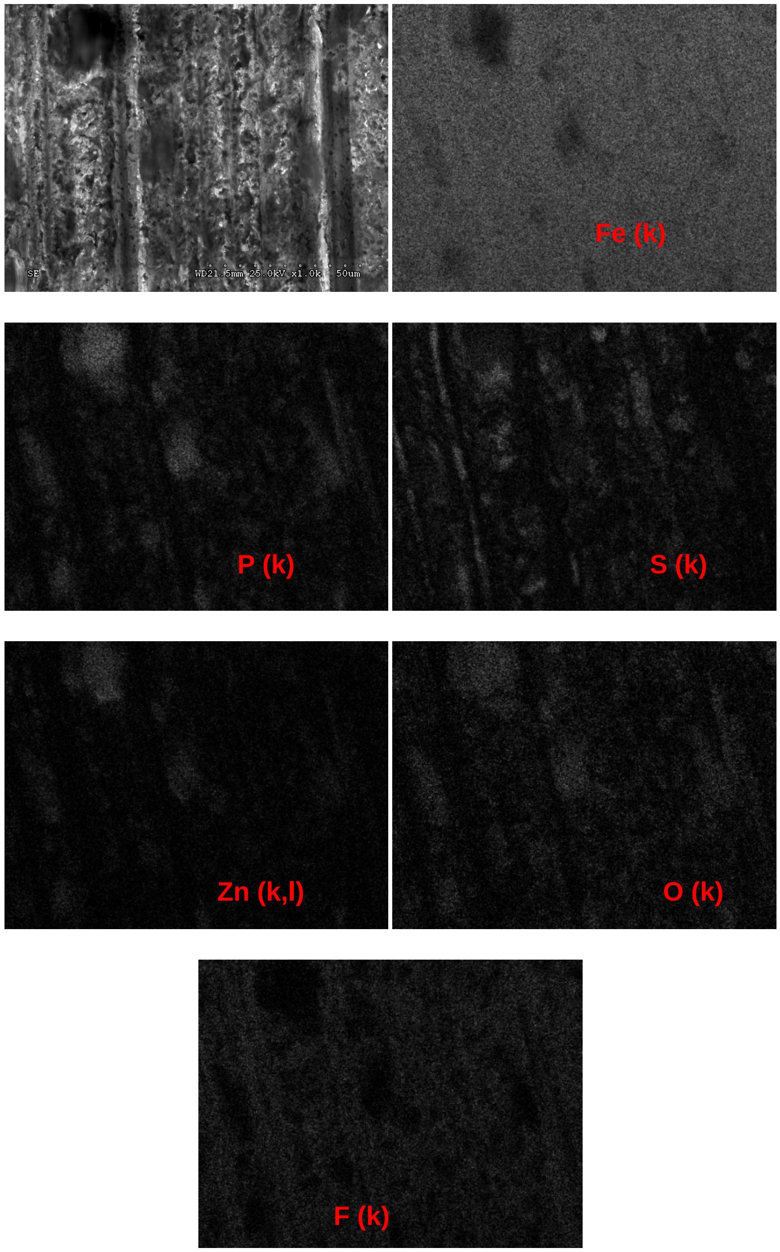


Figure 6.11 Elemental maps of the various elements found on the wear track formed from VL SB+ ZDDP+PTFE-containing Li-base grease

The SEM image of the wear track (Figure 6.11) appears patchy, with ridges and valleys, characteristic of tribofilms formed from ZDDP. The ridges show raised patched of the film, termed as antiwear pads and these pads are responsible for bearing the load between the rubbing surfaces and these pads are responsible for bearing the load between the contacting surfaces and limiting the contact between the asperities, thereby reducing wear [60]. The thick zinc phosphate (ZP) pads are separated by valleys, which contain thinner layers of ZPs. Studies indicate the tops of the pads are hardest and show spectra suggestive of long-chain ZPs and are the load-bearing points experiencing highest pressures during sliding. The valleys contain softer short-chain ZPs [60]. Upon careful examination of the elemental maps, it can be seen that Zn, P and O occur at similar zones on the maps, thus suggesting the formation of zinc phosphates. Fe map shows the presence of the elements throughout except at zones where the ZP pads occur. At the same locations can be seen the presence of sulfur, indicating the formation of iron sulfides. This is in accordance with the theory suggested by Uetz et al. [53] who suggest that in additives based on sulfur, the iron from the bulk is participative in the formation of reaction layer. However, iron does not necessarily participate in the formation of reaction layer with additives based on organometallic dithiophosphates of metals like lead and zinc. FeS may be formed between the phosphate layer and the iron substrate and may serve as an adhesive layer as well as a seizure-resistant [54]. Thus, the low WSD value and high weld load numbers.

The AW/EP action of ZDDP comes from the zinc polyphosphates and iron sulfides in the tribofilms. Komvopoulos et al. [56] report that iron sulfide acts as an excellent solid lubricant because of its high melting point (1100℃), relativ ely low hardness and shear strength, and good adhesion to iron and steel surface. The sulfide film typically consists of FeS with a layered hexagonal lattice and some amount of FeS_2 and exhibits good solid lubrication behavior. The zinc phosphate pads, on the other hand, correspond to experience highest pressure during sliding and the pads of zinc phosphates act as load-bearing points. This accounts for the good wear and EP properties of the grease chemistry with ZDDP+PTFE.

6.1.2.3 VL 7723

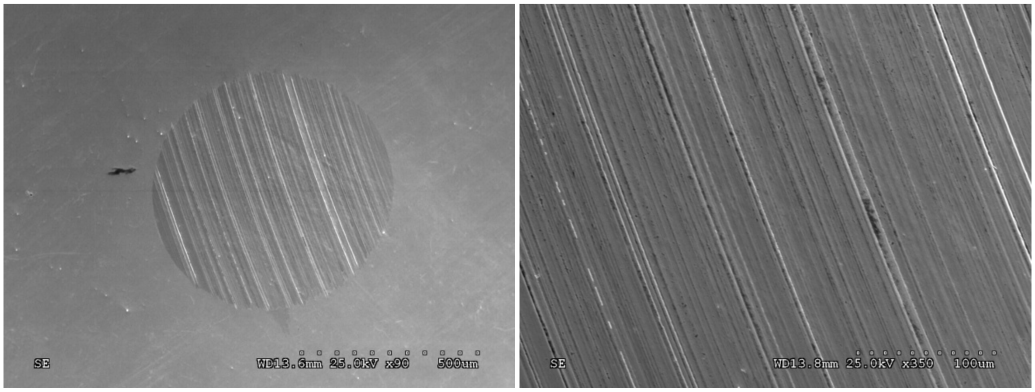
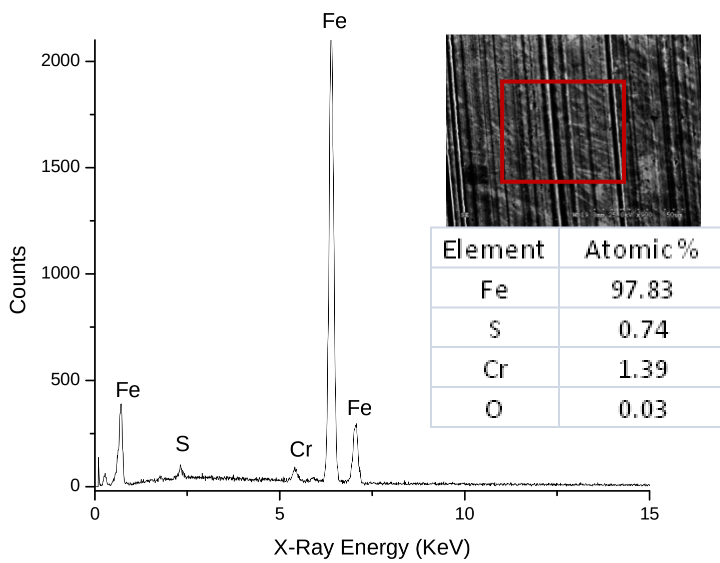


Figure 6.12 SEM images of the wear track formed through a Four-ball wear test (ASTM D 2266) from a Li-base grease containing 3%VL 7723

The presence of plowing grooves running parallel to the direction of sliding suggests the occurrence of abrasive wear (Figure 6.12). The appearance of the wear track does not show presence of a sufficient tribofilm. The wear scar diameter of this grease chemistry (0.63mm) is almost in line with the wear scar diameter value for the base grease (0.70mm).



Element	Atomic%
Fe	97.83
S	0.74
Cr	1.39
O	0.03

Figure 6.13 EDS spectrum performed on the wear track with grease chemistry VL 7723 (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.13) and elemental mapping (Figure 6.13) of the wear track created by the grease containing VL 7723 shows some presence of S on the surface.

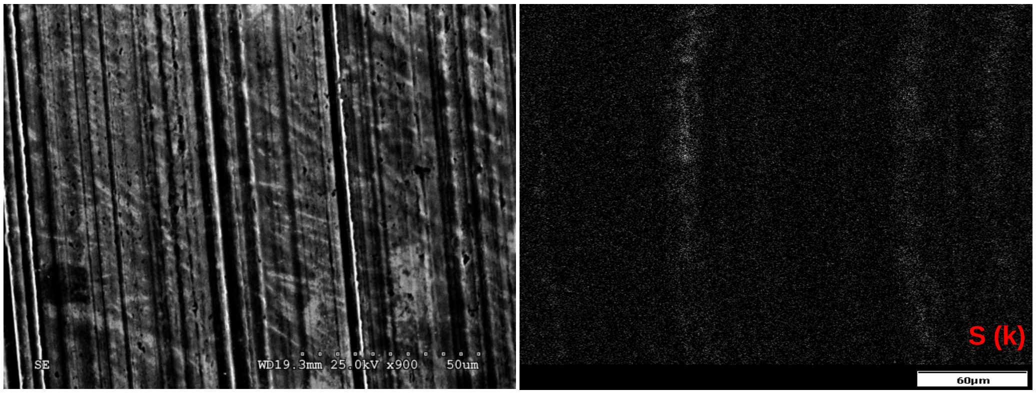


Figure 6.14 Elemental map sulfur found on the wear track formed from VL 7723-containing Li-base grease

