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SYNTHESIS OF DITHIOPHOSPHATE COMPOUNDS AND EVALUATION OF PERFORMANCES AS ANTIWEAR AND ANTIFRICTION LUBRICANT ADDITIVES

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ABSTRACT

ZDDPs are the most widely used antiwear additive in lubricants. It adds several performances attributes to lubricant but also adds to metal ashes produced due to the aging and burning of the lubricants. Being the major contributor to the ash produced by lubricants, Zinc needs to be replaced or removed out to claim lubricants ashless. This paper gives insights on various dithiophosphate compounds that can be considered a replacement to the ZDDP without compromising the performance of lubricants. In this study, the synthesis methods were analyzed for ashless dithiophosphate compounds. These compounds were tested on a four-ball machine to compare their performance with ZDDP. The effect of the carbon chain length of the alkyl group attached to the dithiophosphate group was also analyzed.

Keywords: Dithiophosphate, ZDDP, Antiwear, Antifriction, Lubricant.

1. INTRODUCTION

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 increasingly attract mass awareness. 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%) [1].

In lubricants, the lube oil base stock is a building block for which appropriate additives are selected and properly blended to achieve a delicate balance in the performance characteristics of the finished lubricant. Additives are chemically synthesized compounds 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 "Base Oil") [2].

Grease is a liquid lubricant thickened to provide properties not available in the liquid lubricant alone. Dithiophosphate and Dithiocarbamate are two widely used chemical compounds in Lubricants and Greases. Zinc Dialkyl Dithiophospahte (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 and friction. Though widely used in many commercial formulations of lubricants, ZDDP and MoDTC have several drawbacks. Zinc and Moybdenum metals are major contributors of ash formed by the burned lubricants. This research is aiming to study various Dithiophosphate 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.

1.1. Dithiophospahte in lubricants and greases

Phosphate esters, with sulfur and metals added, such as ZDDP, have found wide applications because of their ability to form tribofilms on a wide range of metals or materials. The tribofilms are all similar in chemical composition, with iron phosphate or iron polyphosphate being a significant component. The films adhere firmly to the substrate, are durable, and continue to form as long as the additive remains. An important feature is films can form by different mechanisms depending on the amount of oxygen present. An essential aspect of the films formed is that their modulus increases in response to stress, allowing them to maintain their integrity under extreme loads [3].

The documented introduction of lubricant additives containing Zinc, phosphorus, and sulfur can be found in number of patents by Lubri-zol [4], American Cyanamid [5] and Union Oil [6] in 1941, claiming the mixtures, now known to be zinc dialkyldithiophosphate, ZDDPs to function as corrosion and oxidation inhibitors. Zinc dialkyldithiophosphate was initially prepared by the reaction of phosphorus pentasulfide (P_2S_5) and one or more different alcohols to give the dialkyldithio-phosphoric acid, neutralized by adding zinc oxide to give the product, as shown in Fig. 1 [7].

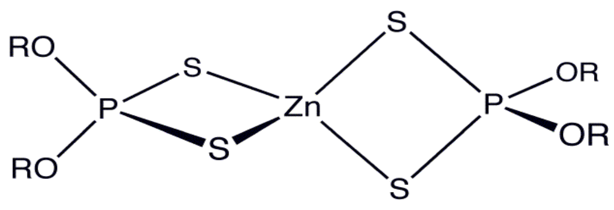


Fig. 1: Structure of a Zinc dialkyl dithiophosphate (ZDDP)

The ability to use a mixture of different primary and secondary alcohols, resulting in a statistical mixture of products, allows the resulting additive's chemical and physical properties to vary significantly. The properties of these additives can be varied based on zinc oxide's ratio to the dialkyldithiophosphoric acid by formation of acidic, neutral, or basic ZDDPs, each having a different reactivity [8]. This method of synthesis is still in use industrially today.

The application of ZDDP in lubricating oils was as an antioxidant initially. The antioxidant mechanism of ZDDP's action appears to be through reaction with peroxy radicals [9]. It was not until 1955 when it was demonstrated that ZDDPs were effective antiwear additives [10], this led to its rapid and wide adoption by the automobile industry [11]. Present environmental limits on phosphorus and sulphur in lubricant formulations and the concern regarding heavy metal emissions threaten the use of ZDDP in engine oil. They have enforced an increase in research to find replacement chemistries of additives that do not contain phosphorus. The history of ZDDP and much of the early research has been reviewed by Spikes [12].

