

**A STUDY OF DITHIOPHOSPHATE COMPOUNDS AS LUBRICANT
ADDITIVES****SACHIN KUMBHAR, DR. SHILPI SHRIVASTAVA**RESEARCH SCHOLAR, DEPT. OF CHEMISTRY, KALINGA UNIVERSITY,
RAIPUR, CHHATTISGARHASSOCIATE PROFESSOR, DEPT. OF CHEMISTRY, KALINGA UNIVERSITY,
RAIPUR, CHHATTISGARH**ABSTRACT**

The most crucial function of lubricants is to reduce friction and wear. Thus, when saving energy and resources and cutting emissions have become central environmental matters, lubricants are attracting mass awareness increasingly. On average, lubricating oils, which quantitatively account for about 90% of lubricant consumption, consist of about 93% base oils and 7% chemical additives and other components (between 0.5 and 40%). In lubricants, the lube oil base stock is building block with respect to which appropriate additives are selected and properly blended to achieve a delicate balance in performance characteristics of the finished lubricant. Additives are chemical compounds that added to lubricating oils to impart properties to the finished oil which are inadequate or lacking in the lube oil base stocks (can be called as “Base Oil”).

KEYWORDS: Dithiophosphate Compounds, Lubricant Additives, lubricating oils, environmental matters, chemical compounds.

INTRODUCTION

Lubricants are classified into two main groups such as liquid lubricants and greases. A liquid lubricant contains 90 percent of oil and 10 percent of additives serving for reduced friction and wear. Grease acts as a mechanical carrier for the lubricant. Liquid lubricants are further classified into Automotive liquid lubricants, Industrial liquid lubricants and metalworking fluids. Metalworking fluids can be sub-divided into water-soluble, neat/ oil-based, rust preventive.

Types of Industrial liquid lubricants are hydraulic oil, gear oil and compressor oil.

Hydraulic oils are non-compressible fluid that is used to transfer power within hydraulic machinery and equipment. Hydraulic fluids can act as a sealant, coolant and lubricant within machinery and equipment and reduces friction. Hydraulic oils are synthetic or mineral-based.

Optimal properties of hydraulic oil are achieved by combining base oil and additives (anti-wear additives, detergents, Anti-oxidants, anti-foaming agents, Corrosion inhibitors etc.). Types of hydraulic oils are mineral oil, phosphate esters, polyol ester, water glycol, vegetable hydraulic oil. Mineral based oils (petroleum base) are the most common and low cost hydraulic fluids. The disadvantages of mineral (petroleum) base oils are their low fire resistance (low flash point), toxicity and very low biodegradability. Phosphate esters are manufactured by the reaction of phosphoric acid with aromatic alcohols. Phosphate esters based hydraulic fluids possess excellent fire resistance, however they are not compatible with paints, adhesives, some polymers and sealant materials. They are also toxic. Polyol esters are produced by the reaction of long-chain fatty acids and synthesized alcohols. Polyol ester based hydraulic fluids are fire resistant and possess very good lubrication properties. They are environmentally friendly but their use is limited by high cost. Water glycol based fluids contain 35-60% of water in form of solution (not emulsion) and additives (antifoam, anti-freeze, rust and corrosion inhibitors, anti-wear etc.). Water & glycol based hydraulic fluids possess excellent fire resistance, they are non-toxic and biodegradable. However their temperature range is relatively low: 32°F - 120°F (0°C - 49°C). Water evaporation causes deterioration of the hydraulic fluids properties. Vegetable hydraulic oils are produced mainly from Canola oil. Their chemical structure is similar to that of polyol esters. Vegetable hydraulic oils possess very good lubrication properties and high viscosity index (low temperature sensitivity of viscosity). They are non-toxic and biodegradable. The main disadvantage of vegetable hydraulic oils is their relatively low oxidation resistance [4]. Metalworking fluids (MWF) are the lubricants which are used for cutting, forming, and cooling of metals. Metalworking fluids are of two types such as water-based and oil-based metalworking fluids. Water-based are sub-divided into emulsions and solutions. Two types of emulsions are microemulsion and macroemulsion. MWF-emulsions are stabilized to an oil-in-water (O/W) emulsion by an emulsifier system [5]. Grease is a solid to semi-solid mixture of fluid lubricants, thickener and additives. The fluid lubricant (oil in the grease bonded with thickener) performs the lubrication. Greases are composed of base oil, thickener and additives. Base oils are mineral oil and synthetic oil. Thickening agents are simple metal soap, complex metal soap and non- soap thickeners.