6.1.2.4 VL 7723_280L

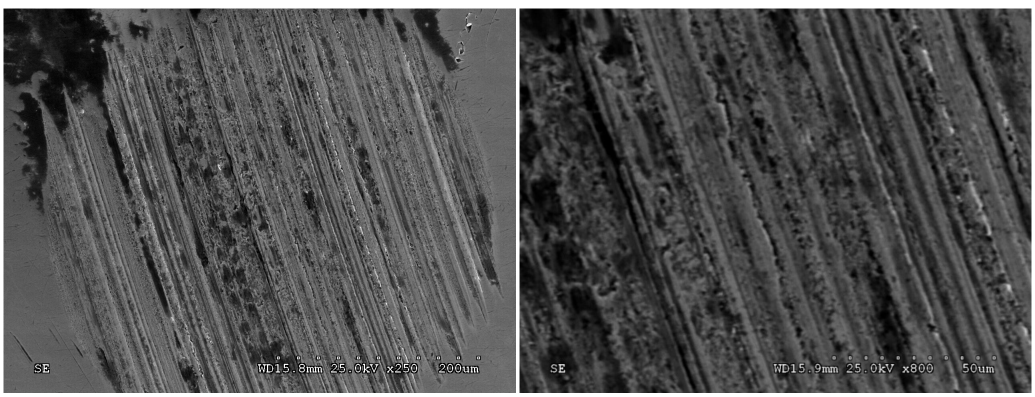
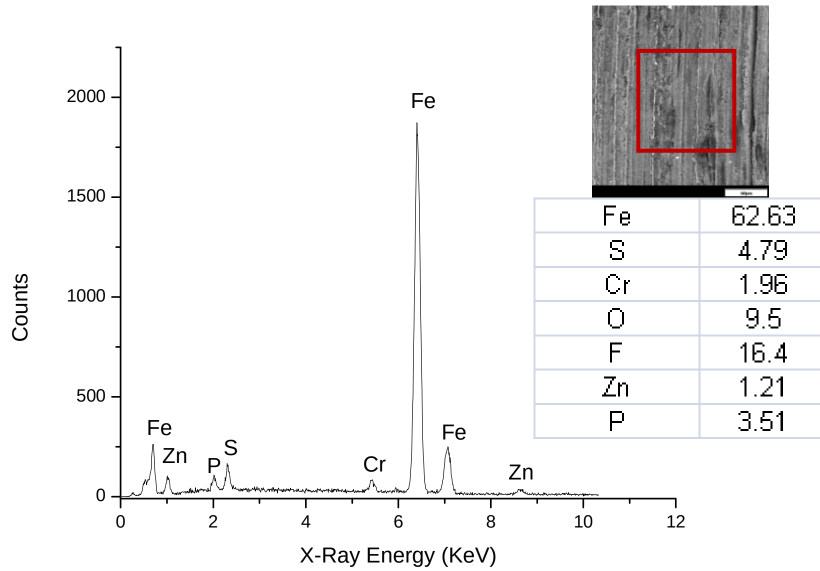


Figure 6.15 SEM images of the wear track formed through a Four-ball wear test (ASTM D 2266) from a Li-base grease containing 3%VL 7723+ ZDDP+ PTFE

The appearance of the wear tracks is as was observed with that of the chemistries containing ZDDP and PTFE (Figure 6.15). The wear track is representative of abrasive wear and mild adhesive wear with features of plowing grooves, pull-outs and plastic flow.



Fe	62.63
S	4.79
Cr	1.96
O	9.5
F	16.4
Zn	1.21
P	3.51

Figure 6.16 EDS spectrum performed on the wear track with grease chemistry VL 7723+ZDDP +PTFE (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.16) shows the presence of elements of S,O,Zn and P. The area of interest is rich in sulfur and phosphorus.

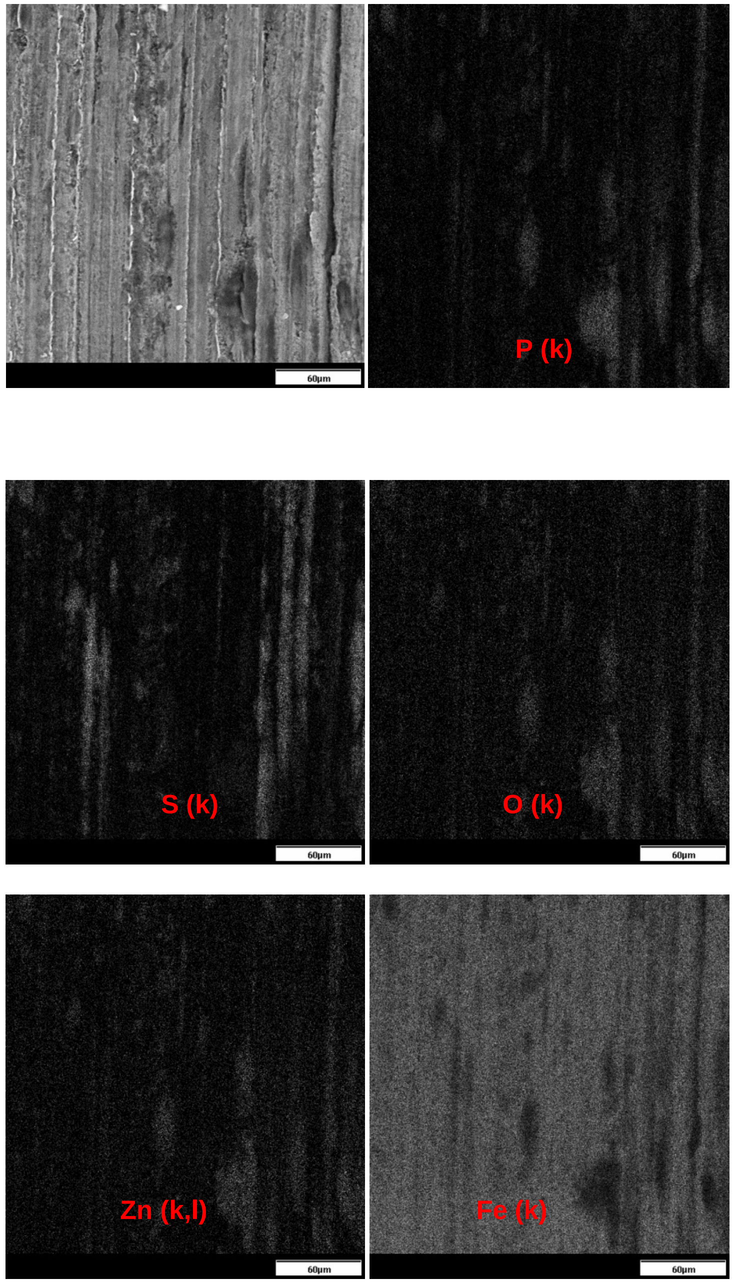


Figure 6.17 Elemental maps of the various elements found on the wear track formed from VL 7723 + ZDDP+PTFE-containing Li-base grease

On examination of the elemental maps (Figure 6.17), it can be deduced that Zn, P and O occur at similar locations, thus suggesting zinc phosphate is formed on the track, hence decomposition of ZDDP. This result is similar to that in VL SB. However, the S in the chemistry with VL 7723 does not occur at locations similar to Fe. This suggests that the additive could have been adsorbed on the steel substrate without scission of the S-S bonds. Had the S-S bonds been broken, an iron sulfide film would have resulted since the reactivity of elemental S with steel has been known to be high [4].

6.1.2.5 VPS 15

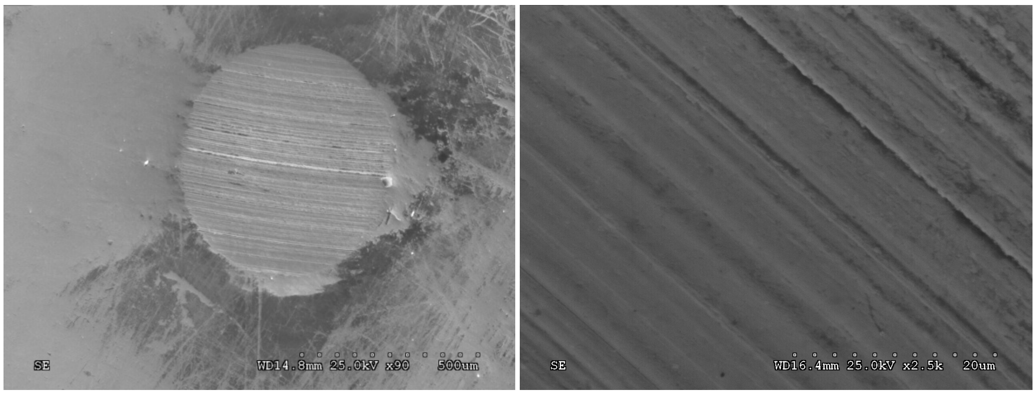
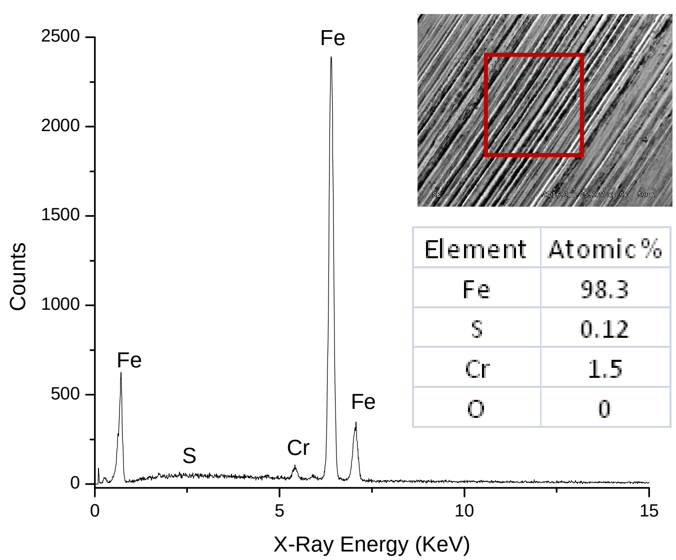


Figure 6.18 SEM images of the wear track formed through a Four-ball wear test (ASTM D 2266) from a Li-base grease containing 3%VPS 15



Element	Atomic %
Fe	98.3
S	0.12
Cr	1.5
O	0

Figure 6.19 EDS spectrum performed on the wear track with grease chemistry VPS 15 (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.19) of this grease does not reveal a distinct S peak, the atomic percent of S being only 0.12%. It could be hypothesized that although VPS 15 is highly polar in nature, it has to compete for the surface with the thickener fibers in the grease that are polar too. With very low amounts of S, the additive may be forming a very thin adsorbed layer that is beyond the detection limit of this instrument.

The elemental map of S (Figure 6.20) does not reveal any distinct distribution of S on the wear track suggesting that either the tribofilm was insufficiently formed on the surface or the sulfur additive was partially adsorbed on the surface and would require the presence of ZDDP and PTFE for AW/EP action.