Modern engines use exhaust treatment filters or catalysts to meet current environmental emissions requirements for particulate emissions. It is well known fact that phosphorus, sulphur, and metals in the exhaust stream can block filters and poison catalysts [13]. Further, lubricants and lubricant additives have been identified as an important contributor to all these components on the exhaust stream. Efforts to reduce ash while maintaining the effectiveness of a ZDDP-like additive with similar reaction temperature have led to the investigation of several substituted thiophosphate ester and phosphorothionate ester-based antiwear additives [14]. The development of "ashless" antiwear additives for automotive applications has focused O,O′-dialkyl-dithiophosphoric acids which can be viewed as ZDDP without the Zinc. Di-alkyl dithiophosphoric acid can be further reacted with an amine to reduce the acid number [15]. The properties can be optimized by the degree of substitution on the amine. These additives often offer the highest load-carrying capability; however suffer from reduced hydrolytic stability and higher resulting acidity when compared to other additives [16]. A typical class of ashless additives can be prepared by adding amines to an appropriate thiophosphoyl chloride to form the amidothiophosphate [17]. Other additives can be prepared by adding the sulphur atoms across the double bond of acrylic acid or an acrylate ester [18]. An alternate approach relies on oxidation of hydrogen peroxide dimerize the dialkylthiophosphate [19]. Several ashless dialkyl dithiophosphate have been studied, indicating that they form thermal films at about 150°C. The tribofilms consist of a mixture of iron(II) polyphosphate and iron(II) sulphate [20]. In tribological testing done by Kim, et.al, the ashless antiwear additives gave thicker surface films and better tribological performance than ZDDP. The film formed from the ashless additive consisted of shorter chain ferrous polyphosphates than ZDDP but with thicker films of an average film thickness of 400 nm [21].

Another class of molecules that have received substantial attention as antiwear additives are the triarylphos-phorothionates. These molecules are very similar to the phosphate esters structurally, except the oxygen is replaced with a sulphur atom. The parent in the series, triphenylphosphorothionate, has received the most study. Triphenylphosphorothionate is oxidized thermally in solution to eventually form triphenyl phosphate, with no oil insoluble products identified [22]. However, in the presence of iron or steel, catalyzed reaction produces triphenyl phosphate. It results in producing a multilayered solid film on iron or iron oxide [23]. In tribological studies, wear debris were found by transmission electron microscopy to contain Fe_3O_4 particles and amorphous material. A wear mechanism was proposed that included wear particles trapped within the phosphate tribofilm. The antiwear additives that contained the fewest iron oxide particles had the best performance [24].

In Industrial oils-such as Hydraulic oils ZDDP is extensively used for various attributes. Under boundary conditions, sacrificial layers of antiwear additive are established on the load-bearing surfaces of machine components to protect against the results of friction. Antiwear additives are very effective in moderate to severe load applications, while oiliness agents are utilized in mild conditions. Extreme-pressure (EP) additives are best in severe applications. Significant advantage of ZDDP is that it performs several key functions at once. Multiple additives must be employed at higher concentrations and cost to replace the ZDDP.

Whereas, the known disadvantages of zinc-based additives include corrosion of some metals and its environmental impact. Lubricants or greases with very high zinc levels have a history of leading to the corrosion of metals, such as yellow metals, as they chemically react with metal surfaces. These additives are not only non-biodegradable, but research has also indicated that ZDDPs are toxic aquatically. A variety of ZDDP compounds differ in their effects on antiwear, hydrolysis and thermal degradation. However, achieving high-quality levels in all of these categories can be a challenge. Additive alternatives to Zinc have the potential of obtaining these benefits separately [25].

Dialkyldithiophosphate compounds (MDTPs) are being used for a long time as lubricant additives due to their excellent antiwear, friction reduction, extreme pressure, corrosion resistance and antioxidant properties. Different elements such as cadmium, molybdenum, titanium, copper, gadolinium, antimony, iron and other metals have been investigated as multifunctional additives into lubricants. The most extensively used compounds from this group are zinc dialkyldithiophosphates (ZnDTPs). Several mechanisms have been proposed for how ZDDP forms protective tribofilms on solid surfaces. *In-situ* AFM (atomic force microscopy) experiments show that the growth of ZDDP tribofilms increases with the applied pressure and temperature, consistent with a stress-promoted thermal activation reaction rate model. Subsequently, experiments with negligible solid-on-solid contact demonstrated that film formation rate depends on the applied shear-stress [26].