In a variety of different sectors, lubricants play an essential part in guaranteeing the smooth running of machinery and equipment as well as facilitating their life. These compounds, which are often disregarded despite their necessary nature, are available in a wide variety of

forms and compositions, custom-tailored to fulfill the particular requirements of various applications. The categorization of lubricants is a complex and subtle procedure that takes into consideration a variety of aspects, including the kind of base oil, additives, viscosity, and the use that is intended for the lubricant. It is crucial to have a solid understanding of these categories in order to pick the appropriate lubricant for a certain application, which will ultimately lead to increased efficiency, dependability, and cost-effectiveness.

One of the most important distinguishing characteristics of lubricants is the kind of base oil that is used. The basic component of lubricants, base oils are responsible for delivering the essential lubricating qualities that are required for lubrication. Mineral oils are a key category of base oils since they are obtained from crude oil via a process that is known as refining. Because they are adaptable and economical, they are suited for a broad variety of applications because of their overall versatility. On the other hand, synthetic base oils, which include polyalphaolefins (PAO), esters, and polyalkylene glycols (PAG), provide superior performance in terms of temperature stability, resistance to oxidation, and viscosity index. These synthetic lubricants are used in challenging settings, such as those that are characterized by high temperatures and high pressures.

The presence of additives is in addition to being an essential component of the categorization of lubricants. Additives are chemical substances that are used with base oils in order to improve certain attributes or for the purpose of addressing certain issues. For instance, anti-wear chemicals provide a protective coating on metal surfaces, which in turn reduces the amount of friction and wear that occurs. In a similar manner, antioxidants and anti-corrosion additives shield lubricants from oxidative deterioration and corrosion, therefore increasing the total lifetime of the lubricant as well as the equipment that it supports. The creation of deposits and sludge may be avoided with the use of detergents and dispersants, which contribute to the engine's cleanliness. Lubricants' total performance and efficacy are strongly impacted by the careful selection and mix of additives, which contribute considerably to the overall performance.

The thickness of a lubricant, often known as its viscosity, is an important metric that plays a role in determining its performance. Lubricants are often classified according to their viscosity, with thinner oils being an appropriate choice for applications that involve low temperatures and thicker lubricants being chosen for applications that include high temperatures and heavy-duty workloads. There is a viscosity classification system that has

been created by the Society of Automotive Engineers (SAE), and the grades range from 0 to 60. Multigrade oils, such as 10W-30, are intended to give appropriate viscosity throughout a wide temperature range. This ensures that the lubrication is constant regardless of the operating circumstances that are present. It is essential to pick the appropriate viscosity in order to avoid problems such as excessive friction and wear, as well as to keep the fuel economy at a satisfactory level.

CHARACTERISTICS OF GREASE:

Characteristics of Grease are as follows:-

1. Consistency.
2. Oil separating Test.

Consistency of grease is determined by cone penetration test.

CLASSIFICATION OF BASE OIL:

Base oil is classified into crude (hydrocarbon) petroleum oil and synthetic oil. Hydrocarbons are further subdivided into the following:

1. Alkanes, known as paraffins, with saturated linear or branched-chain structures,
2. Alkenes, known as olefins, unsaturated molecules, but comparatively rare in crude oils.
3. Alicyclics, known as naphthenes, are saturated cyclic structures based on five- and six-membered rings,
4. Aromatics, cyclic structures with conjugated double bonds, mainly based on the six-membered benzene ring.

According to API Base oils are classified into Group I,II,III,IV and V. Group I, II and III constitutes mineral oils. Group IV and V constitutes synthetic oils.

DISTINGUISHING FACTOR OF BASE OIL (Group I, II and III):

1. Saturated and Unsaturated: From Group I to III, Unsaturated compounds decrease and saturated increases.
2. Aromatic Content: From Group I to III, Aromatic compounds decrease.
3. Presence of elemental sulphur: Presences of sulphur causes corrosion. Content of elemental sulphur decreases from group I to III.