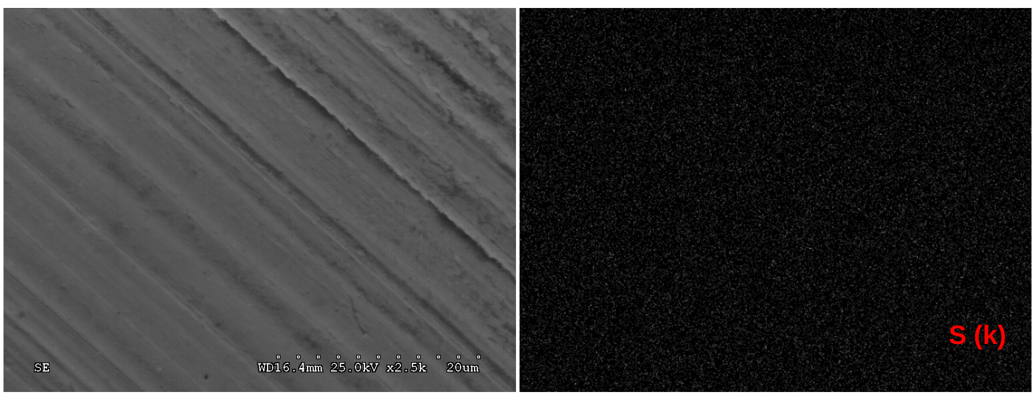
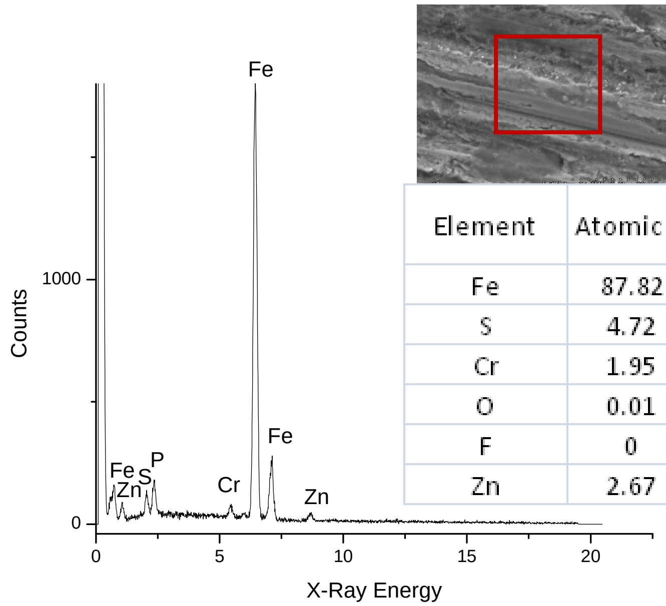


Figure 6.20 Elemental map of sulfur as found on the wear track formed from VPS 15-containing Li-base grease

6.1.2.6 VPS 15_280L



Element	Atomic %
Fe	87.82
S	4.72
Cr	1.95
O	0.01
F	0
Zn	2.67

Figure 6.21 EDS spectrum performed on the wear track with grease chemistry VPS 15+ PTFE + ZDDP (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.21) shows the presence of important elements like S,P, and Zn. The spatial distribution of these elements can be observed through the elemental maps. There is some oxygen detected at location also containing Zn and P suggesting the formation of zinc phosphates.

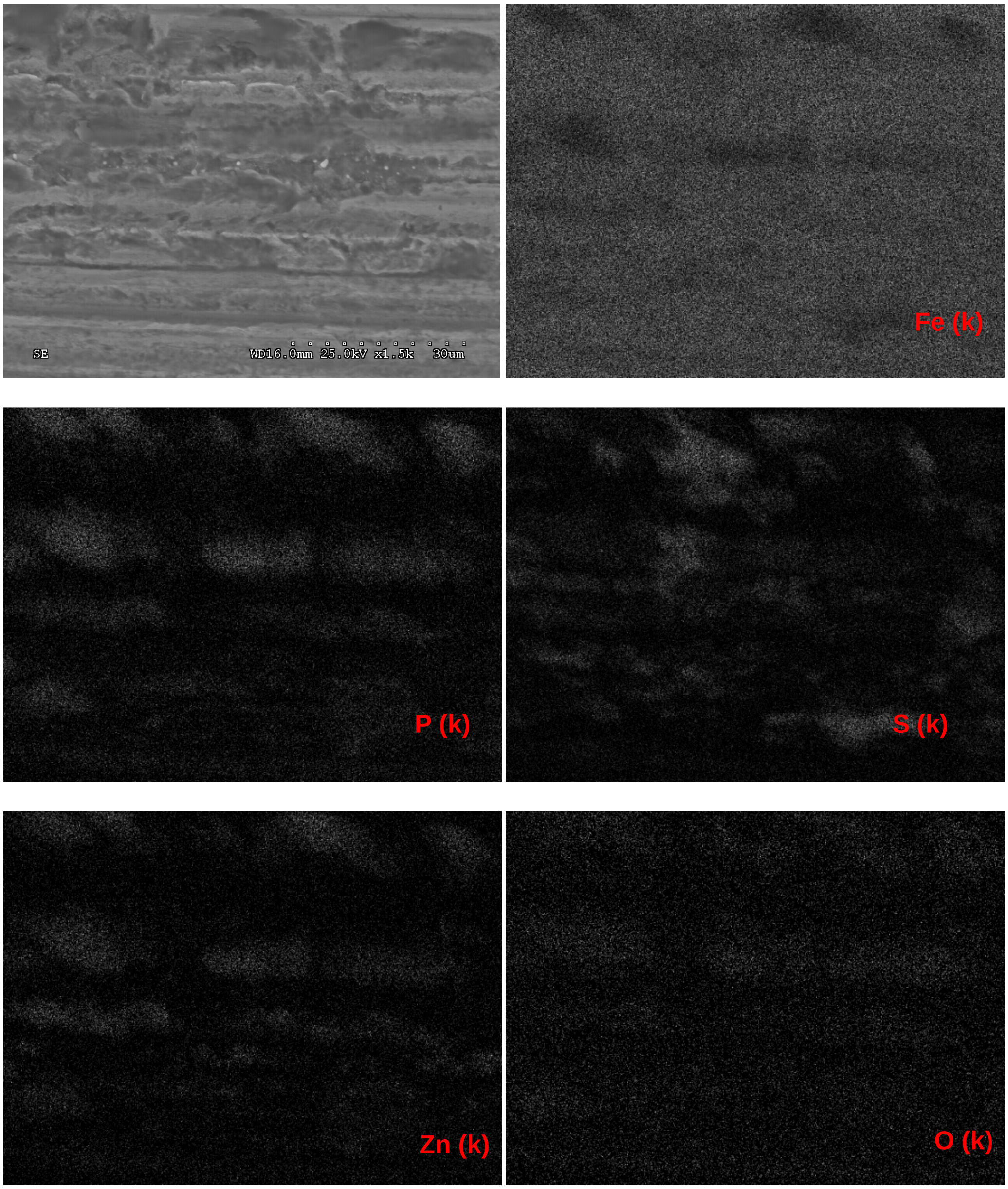


Figure 6.22 Elemental maps of the various elements found on the wear track formed from VPS 15+ ZDDP + PTFE-containing Li-base grease

The maps (Figure 6.22) indicate that Zn and P occur at similar locations. There are traces of oxygen found on the track. Fe and S do not occur at similar locations. These results are different from what was seen with the other additives dealt with so far. Thus, it can be commented that zinc phosphide is formed; the formation of zinc phosphate is not conclusive from the data.

Moreover, no iron sulfide is formed in this case. This result is consistent with the fact that VPS 15 is an inactive sulfur additive and is very stable to release the sulfur and react with the substrate to form iron sulfide. Sulfur could be present as an organosulfur on the track and occurs in sites where zinc phosphides are not formed. Kulczycki [50] mentions that in the low-load regimes, the sulfur additive get physically adsorbed on the metal surface and increase the durability of the lubricating film; in the high load regime, where the durability of the lubricating film is limited, the sulfur additives form tribologically active mercaptide compounds and form metal sulfides layer when loads damaging the film are applied. However, the mapping results do not indicate the formation of either iron sulfide or iron mercaptide. It is likely that the organosulfur has been physically adsorbed on the surface andno cleavage or decomposition has occurred since VPS 15 is a stable polysulfide with inactive sulfur.

6.1.2.7 TPS 44

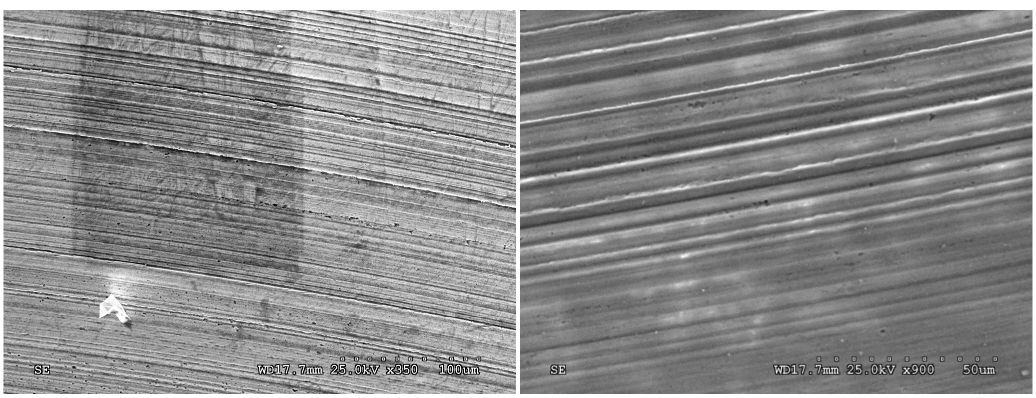


Figure 6.23 Wear track formed from TPS 44-containing Li-base grease

The wear track (Figure 6.23) of this chemistry shows plowing grooves running in a direction parallel to the sliding direction and few cavities that suggest the occurrence of abrasive wear.

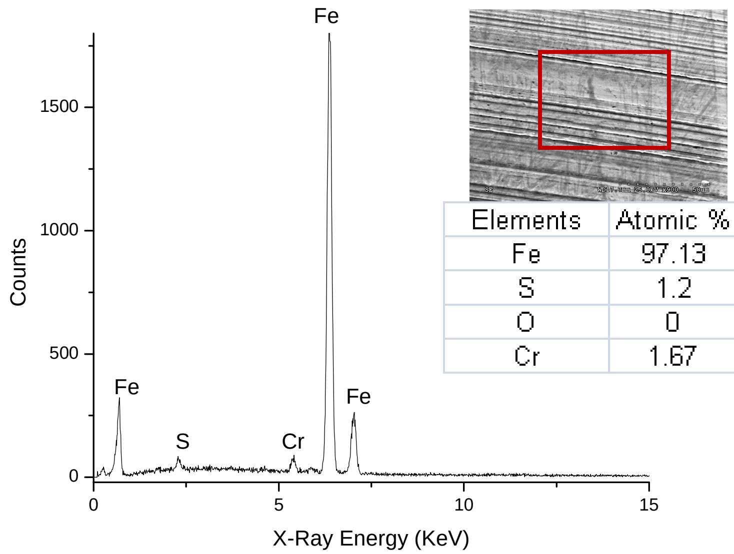


Figure 6.24 EDS spectrum performed on the wear track with grease chemistry TPS 44 (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.24) shows the presence of S on the wear track The elemental map (Figure 6.25) suggests the presence of some sulfur on the wear track of the steel ball after running the Four-ball wear test at standard ASTM D 2266 conditions of 40kg/1200rpm/1 hour suggesting that either TPS 44 or its decomposition products have been adsorbed on the surface since TPS 44 contains higher amount of active sulfur (18 weight percent); though the amount of sulfur on the wear track is not significant enough better the wear performance of the grease with TPS 44(WSD= 0.64mm) than when the grease is used without the additive (WSD of Li-base grease= 0.70mm).