Reaction mechanisms of ZnDTP additives under rubbing conditions on steel surfaces have been proposed by Willermet and co-workers in four steps as following [27]:

- Adsorption of ZnDTP on the substrate steel surfaces
- Reactions between ZnDTP and the surface and formation of phosphates and phosphothionates bound to the metal surface.
- Formation of phosphate film from oxidation reactions of ZnDTP.
- Condensation of the phosphothionates and phosphates in polymeric chains, which are then terminated by Zinc based compounds or other metal ions present in the lubricant.

2. EXPERIMENTAL

ZDDPs were synthesized in two step reaction. In the first step, phosphourus pentasulfide was treated with appropriate alcohol (primary or secondary) producing dithiophosphoric acid. Various alcohols can be used, which allows the lipophilicity of the final zinc product to be fine-tuned. Zinc oxide was then added to neutralize dithiophosphoric acid producing ZDDP [28-29].

P_2S_5 + 4 ROH $\rightarrow$ 2 $(RO)_2PS_2H$ + H_2S------Step (I)

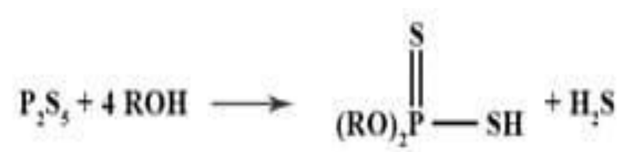
2 $(RO)_2PS_2H$ + ZnO$\rightarrow$Zn [($S_2P(OR)_2$]$_2$ + H_2O-----Step(II)

Scheme 1: Synthesis of ZDDP

The FT-IR spectrum confirms the P-O-C presence with wavelength of 972 & 654 cm^{-1} as below.

2.1. Synthesis of Ashless dithiophosphate compounds

Ashless Dithiophosphate can be synthesized in two steps similar to ZDDP. In the first step, Dithiophosphoric acid is synthesized by reaction Alcohol and Phosphorus pentasulfide.



Scheme 2: Synthesis of Ashless Dithiophosphate (Step I)

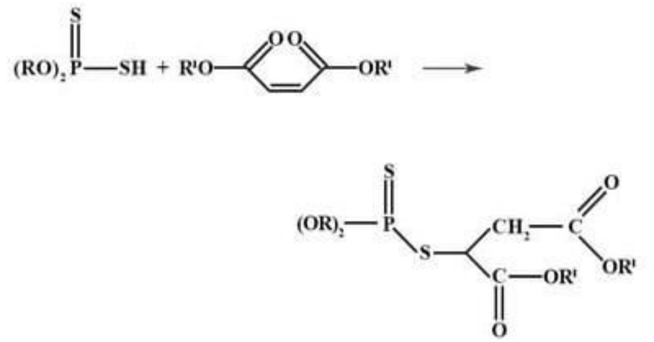
By selecting appropriate alcohol of short or long carbon chain length, properties such as antiwear, hydrolytic stability, and thermal stability can be controlled.

In the second step, Dithiophosphoric acid is reacted with Maleate, which gives dithiophoric acid ester, which is an ashless Dithiophosphate [30].

Two commercial ashless dithiophosphate additives were selected for experimental analysis having variable R groups as C_3 and C_8.

IR spectrum of short-chain diakyldithiophsphate with C_3 length is as below:

IR spectrum of ashless dialkyldithiophosphate with a longer carbon chain of alkyl group is as below with C_8 chain.



Scheme 3: Synthesis of Ashless Dithiophosphate (Step II)