Since the unsaturated, aromatic and sulphur content is decreasing from group I to III, Aniline point increases and Polarity decreases from group I to III.

FACTORS AFFECTING BASE OIL:

1. Addition of Additives: Additives are highly polar in nature. From Group I to III polarity of base oil decreases so, the solubility of additives also decreases.
2. Viscosity Index: From Group I to III, Viscosity Index increases. Thus, Group III base oil works under varying temperature ranges due to high Viscosity Index.
3. Oxidation and thermal stability: Decrease in the unsaturated compounds from group I to III increases the oxidation and thermal stability of base oil.
4. Pour point: Pour point increases from group I to III.
5. Flash Point: Increase in Saturated compounds and decrease in impurities results in increase in flash point from group I to III.

Group IV constitutes one base oil i.e. Polyalphaolefins. Polyalphaolefins have high thermal and oxidation stability. It has a high aniline point.

Group V (Miscellaneous group): Group V constitutes ester, polyalkylene glycols (PAG), alkylated naphthalene, alkylated benzene, silicon oils. Esters are used as lubricating enhancers. Esters are used as base oil or Co-base oil. Silicon oils are electrically inert even at high temperature.

Dithiophosphate and Dithiocarbamate are two widely used chemical compounds in Lubricants and Greases. Zinc Dialkyl Dithiophosphate (ZnDTP or ZDDP) is known for its

antiwear and antioxidant property in Engine oil, Hydraulic Oil, Greases, etc. Molybdenum Dialkyldithiocarbamate has gained popularity as Friction Modifier and Antioxidant for Engine Oil and Greases. Frequently, both of these compounds are used in combination to get the synergistic effect for reduction of Wear & Friction.

Though widely used in many commercial formulations of Lubricants, ZDDP and MoDTC have several drawbacks. Zinc and Molybdenum metals are major contributors of ash formed by the burned lubricants.

This research is aiming to study various Dithiophosphate and Dithiocarbamate compounds in lubricant formulations. The major objective of this research is to obtain the direction for formulating Lubricants and Grease containing lesser to no metals while maintaining the performance attributes same as metal containing Lubricants and Greases – where the major source of metal is additives.

Lubricant & Grease

The function of lubricants and greases is to lubricate, reduce friction and wear, offer protection to moving metal parts, dissipate heat among many other. Additives are generally used in lubricants and greases to improve certain properties or to impart the properties to the base oil which is lacking completely. These additives can perform on the moving metal surface, also called as film forming additives or in the bulk fluid. The example of additives which perform in the bulk are antioxidants, viscosity Index improvers, dispersants and detergents, grease thickeners, emulsifiers & demulsifiers to name a few. Antiwear, Extreme Pressure, Rust & corrosion inhibitors are some examples of additives which perform on the moving metallic surface. Among these surface active additives, some are chemically active such as Antiwear and Extreme Pressure additives. These chemically active additives have ability to form chemical bond with Iron (Fe^{2+} or Fe^{3+}) forming an Iron compounds which protects Metal from wearing and tearing under extreme conditions such as high temperature, extreme loads, low and high speeds, shocks, etc.

Base Oils

Base oils, which are also sometimes referred to as base stocks, are an essential component of lubricants. They play an essential part in guaranteeing the efficiency and durability of machinery and equipment across a wide range of sectors. Lubricant formulations are built on

these oils, which provide the necessary lubricating qualities that decrease friction, disperse heat, and protect against wear and corrosion. Lubricant formulations include these oils as their basic base. To choose the appropriate lubricant for a particular application, it is crucial to have a thorough understanding of the features and kinds of base oils. When making this selection, it is important to take into consideration aspects such as viscosity, oxidation resistance, and thermal stability.

It is the fundamental purpose of base oils in lubricants to create a coating that is both stable and long-lasting between moving surfaces, therefore preventing metals from coming into direct contact with one another. The friction and wear that are caused by this lubricating coating are reduced, which results in an increase in the overall efficiency of the system and a longer lifetime for the components. There are many different sources from which base oils are generated, and they may be categorized according to their origin, content, and the techniques by which they are processed.