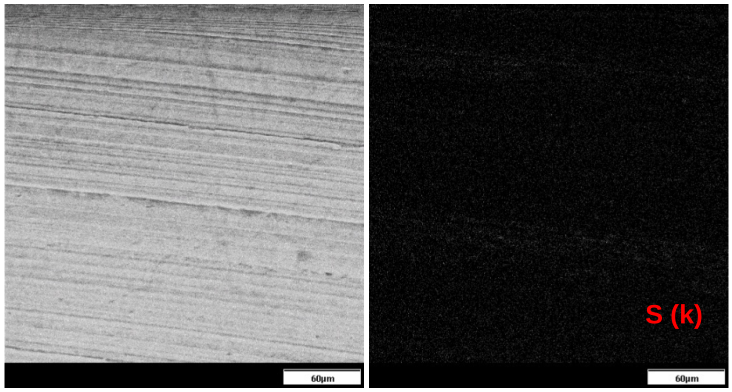


Figure 6.25 Elemental map of sulfur on the wear track formed from TPS 44 -containing Li-base grease

6.1.2.8 TPS 44_280L

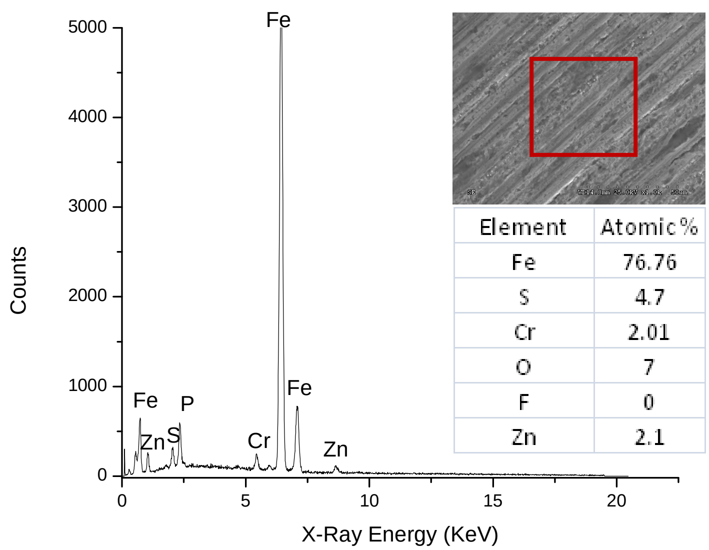


Figure 6.26 EDS spectrum performed on the wear track with grease chemistry TPS 44+ PTFE + ZDDP (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.26) gives first-hand information of the presence of various elements on the wear track, as Zn, P, O, and S. The distribution of these elements can be observed through the elemental maps.

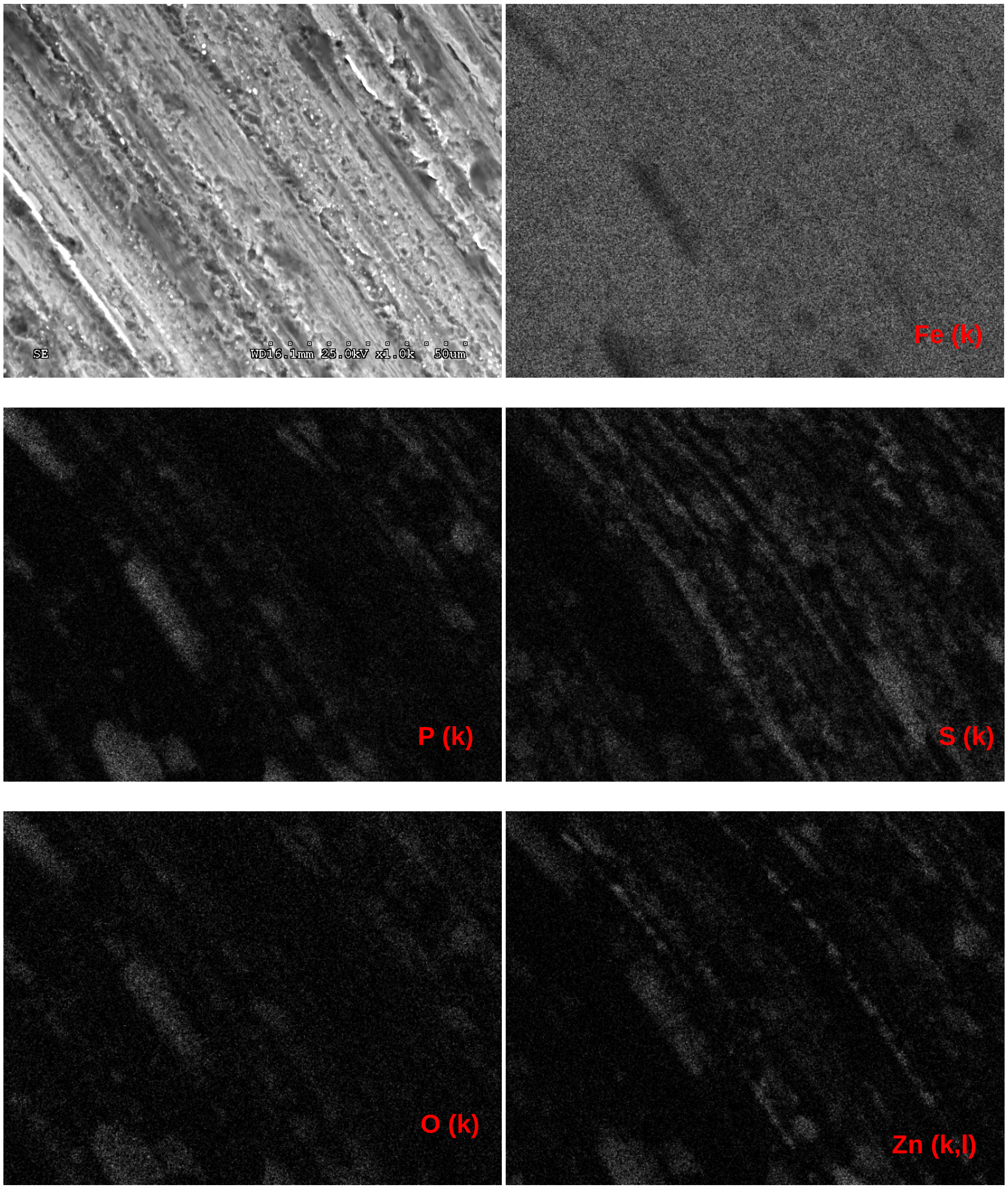


Figure 6.27 Elemental maps of the various elements found on the wear track formed from TPS 44+ ZDDP + PTFE-containing Li-base grease

The maps (Figure 6.27) suggest that zinc phosphates patches are formed. In the regions deprived of zinc phosphate, iron sulfide-rich areas can be seen. Since this additive is an active sulfur carrier, it forms iron sulfide layers under the given test conditions and provides adequate wear and EP protection. The proposed mechanism of antiwear/EP action for oraganosulfur compound is such that the organosulfur compound is initially adsorbed on the iron surface and iron mercaptide is formed due to cleavage of the S-S bonds. It is, however, not certain whether decomposition occurs before initial adsorption or vice-versa. When loads approach EP conditions, much higher temperatures are reached in the contact zone, and cleavage of the S-C bond occurs to form an inorganic sulfur-containing layer [51].

6.1.2.9 VL AZ

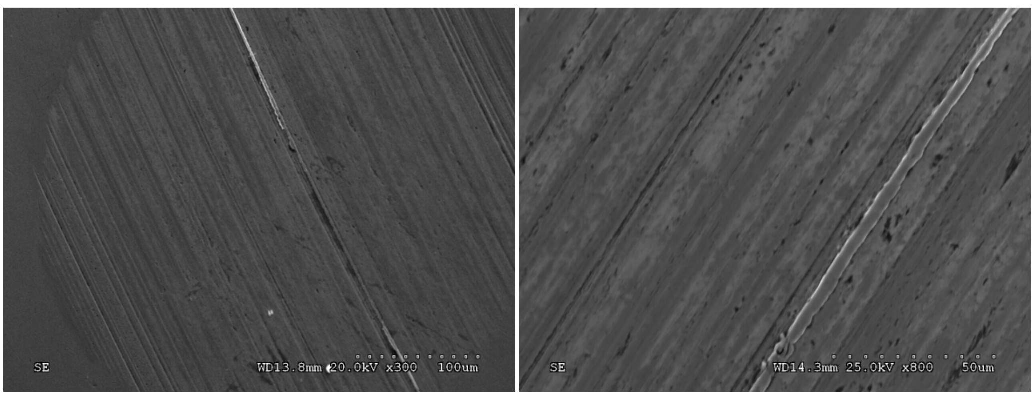


Figure 6.28 Wear track formed from VL AZ-containing Li-base grease

The wear track (Figure 6.28) for this grease chemistry is similar to that obtained for samples exhibiting abrasive type of wear with presence of plowing grooves and few cavities.

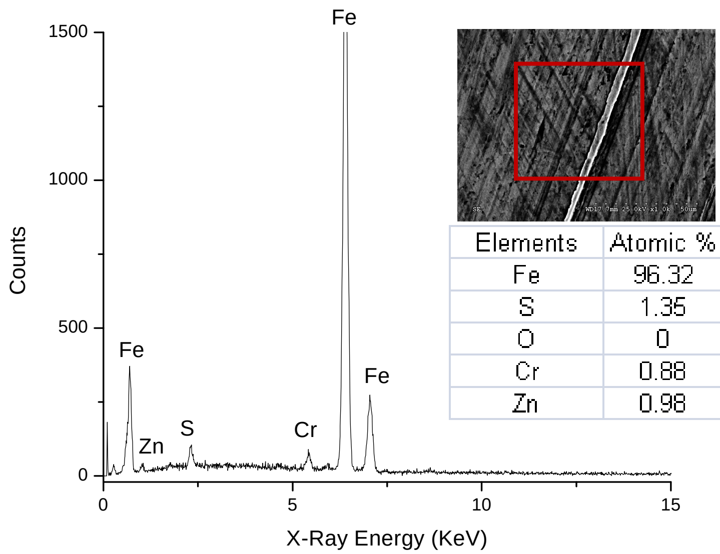


Figure 6.29 EDS spectrum performed on the wear track with 3% VL AZ in Li-base grease. (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.29) shows presence of some amount of sulfur and zinc on the wear track suggesting the presence of the additive or its decomposed product on the surface.