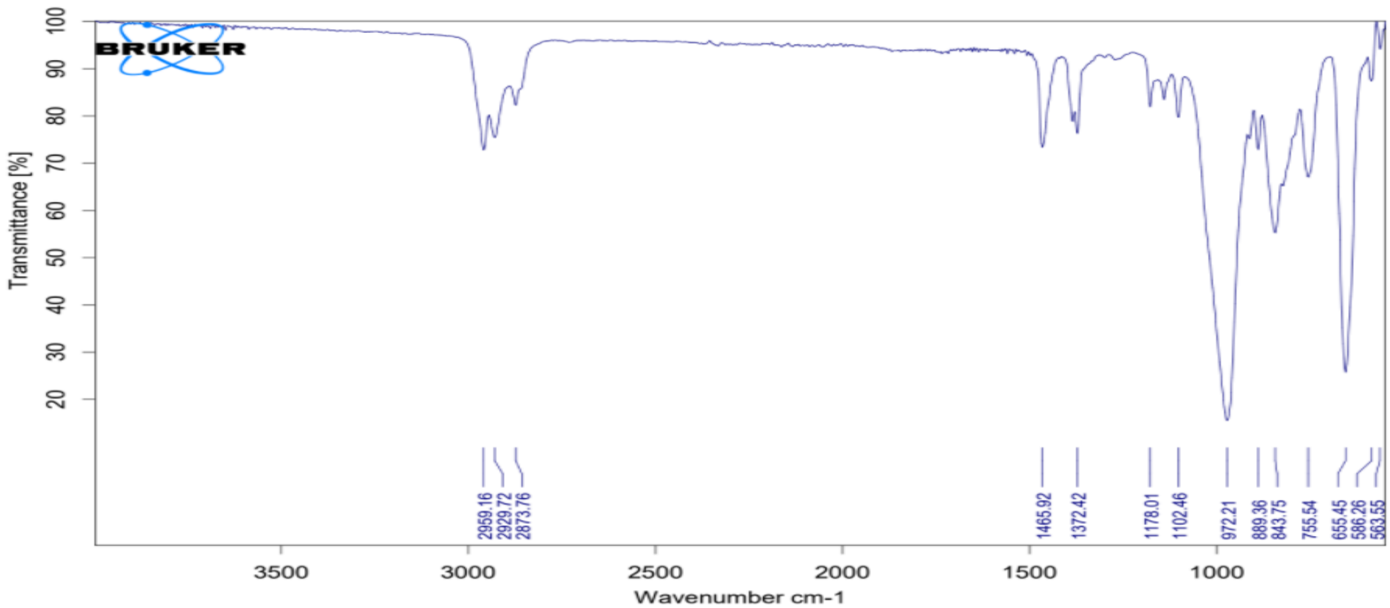


Fig. 2: FT-IR spectrum of ZDDP

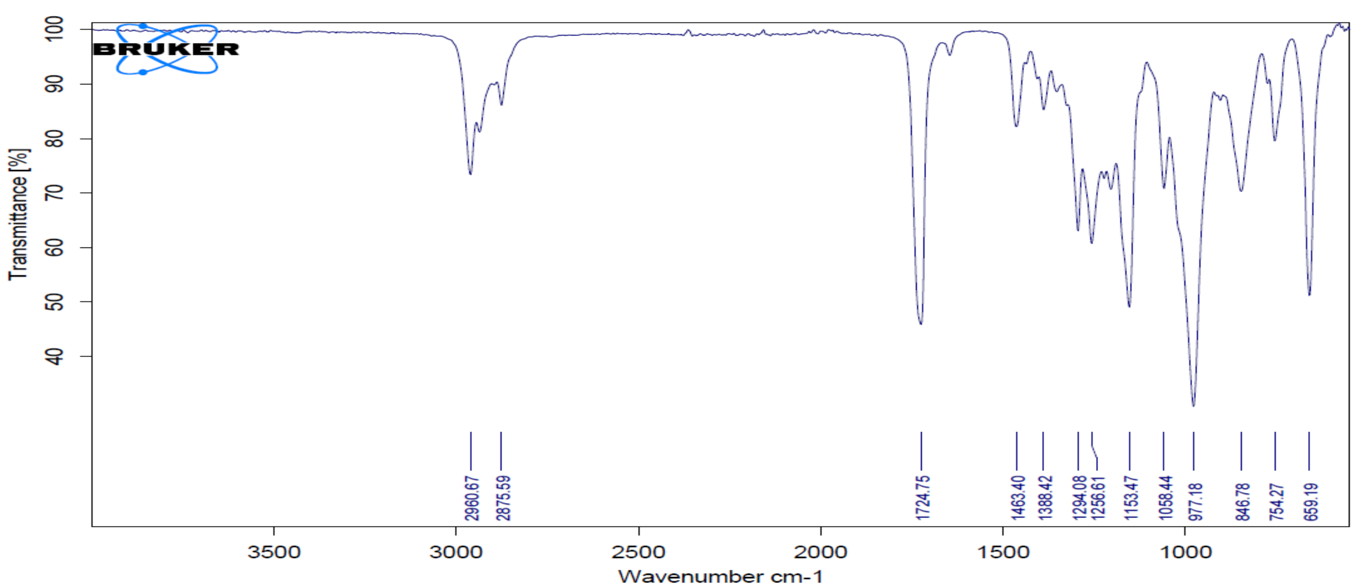


Fig. 3: IR spectrum of short-chain dialkyldithiophosphate compound

2.2. Experimental analysis of metal-free Dithiophosphate compounds

Two commercial ashless dithiophosphates were identified having different alkyl groups (i.e., short and long-chain). Further, Antiwear and Coefficient of friction were analyzed of these ashless dithiophosphates compared to ZDDP by adding these compounds in the Mineral oil at equal treat rates.