Base oils are classified according to their origin, which is an important classification criteria. A significant portion of the basic oils that are available are mineral oils, which are obtained from crude oil via the process of refining. During the distillation and refining processes, crude oil, which is a complex combination of hydrocarbons, is separated into fractions depending on the boiling points of the individual components. Saturated hydrocarbons, principally alkanes, are the fundamental components of mineral oils, and the base oil portion is made up of these hydrocarbons. These oils are extensively utilized in a variety of applications, ranging from lubricants for automobiles to equipment used in industrial settings. They are also very cost-effective.

One further significant category is synthetic base oils, which are manufactured via chemical engineering in order to obtain certain performance characteristics. Polyalphaolefins (PAO), for example, are synthetic hydrocarbons that have a molecular structure that is homogeneous and constant throughout. In order to meet the requirements of demanding applications like high-performance automobile engines and industrial gearboxes, PAOs are appropriate because they have great thermal stability, resistance to oxidation, and a wide temperature range. Some examples of synthetic base oils are polyalkylene glycols (PAG) and esters. Each of these types of base oils has distinctive characteristics that are tailored to meet certain lubricating needs.

Group III base oils are an intermediate category that are often regarded as synthetic owing to the extra refining operations that are done to traditional mineral oils. Through the use of these methods, contaminants are eliminated and unsaturated hydrocarbons are saturated, which ultimately results in base oils that have enhanced performance qualities. As a result of their superior oxidation stability and viscosity index in comparison to conventional mineral oils, Group III base oils are well-suited for use in applications that call for greater levels of performance.

Base oils belonging to Group IV, which are often referred to as polyalphaolefins (PAOs), are considered to be completely synthetic and possess exceptional performance qualities. They have been chemically developed to have a molecular structure that is constant and predictable, and they provide good viscosity-temperature behavior, thermal stability, and shear stability. Among the many applications that need high-performance lubrication, PAOs are used extensively. These applications include industrial gear oils and automobile gear oils.

Base oils that are classified as belonging to Group V include a wide variety of synthetic oils that do not belong to any of the other groups. Among the several specialized fluids that fall under this category are esters, polyalkylene glycols (PAGs), and others. PAGs, which are characterized by a high viscosity index and good thermal stability, find use in applications that are subjected to extreme temperature conditions. Esters, which are derived from organic acids and alcohols, offer excellent lubricity, biodegradability, and oxidative stability, which make them suitable for applications such as aviation lubricants.

Characteristics of the Hydrocarbons for Lubricant Performance

The majority of lubricants that are used in a variety of sectors are made up of hydrocarbons, which are molecules that are formed of hydrogen and carbon atoms. The performance of lubricants is mostly determined by the features of hydrocarbons, which play a paramount role in the process. For the purpose of developing lubricants that are capable of satisfying the varied and demanding needs of machinery and equipment, it is vital to have a solid understanding of these features. In order to understand the complex link that exists between hydrocarbons and lubricant performance, this investigation will focus on essential characteristics such as molecular structure, viscosity, volatility, and thermal stability.

Lubricant behavior is significantly impacted by a number of basic factors, one of which is the molecular structure of hydrocarbons. Alkanes, which are saturated hydrocarbons, alkenes,

which are unsaturated hydrocarbons with double bonds, and alkynes, which are unsaturated hydrocarbons with triple bonds, are the three primary forms of hydrocarbons that may be classified in a generally accepted manner. Lubricant characteristics are substantially influenced by the fact that the length of hydrocarbon chains, the branching of those chains, and the existence of double or triple bonds are all present.

It is possible for saturated hydrocarbons, often known as alkanes, to have structures that are either straight-chain or branched because they include single bonds between carbon atoms. Each of these molecules, whether they are linear or branching, contributes to the viscosity of lubricants. One of the factors that determine whether or not a lubricant is able to create a stable lubricating coating between moving surfaces is its viscosity, often known as its thickness. When seen from this perspective, longer hydrocarbon chains have a tendency to enhance viscosity, which results in improved film strength and protection against wear. The presence of an overly high viscosity, on the other hand, may result in difficulties with low-temperature fluidity. In order to attain the appropriate viscosity properties for certain operating situations, lubricant compositions often incorporate a mixture of hydrocarbons. Although striking this delicate balance may be challenging, it is essential.