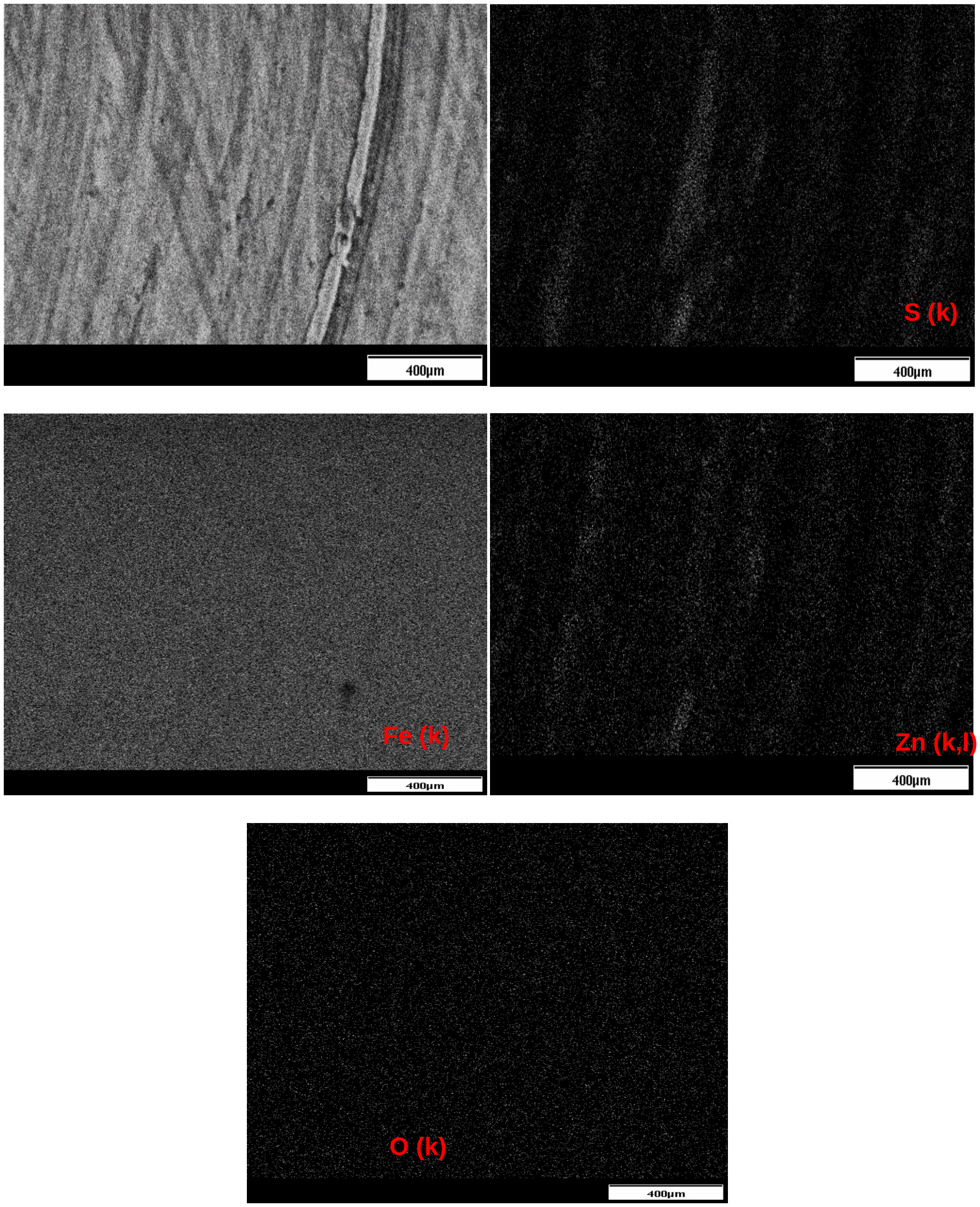
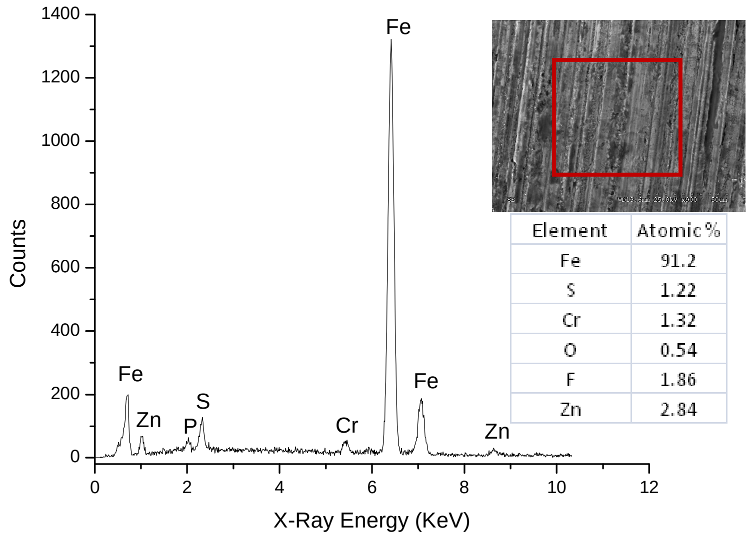


Figure 6.30 Elemental maps of the various elements found on the wear track formed from VL AZ-containing Li-base grease

It can be speculated from the elemental maps (Figure 6.30) that the additive was physically adsorbed on the surface and could have decomposed to form zinc sulfides that is responsible for giving good wear numbers..

6.1.2.10 VL AZ_280L



Element	Atomic %
Fe	91.2
S	1.22
Cr	1.32
O	0.54
F	1.86
Zn	2.84

Figure 6.31 EDS spectrum performed on the wear track with grease chemistry ZDDP+PTFE+VL AZ. (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.31) done on the wear track of one of the three stationary balls after running the ASTM D2266 on the Four-ball wear tester for the grease chemistry containing 5% (3%ZDDP, 2% PTFE) and 3% VL AZ, reveals the presence of Zn, P, S. O.

Considering the atomic percent of P, it remains unchanged in both cases and it comes from the decomposition of ZDDP (since VL AZ contains no P). The amount of Zn and O are slightly higher in the case of ZDDP+PTFE, while the amount of S recorded is somewhat higher in VL AZ+ZDDP+PTFE.

The zonal distribution of the various elements in VL AZ+ZDDP+PTFE is shown in the elemental maps (Figure 6.32), obtained individually for all the plausible elements in the wear track:

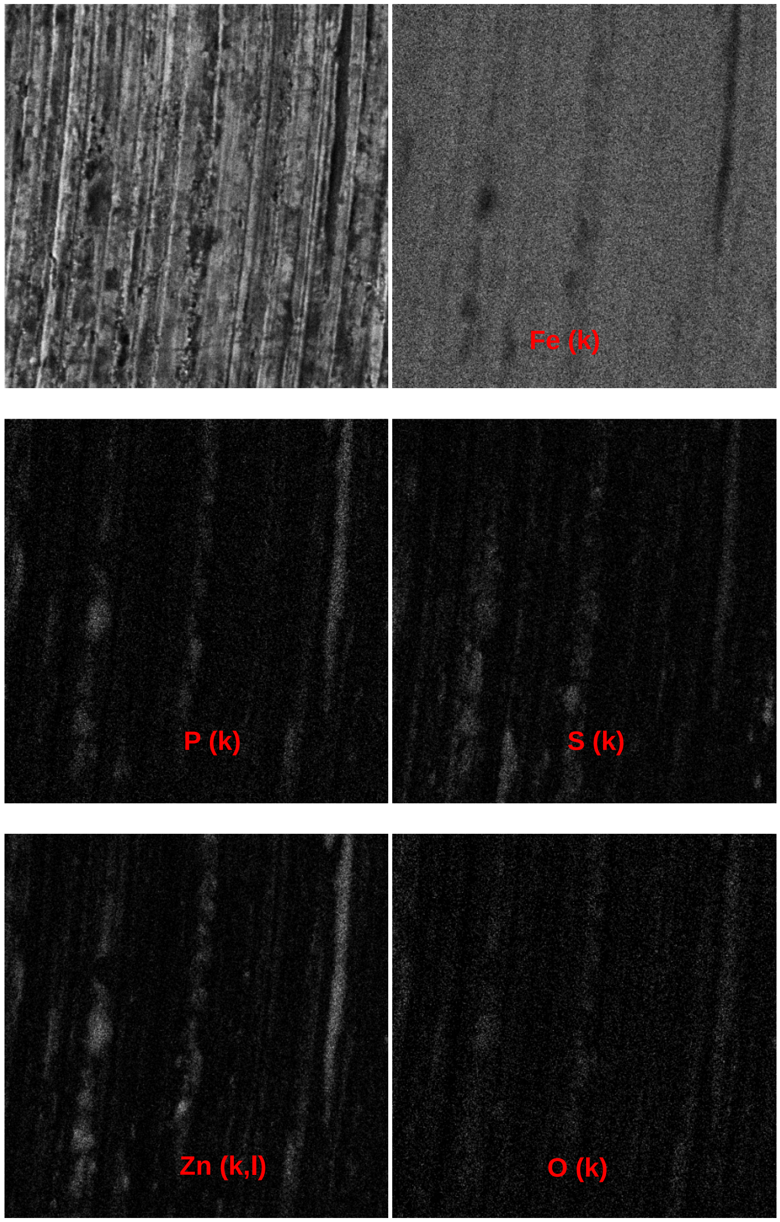


Figure 6.32 Elemental maps of the various elements found on the wear track formed from VL AZ+ ZDDP + PTFE-containing Li-base grease

As can be observed from the maps (Figure 6.32), Zn, P and O occur in distinct areas on the wear track suggesting the formation of zinc phosphates (ZP) from the decomposition of ZDDP. In these regions, the Fe regions appear dark with little or no Fe. However, Fe and S occur at similar areas, and suggest the presence of iron sulfides. The maps also suggest the formation of trace amounts of iron sulfates which are more abrasive than the sulfides and phosphates, thus detrimental to the tribofilm formation.

6.1.2.11 VL 622

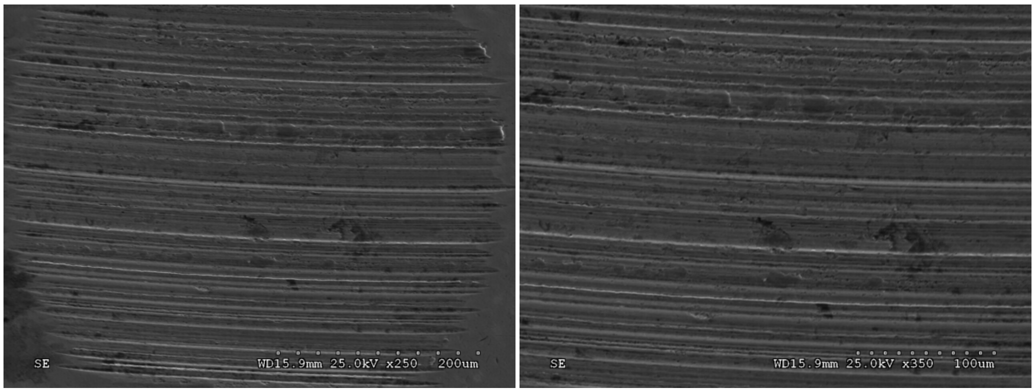
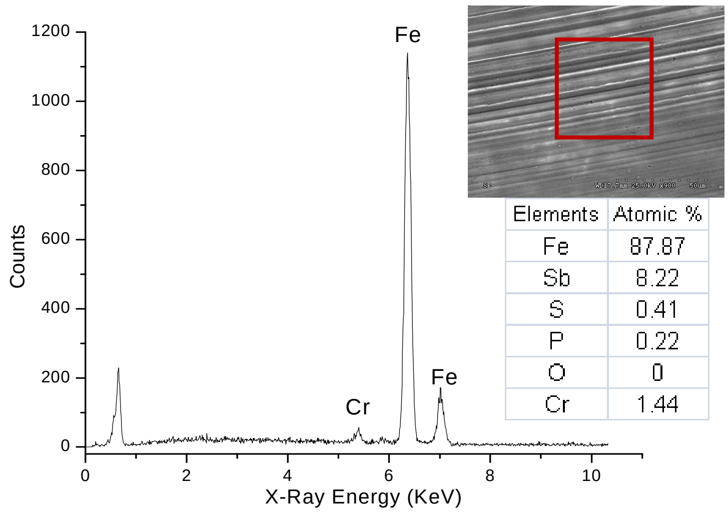


Figure 6.33 Wear track formed from VL 622-containing Li-base grease

The wear tracks (Figure 6.33) suggest the occurrence of abrasive wear and mild adhesive wear.