The test method used was ASTM D4172 (Commonly known as Four-ball wear test)

Three steel balls were clamped together and covered with the lubricant to be evaluated. A fourth steel ball, referred to as the top ball, was pressed with the mechanical force into the cavity that was formed because of the clamping of the three balls for three-point contact. Lubricants were compared by the average size of the scar diameters formed on the three lower clamped balls. Smaller the diameter of wear circle indicates better antiwear property of the lubricant. Meanwhile, the friction coefficient can be recorded.

Test conditions were, Rotating speed of 1200 rpm, load of 392N, temperature of 75°C, time duration of 60min.

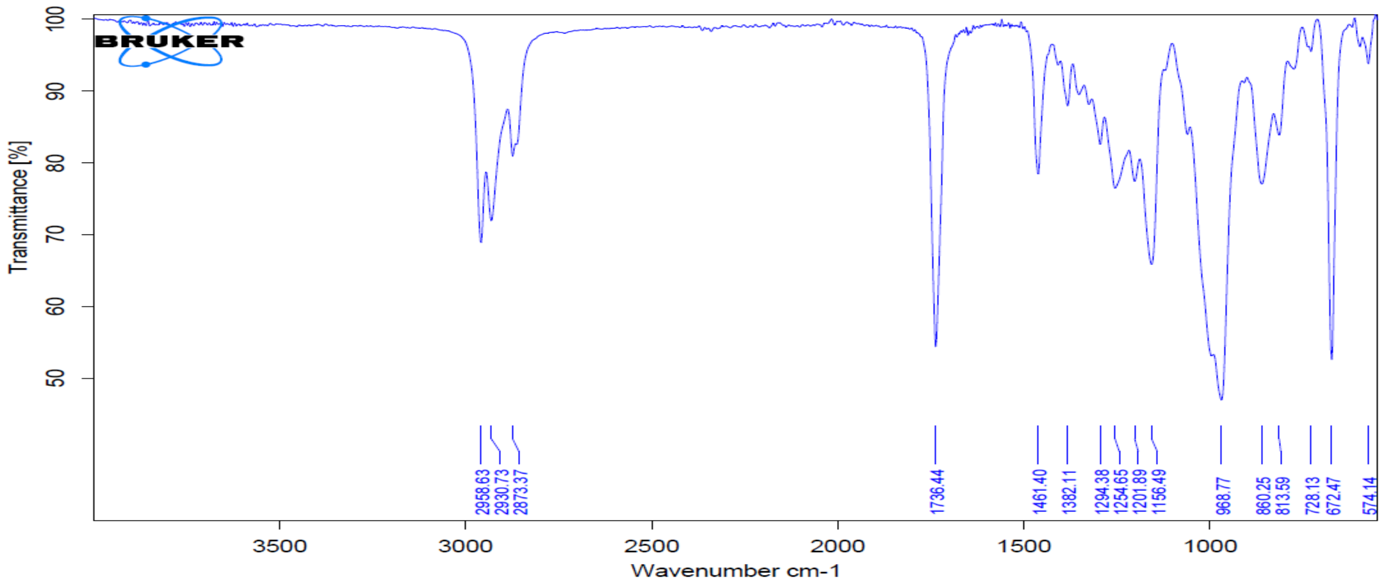


Fig. 4: IR spectrum of long-chain alkyldithiophosphate compound

Mixture of Mineral Oil	Four ball Wear Scar diameter in mm	Coefficient of Friction at 1200 RPM, 75°C
Mineral Oil ISO VG 32 Group I (MO)	1.161	0.38
MO + 1% ZDDP	0.492	0.105
MO + 1% Short alkyl chain ashless DTP	0.692	0.117
MO + 2% Short alkyl chain ashless DTP	0.603	0.109
MO +1% long chain ashless DTP	0.928	0.111
MO +2% long chain ashless DTP	0.576	0.111

3. RESULTS AND DISCUSSION

Four-ball wear results confirmed that ashless Dithiophospahte is effective in reducing wear substantially. Compared with ZDDP, the antiwear property of ashless dithiophosphate is slightly inferior but enough for considering as a replacement to Zinc or other metal-based antiwear additives.

It was also observed that short alkyl chain ashless dithiophosphate performed better at a lower treat rate than longer alkyl chain ashless Dithiophosphate. It is prominently because of the higher amount of Phosphorus and Sulphur in short-chain DTP. With an increased treat rate (2% by weight), long-chain DTP outperformed short-chain DTP at the same treat rate. This confirms that DTP compounds after a certain treat level does not reduce wear, pointing towards the need to optimize the treat rate in lubricants.