CONCLUSION

In addition, lubricants may be categorized according to the kinds of applications they are designed to serve. Engine oils, gear oils, and transmission fluids are all examples of items that fall under the category of automotive lubricants. Internal combustion engines are lubricated using engine oils, which are meant to reduce friction, dissipate heat, and protect against wear and tear. When it comes to automatic and manual transmissions, gear oils are responsible for providing lubrication in differentials and gearboxes, while transmission fluids are responsible for facilitating smooth gear changing. On the other hand, industrial lubricants are designed to meet the requirements of a diverse range of machinery and equipment that are used in manufacturing, processing, and other functions within the industrial sector. Hydraulic oils, compressor oils, and turbine oils are all examples of these types of lubricants. Each of these oils is designed to comply with the particular specifications of the machinery that they support. When classifying lubricants, it is necessary to take into consideration a variety of aspects, including the kind of base oil, the additives, the viscosity, and the purpose for which the lubricant is meant to be used. With the help of this categorization system, businesses are able to choose the lubricant that is most suited for their particular applications. This helps to

ensure that machinery and equipment function at their highest level, run efficiently, and last as long as possible. The development of new lubricant formulas continues, which further expands the variety of alternatives that are accessible to companies all over the globe. This is necessary since environmental concerns are becoming more important as technology continues to grow.

REFERENCES

1. **Li, Meng, et al.** Experimental study and modeling of atomic-scale friction in zigzag and armchair lattice orientations of MoS₂. *Science and Technology of Advanced Materials Volume 17*. 2016.
2. *A Computational Chemistry Study on Friction of h-MoS₂. Part II. Friction Anisotropy.* **Tasuku Onodera, Yusuke Morita, Ryo Nagumo, Ryuji Miura, Ai Suzuki, Hideyuki Tsuboi, Nozomu Hatakeyama, Akira Endou, Hiromitsu Takaba, Fabrice Dassenoy, Clotilde Minfray, Lucile Joly-Pottuz, Momoji Kubo, Jean-Michel Martin, and Akira Miyamoto.** 2010, *J. Phys. Chem. B*, pp. 15832-15835.
3. **Topolovec Miklozic, Graham, J and Spikes, H.** Chemical and physical analysis of reaction films formed by molybdenum dialkyl-dithiocarbamate friction modifier additive using raman and atomic force microscopy. *Tribology Letter 11*. pp. 71-81.
4. **Kalin, M.** Influence of flash temperatures on the tribological behaviour in low-speed sliding: A review. *Materials Science and Engineering*. 2004, pp. 390-397.
5. **Hsu, S M and Gates, R.** Boundary lubricating films: formation and lubrication mechanism. *Tribology International 38(3)*. 2005, pp. 305-312.
6. **Hsu, S, Klaus, E and Cheng, H.** A mechano-chemical descriptive model for wear under mixed lubrication conditions. *Wear 128(3)*. 1988, pp. 307-323.
7. **Hsu, S M, Zhang, J and Yin, Z.** The nature and origin of tribochemistry. *Tribology Letters 13(2)*. 2002, pp. 131-139.
8. **Williams, J A.** *Engineering Tribology vol. 10*. s.l. : Cambridge Univ Pr, 2005.
9. **Boyde, S.** *Green lubricants - Environmental benefits and impacts of lubrication*. 2002.
10. **Taher, M.** Tribological Performance of Novel Boron. *Masters Thesis - Luleå University of Technology*.
11. *Development of a set of Stribeck curves for conformal contacts of rough surfaces.* **Wang, Y, et al.** 2006, *Tribology Transactions 49 (4)*, pp. 526-535.



12. **Najman, M N, Kasrai, M and Bancroft, G M.** Chemistry of antiwear films from ashless thiophosphate oil additives. *Tribology Letters* 17. pp. 217-229.
13. **Kim, B, Mourhatch, R and Aswath, P.** Properties of tribofilm formed with ashless thiophosphate and zinc dialkyl dithiophosphate. *Tribology Letters* 6. 2010, pp. 1-8.
14. *Tribofilm generated from ZDDP and DDP on steel surfaces - Part 1 Growth, wear and morphology.* **Zhang, Z, et al.** Washington DC : s.n. World Tribology Conference III. pp. 617-618.
15. **Martin, J M, et al.** Superlubricity of molybdenum disulphide. *Physical Review B* 48 *condensed matter and materials physics*. 1993, pp. 10583-10586.