The EDS spectrum (Figure 6.34) shows the presence of elements of Sb, P,S on the wear track as is given in the figure. The spectrum suggests that the additive is physically adsorbed on the surface of the steel balls. No further conclusions can be drawn from the spectrum obtained.



Elements	Atomic %
Fe	87.87
Sb	8.22
S	0.41
P	0.22
O	0
Cr	1.44

Figure 6.34 EDS spectrum performed on the wear track with grease chemistry VL 622 (Inset: SEM image of the wear track)

The distribution of these elements can be observed through the elemental maps (Figure 6.35). The maps show the presence of some amount of S, P, Sb, suggesting the adsorption of the additive on the surface of the steel balls. However, much conclusion cannot be drawn from the elemental maps and more sophisticated characterization techniques are required to predict the nature of formation of films.

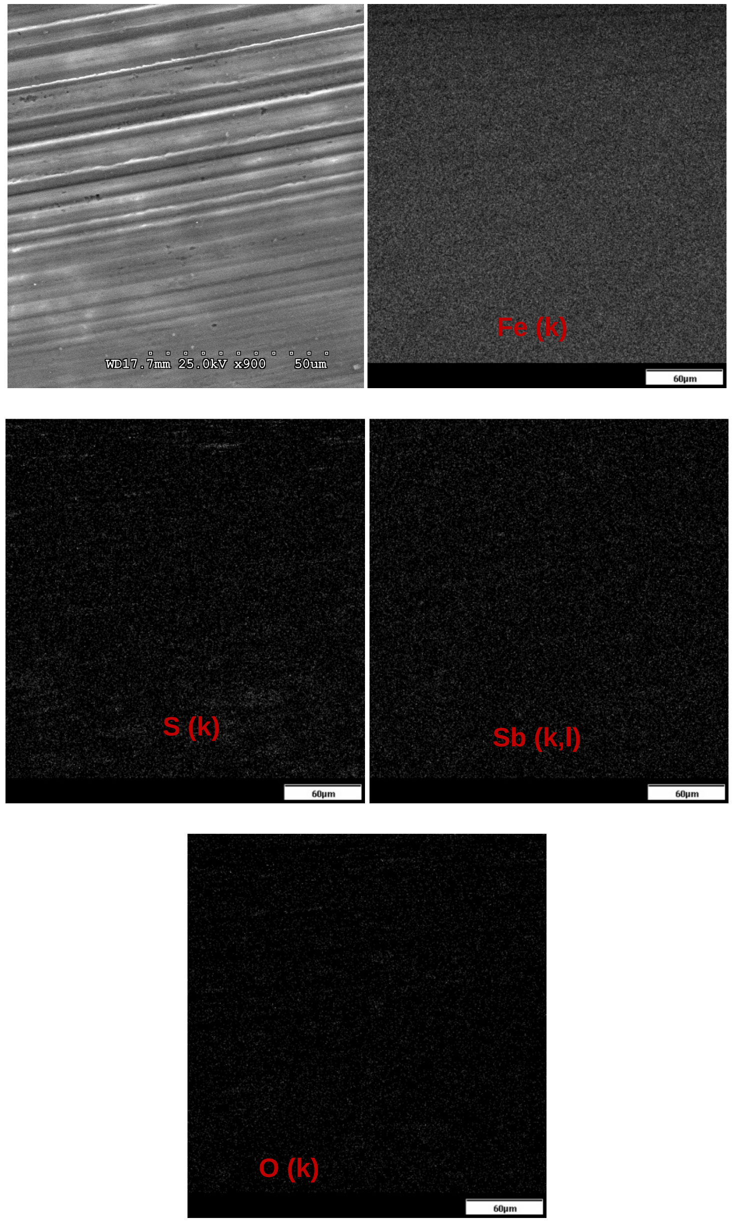
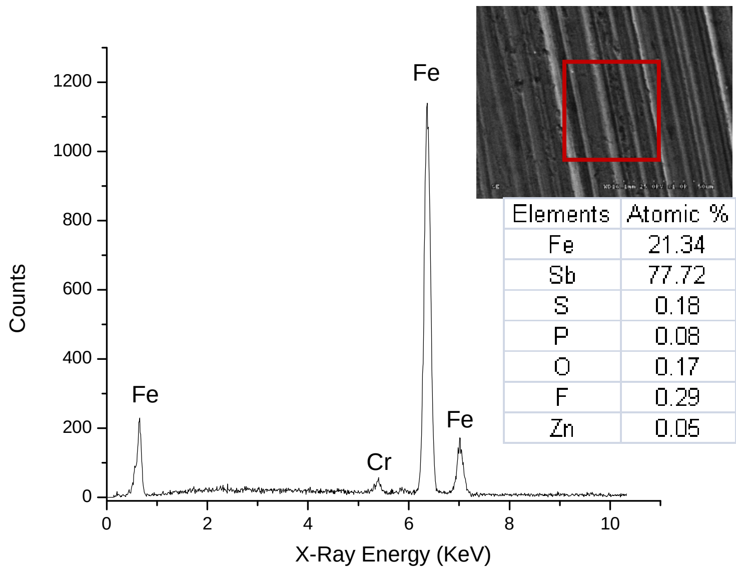


Figure 6.35 Elemental maps of the various elements found on the wear track formed from VL 622-containing Li-base grease

The elemental maps (Figure 6.35) show distinct regions of P, S and O suggesting the various compounds that could have been formed of sulfides, phosphates or even antimony phosphorodithioate. Antimony phosphorodithioate incorporated into greases as a solid additive imparts outstanding extreme-pressure properties and is considered to be a candidate additive for use under extremely high loads where conventional solid lubricants are found to be inadequate

[57]. This could explain good wear numbers obtained for this chemistry (0.47mm) and weld load of 400kgs.

6.1.2.12 ZDDP+PTFE+VL 622



Elements	Atomic %
Fe	21.34
Sb	77.72
S	0.18
P	0.08
O	0.17
F	0.29
Zn	0.05

Figure 6.36 EDS spectrum performed on the wear track with grease chemistry ZDDP+PTFE+VL 622 (Inset: SEM image of the wear track)

The EDS spectrum (Figure 6.36) reveals the presence of Sb, S, O and traces of Zn, and P on the wear track. The elements have not been marked on the EDS spectrum since they are present in insignificant amounts on the tribofilm.

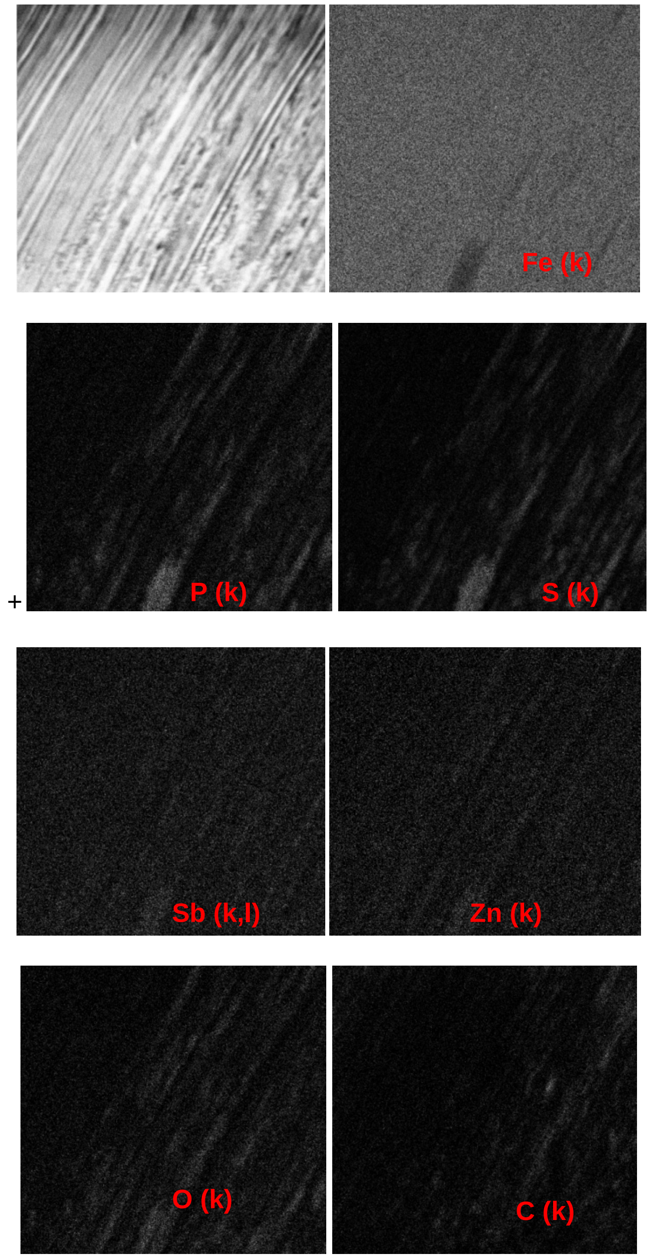


Figure 6.37 Elemental maps of the various elements found on the wear track formed from VL 622-containing Li-base grease

The elemental maps (Figure 6.37) show strong signals of P and S in certain distinct regions of the wear track. Presence of S, P, O and Zn at similar locations suggest that there might have been formation of some amounts of zinc sulfates and zinc phosphates. Zinc phosphates have a positive influence on the wear and EP properties of the grease, whereas zinc sulfates adversely affect the wear performance. The presence of two cations could suggest a competition for surface. It could be hypothesized that VL 622 could have formed antimony thioantimonate [Sb(SbS_4)], which is a known lubricant additive in oils and greases. However, the presence of ZDDP has some antagonistic effect on the wear behavior of VL 622.