With increased treat rate of short-chain DTP compound though the average four-ball wear scar diameter was not reduced substantially, the effect was seen in the microscopic image of scars. The scars formed on three balls were smoother, showing lesser deformation with a 2% treat rate of short-chain alkyl Dithiophosphate in mineral oil. This could be because of a decrease in CoF in the formulation consisting of 2% short chain alkyl Dithiophosphate.

In the case of long chain alkyl dithiophosphate, the reduction in wear scar diameter was substantial with an increase in the treat rate in Mineral oil from 1% to 2%. But unlike in short-chain alkyl dithiophosphate, they did not improve the scar's smoothness or deformation. This was also supported by CoF results which did not show a decrease with an increased treat rate of additive.

Along with wear reduction, there was a substantial reduction in friction after the addition of ashless DTPs. However, once again, increasing the treat rate did not help much in lowering friction further. It can be seen that with jumping from 1% treat rate to 2%, there is not a considerable reduction in average CoF. But in the CoF graph, it was evident that the starting friction was reduced drastically with an increased treat rate of short and long-chain DTP.

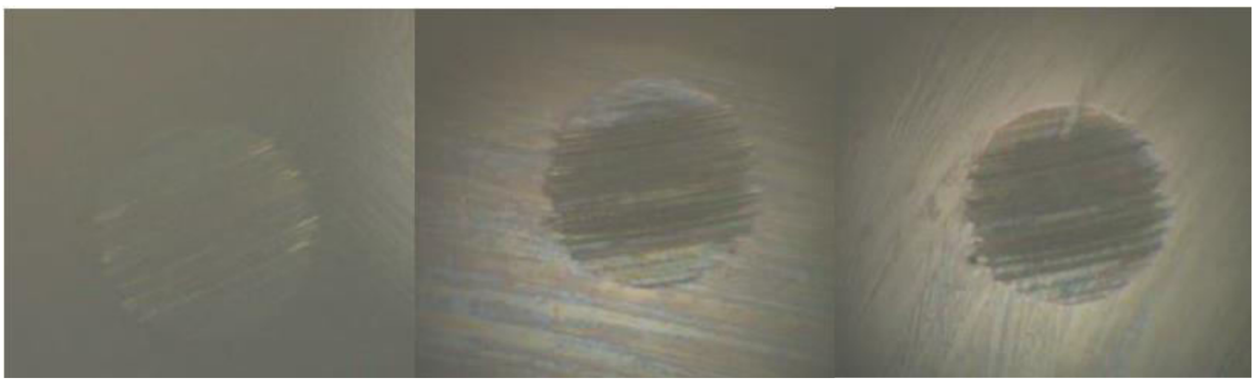


Fig. 5: Microscopic image of Wear scar diameter 1% ZDDP in Mineral oil

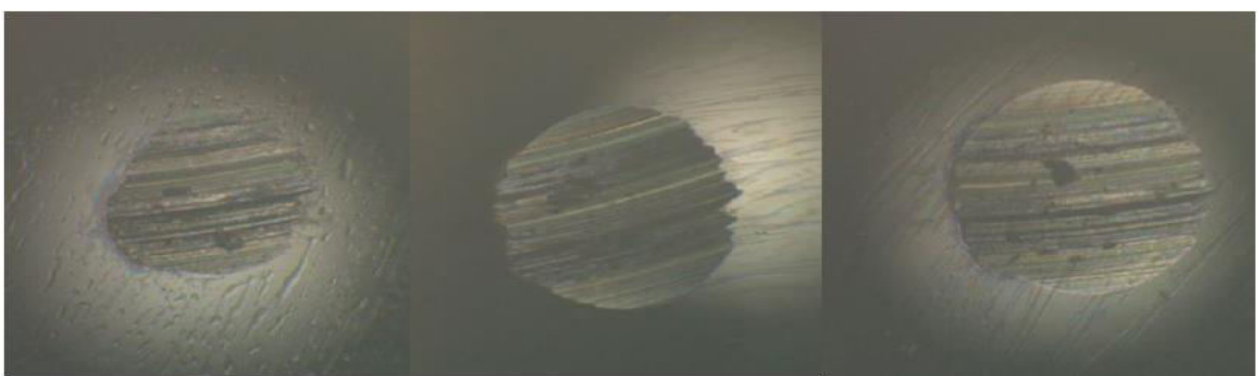


Fig. 6: Microscopic image of Wear scar diameter - 1% short-chain DTP compound in Mineral oil

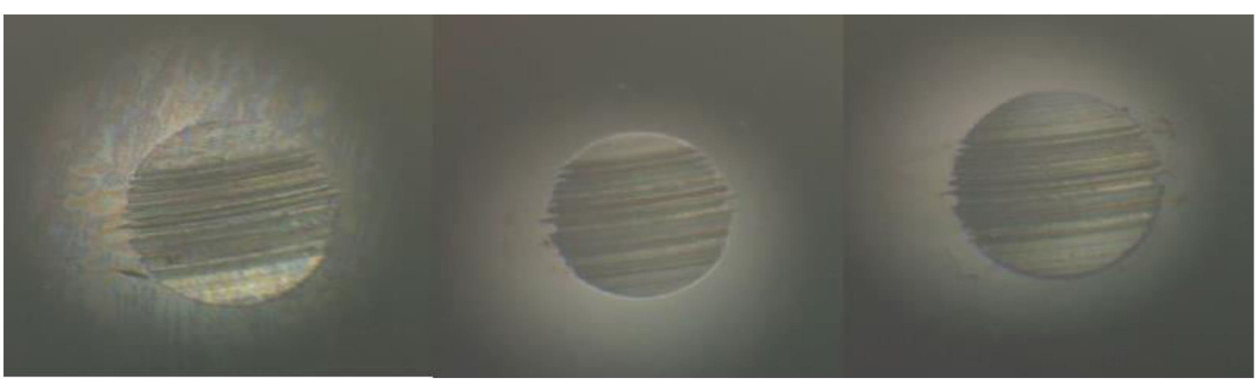


Fig. 7: Microscopic image of Wear scar diameter - 2% short chain alkyl DTP compound in Mineral oil

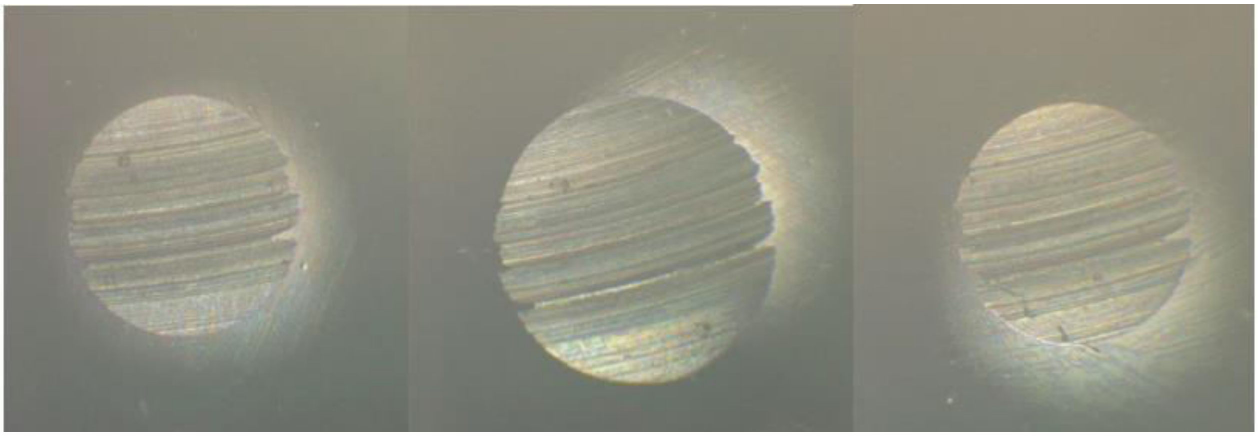


Fig. 8: Microscopic image of Wear scar diameter - 1% long chain alkyl DTP compound in Mineral oil