6.1.2.13 VL 672

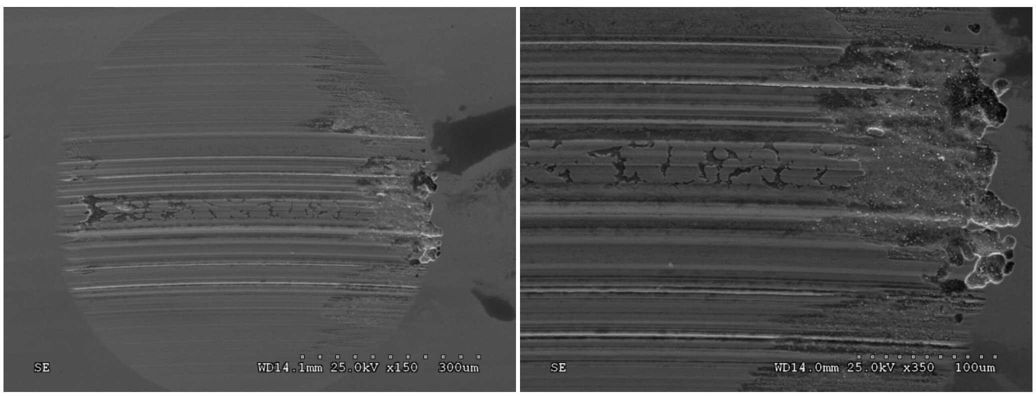


Figure 6.38 SEM images of the wear track formed through a Four-ball wear test (ASTM D 2266) from a Li-base grease containing VL 672

The SEM images (Figure 6.38) of the wear track suggest the occurrence of abrasive and adhesive wear. The presence of grooves, fine wear debris and surface microcracks are indicative of abrasive wear, whereas the pull-outs at the edges of the track suggest adhesive wear and loosely adherent film.

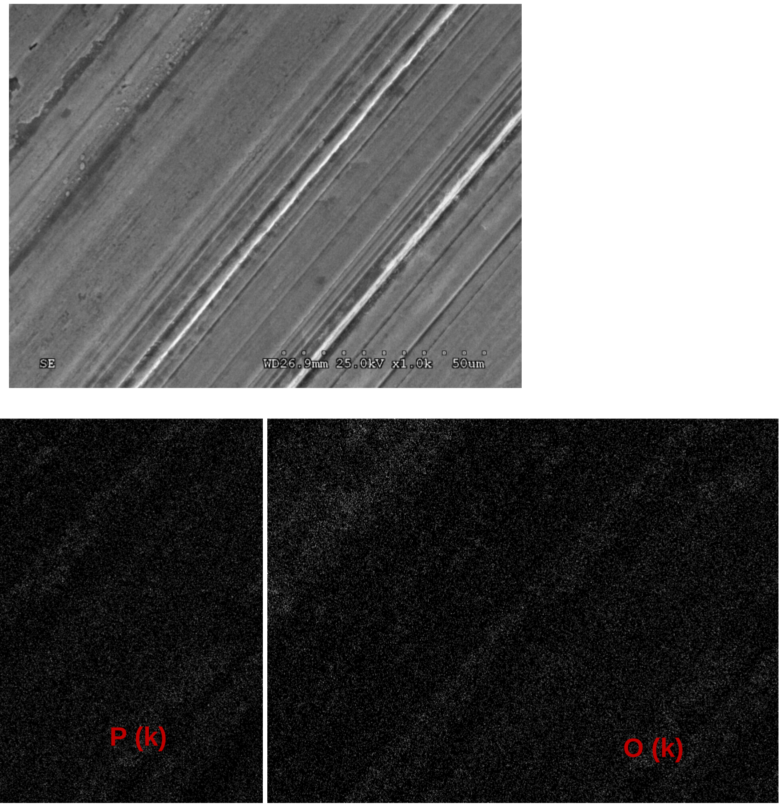


Figure 6.39 Elemental maps of the various elements found on the wear track formed from VL 672-containing Li-base grease

The elemental maps (Figure 6.39) suggest the formation of phosphates on the film formed by VL 672 (Ashless amine phosphate) in Li-base grease. The high wear and low weld load numbers could be due to a loosely adherent film and the occurrence of severe adhesive and abrasive wear.

6.1.2.14 VL 672+ ZDDP+ PTFE

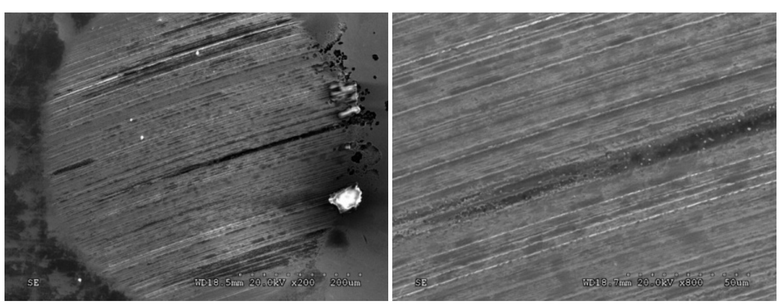
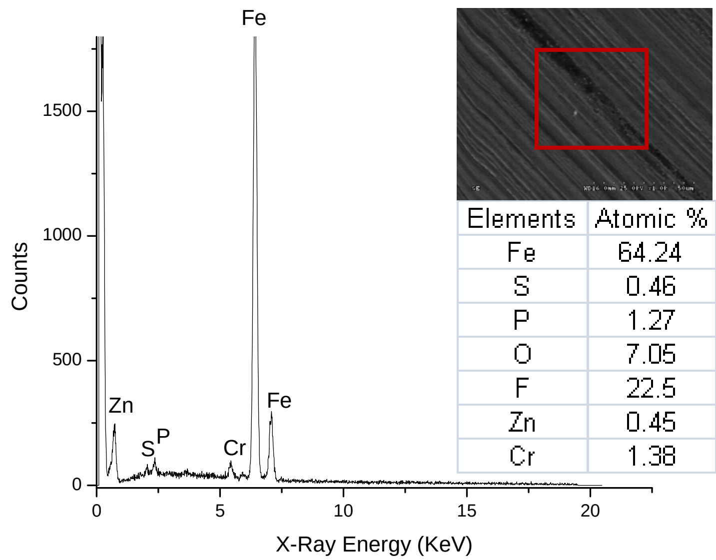


Figure 6.40 SEM images of the wear track formed through a Four-ball wear test (ASTM D 2266) from a Li-base grease containing VL 672+ ZDDP+ PTFE

The SEM images (Figure 6.40) of the wear track for this grease chemistry is suggestive of abrasive showing grooves with some debris formation.

The EDS spectrum as shown in Figure 6.41 reveals the presence of elements Fe, O, P and traces of S and Zn in the wear track. More on the distribution of the elements on the wear track can be seen on the elemental maps obtained for the individual elements through the “Multi-toolbar” option of the “Revolution” software for EDS analysis.



Elements	Atomic %
Fe	64.24
S	0.46
P	1.27
O	7.05
F	22.5
Zn	0.45
Cr	1.38

Figure 6.41 EDS spectrum performed on the wear track with grease chemistry ZDDP+PTFE+VL 672 (Inset: SEM image of the wear track)

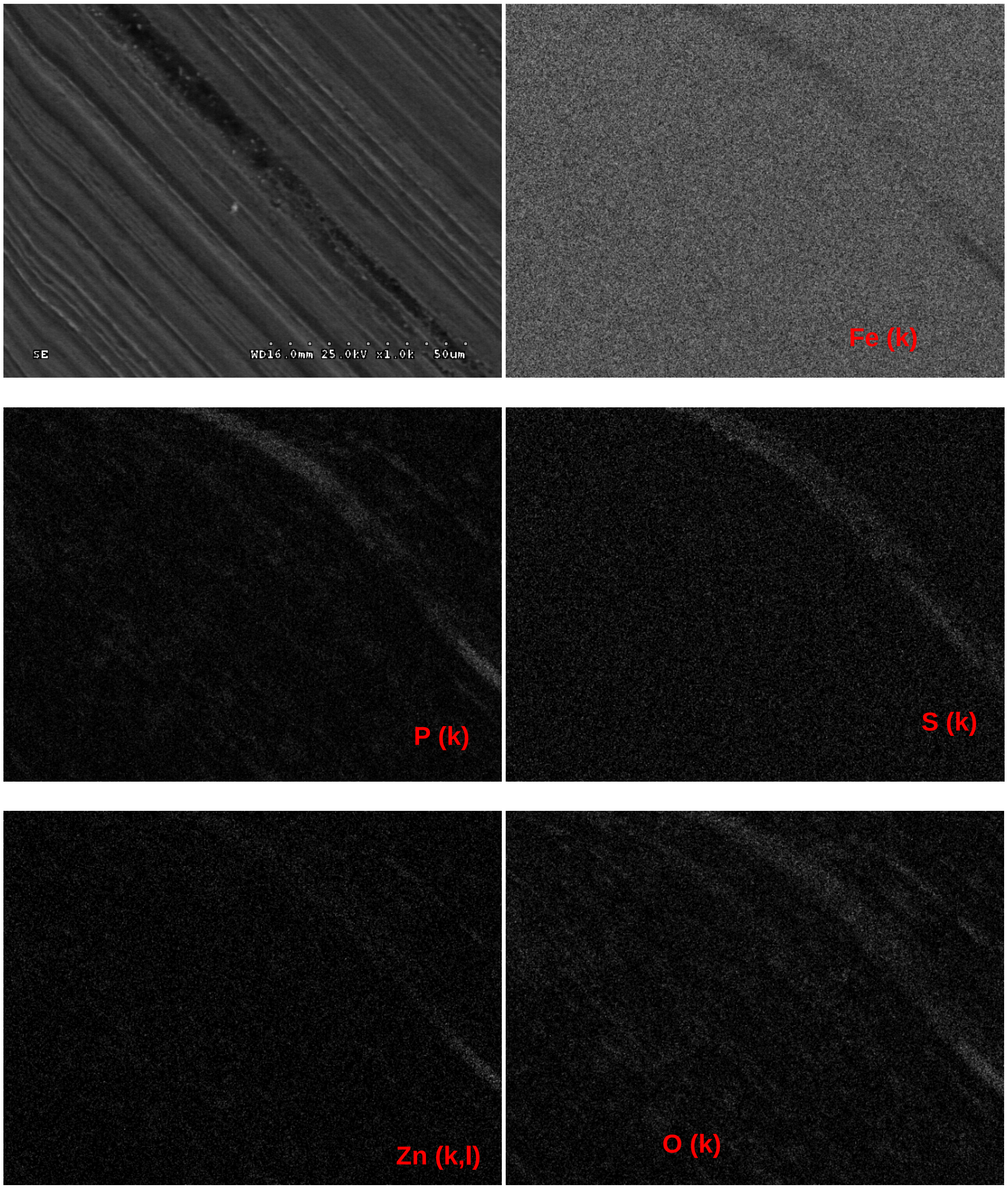


Figure 6.42 Elemental maps of the various elements found on the wear track formed from ZDDP+PTFE+VL 672-containing Li-base grease

The elemental maps (Figure 6.42) suggest the presence of trace amounts of Zn on the wear track. S,P, O and C occur at similar zones. The zones showing higher signals from S are also the zones with absence of Fe. This eliminates the possibility of formation of iron sulfides. The sulfur could be present as zinc sulfides (in traces), or as organosulphates (or simply as organosulfur). Phosphorus could be present as organophosphates or iron phosphates, imparting some antiwear property to the grease. This is in accordance with the theory held by Wan et al. [59] who suggest that P-containing additives can form a $FePO_4$ surface film by adsorption and reaction of the phosphate with the surface. They also suggest that the preferential adsorption of the amine on to the surface reduces the adsorption and reaction of AW agents with the surface. This serves to explain the presence of trace amounts of Zn when an amine phosphate with 0% S is used. The only source of Zn and S, in this grease chemistry, comes from the decomposition of ZDDP. According to the EDS quantitative data, the atomic percents of Zn and S are equal (~0.45%) suggesting the formation of zinc sulfides as ZnS.

CHAPTER 7

CONCLUSIONS

The present study lays the groundwork for understanding various tribological aspects of greases. This chapter summarizes the outcomes important to the study of additives in greases.

1. MoS_2 has detrimental effects on the film formed on the steel surface, such that the hard and rough edges of the particles themselves serve to rip off the film. Moreover, the lubricating action of MoS_2 is realized only when the hexagonal planes of the molecule come parallel to the contact point. Increasing the amount of MoS_2, increases the wear and lowers the weld load numbers.
2. As an effort to replace the black powder (MoS_2) due to its increasing cost and poor AW/EP behavior, the synergistic combination of ZDDP and PTFE was utilized to develop greases with superior AW/EP performance. ZDDP-PTFE when used in lower concentrations (3 and 2 percent respectively) provided superior wear and weld performance compared to MoS_2 greases. Additionally, increasing the amount of ZDDP and PTFE enhanced the AW/EP results.
3. Although ASTM Standard D 2266 has been used to screen the performance of greases, yet the actual bearing conditions may vary significantly with load, rpm and duration of test such that the activation of chemistries is load-driven, the rpm dictates the entry of grease into the contact point and the test duration dictates the durability of greases. Results indicate that the performance of greases varies with the test conditions and this would prove to be very useful for designing greases for extended operating conditions.

4. The weld load numbers obtained for Blend-H were the highest (620kgs) as compared to Blend-L that gave weld load numbers of 400kgs. Thus, ZDDP-PTFE synergism has been established to give superior EP/AW properties to grease.

5. On addition of Blend-L to the VL additives, VL 622, which showed good wear numbers when used alone in the Li-base grease without Blend-L, is antagonistic to ZDDP. This could be attributed to the presence of two metal cations in the grease formulation such that there is competition of surface. The EP action of VL 622 is independent of the ZDDP content and depends solely on the PTFE content. The formation of sulfides of antimony which are thermally stable and have layered structure could be responsible for good wear behavior [64].

6. All of the other VL additives behave in synergism with ZDDP and form sulfides and phosphates in distinct regions on the wear track.

7. Blend-L demonstrates strong synergism with VL SB (sulfurized olefin) and the combination of Blend-L and VL SB produces excellent wear and weld load behavior.

CHAPTER 8

SUGGESTED FUTURE WORK

After performing the elementary tests and characterization, there are some suggestions that would contribute to future work and were beyond the scope of the present research work.

- The chemical composition of the films through more sophisticated characterization like XANES should be performed.

Since there are interactions (antagonistic and synergistic) that occur between additives in greases, it is important to study the chemical composition of the lubricant films formed. This would give an insight into the chemical interactions that may have occurred between additives or between the additives and surface.

- The mechanical properties of the films should be investigated through nanomechanical indentation tests.

Abrasive wear results from a cutting action by (1) a rough, hard surface sliding against a softer surface or (2) contaminant hard particles trapped between the sliding surfaces. In previous work, it has been established that to cut, the hardness of the cutting agent should be greater than about 1.2 times that of the material cut. Thus, by performing nanomechanical tests, correlations between abrasive wear and material properties like hardness, modulus could be established.

- The effect of ball-milling on the particle size of MoS_2, hence its lubricating action, should be carried out.

Since that hard and rough edges of the MoS_2 were considered to be the factors responsible for poor wear performance of greases with MoS_2, ball-milling of the MoS_2 particles could be performed, since ball-milling would generate powders of fine sizes at a relatively low cost and thus, the dependence of particle size on the lubricating behavior of MoS_2 could be established.

APPENDIX A

PROTOCOL FOR GREASE PREPARATION

PROTOCOL FOR GREASE PREPARATION

GREASE BLENDS WERE PREPARED (IN WEIGHT PERCENT) IN BATCHES OF 200 GRAMS.

1. For preparation of (1) and (2) chemistries as was stated in the preceding section, measured amount of Lithium-base grease was taken in a 4.5 quart container and 3 or 5 weight percent of MoS_2 (or 3% Vanlube additives) was carefully added to the container and stirred with a spatula, ensuring that the particles do not stick to the walls of the container. Mixing was done according to the specifications as mentioned in (g) below.
2. Depending on the compositions to be blended (whether (3) or (4)), required amount of ZDDP was measured on a weighing scale (sensitive up to 4 decimal places) and proportionate amount of PTFE was added. The mixture was thoroughly mixed with a spatula to obtain uniform composition. Blend L or Blend H was added to the grease taken in a container and mixed as specified in (g) below.
3. For preparing chemistry (5), MoS2 is first added to the base grease and then followed by PTFE. Finally, proportionate amount of ZDDP is added and the mixture is stirred with a spatula for rough mixing and preventing the particles to fly off when final mixing is done in a Kitchen Aid Blender.
4. (6) can be prepared by adding the required amount of additives (3%) to the base grease and subject it to mixing.
5. For (7), first the concentrate of Blend L is prepared and the appropriate amount is added to the base grease, following which the additive is added and stirred with a spatula for rough mixing. Final mixing is done as described in (g).
6. (7) is prepared by added the measured amount of PTFE to the base grease after which the additive is added and the mixture roughly stirred before subjecting to final mixing.

7. The final mixing is done in a 4.5 quart capacity Kitchen Aid Blender of power rating 250 watts. The blender is run at a speed of 4 for approximately 30 minutes and then turned off to scrub the walls of the container. The blender is restarted and blending is done at speed 6 for 1 hour. The total blending time is 1.5 hours.
8. After blending is done, the formulations are stored in containers with appropriate labeling. The formulation is ready to be tested. (To ensure no contamination, the containers and hardware are cleaned thoroughly with hexane and acetone).

APPENDIX B

PROTOCOL FOR RUNNING THE FOUR-BALL WEAR/EP TESTS AND CLEANING METHODOLOGIES

In order to generate consistent and reproducible outcomes, a test protocol was followed in the laboratory. Details of the test protocol are as follows:

LOADING THE SAMPLE/WEAR TEST

1. Chrome-plated ½ inch diameter stainless steel balls (Bearing Quality Aircraft Grade E52100 Alloy steel) were ordered from McMaster Carr and cleaned thoroughly with hexane.
2. The required grease formulation was taken and the grease-cup in the four-ball tester was filled to 2/3rd the amount. While filling, care must be taken that there are no air-bubbles.
3. Three of the four cleaned steel balls are carefully placed in the grease-filled cup, ensuring that the balls are in contact with each other. The balls are held in place through a Clamp ring.
4. Now the clamp ring is placed slowly such that the steels balls do not come out of the orifice provided in the ring. Otherwise, repeat the above steps till the balls remain clamped by the ring in the grease cup.
5. The grease cup is filled with more grease matching the height of the ball-holder assembly.
6. This whole assembly is placed in the body specimen clamp.
7. The next step is spin the locking nut onto the thread by hand and hand tightened. The box spanner is placed onto the nut and tightened using a torque bar to prevent the movement of the balls.
8. Insert a fresh cleaned ball in the collet and feel the ball snap into place by hand.
9. Insert the collet into the end of the shaft.
10. The thermocouple lead is connected to the thermocouple plug and the door is closed.
11. Clip the protective cover onto the vertical columns before proceeding – this is for the safety of the operator. The test will not run if the cover is removed.
12. The machine is now ready for the 4-Ball test.

13. Using the software ‘Compend’, decide whether the data has to be recorded on the data file and select the appropriate file name for the lubricant/grease being tested.
14. The load, rpm and duration of test are set as desired by the experiment.
15. Start the test by pressing START.

EP TEST

FOR PERFORMING THE WELD POINT (EP) TEST, THE STEPS 1 THROUGH 13 ARE PERFORMED. HOWEVER, THE THERMOCOUPLE LEAD IS NOT CONNECTED TO THE PLUG.

START THE TEST BY PRESSING START.

A VARIABLE TABLE WILL BE PROMPTED TO THE USER INTO WHICH THE REQUIRED LOAD IS PLACED.

APPLY THE CLUTCH BRAKE DURING THE LOADING PHASE OF THE PROGRAM.

THE CLUTCH BRAKE (BLACK HANDLE ON THE TOP OF THE TEST SHAFT) IS TIGHTENED DOWN ONTO THE TOP OF THE CLUTCH. THIS IS DONE TO HAND-TIGHT AND PREVENTS THE SHAFT FROM ROTATING UNTIL THE CLUTCH IS ENGAGED BY THE TEST SEQUENCE FILE.

THE TEST STOPS AUTOMATICALLY AFTER 10 SECONDS. HOWEVER, IF WELDING OCCURS (AS INDICATED BY THE FUMES FROM THE BALL POT OR INCREASED NOISE OF THE MOTOR) THE TEST MUST BE STOP IMMEDIATELY TO AVOID DAMAGE TO THE MACHINE.

UNLOADING THE ASSEMBLY

1. After the test, unplug thermocouple lead and plug (if they are plugged)

2. Remove the whole four-ball assembly before proceeding to the next step and the three stationary balls are retrieved.
3. Remove the ball collet from the test shaft by inserting the long handled extractor rod into the top of the shaft (above the clutch) and screw down the extractor rod.
4. If the shaft rotates while unscrewing, then hold the shaft still by using a C spanner, inserting the nose of the spanner into one of the holes in the shaft at the bottom end.
5. Tighten the extractor rod until the collet falls out. Remove the extractor rod at this point.
6. Remove the old test ball from the collet by inserting the punch provided into the hole at the rear of the collet.
7. Turn upside down and push the punch up into the collet - the ball should pop out.
8. If it does not move, place the collet, ball downwards, on the Holding Block and the punch with a hammer.

FINAL CLEANING

1. Clean the machine off the grease using hexane and get it ready for the next test.
2. For running consecutive tests, it should be ensured that the whole machine assembly cools down to room temperature.
3. Clean the test balls thoroughly for post-test analysis.
4. If the test produces objectionable odor, use hood.

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BIOGRAPHICAL INFORMATION

Arunya Suresh was born in Ajmer,Rajasthan (India) and did her schooling from schools located in different parts of India. She secured admission at Malaviya National Institute of Technology, Jaipur, Rajasthan (India) and graduated with a Bachelor of Technology degree in Metallurgical Engineering. She received the Gold Medal for academic excellence in her undergraduate program. In her undergraduate years, she had the opportunity to carry out Summer project at IIT, Roorkee in Shape Memory Alloys and developed keen interest in Materials Science. After serving at Accenture Ltd. (India) for a year and a half, she came back to school to pursue Master of Science at the University of Texas at Arlington in Materials Science and Engineering. She considers herself extremely fortunate to carry out research in the field of Tribology and Lubrication, under the tutelage of Dr. Pranesh Aswath.