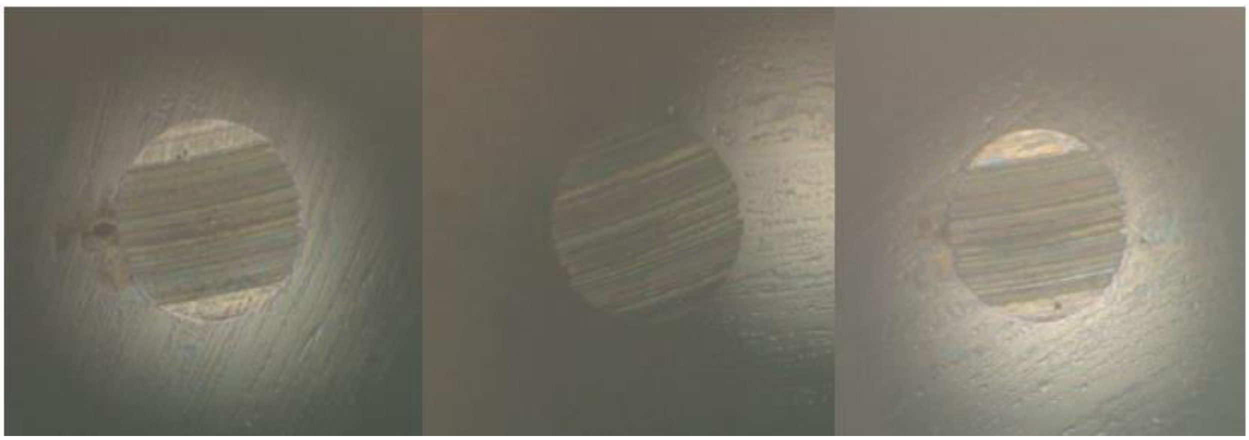


Fig. 9: Microscopic image of Wear scar diameter - 2% long-chain alkyl DTP compound in Mineral oil

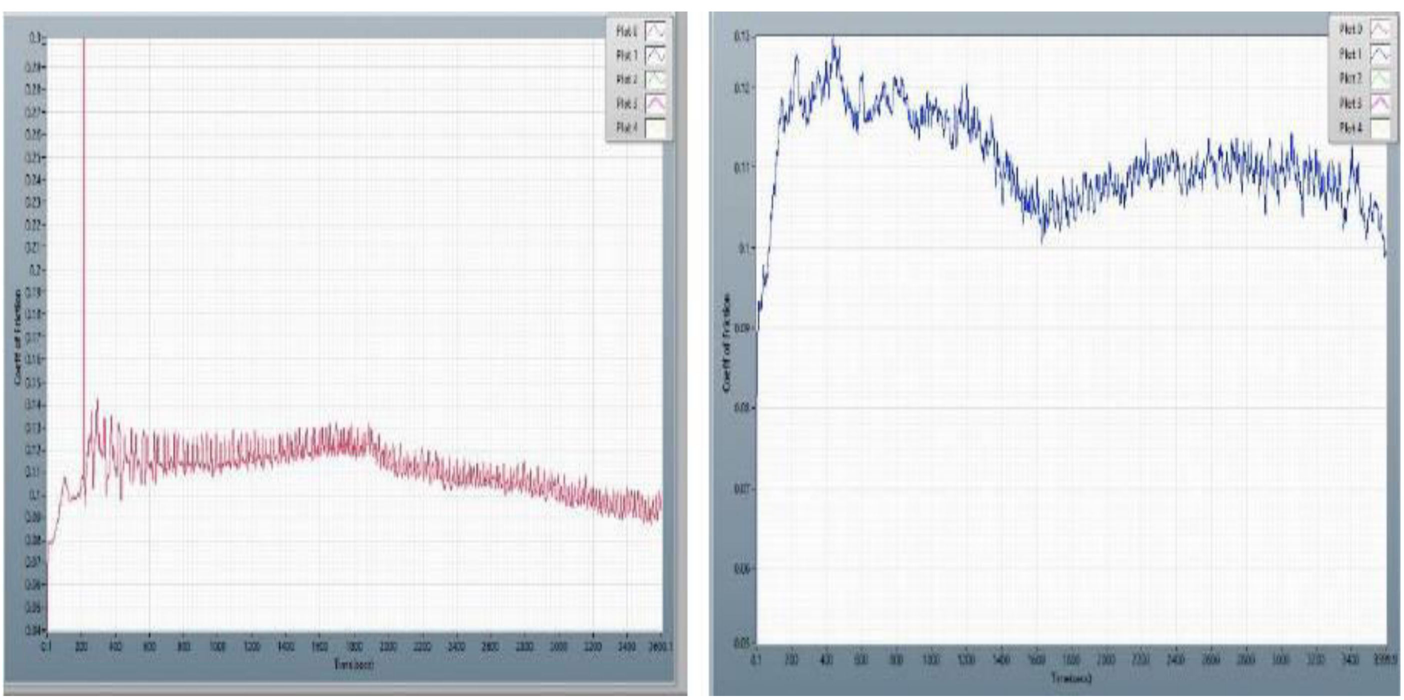


Fig. 10: Graph of CoF showing reduced intial friction with 2% treat rate (right side) of long chain alkyl dithiophosphate

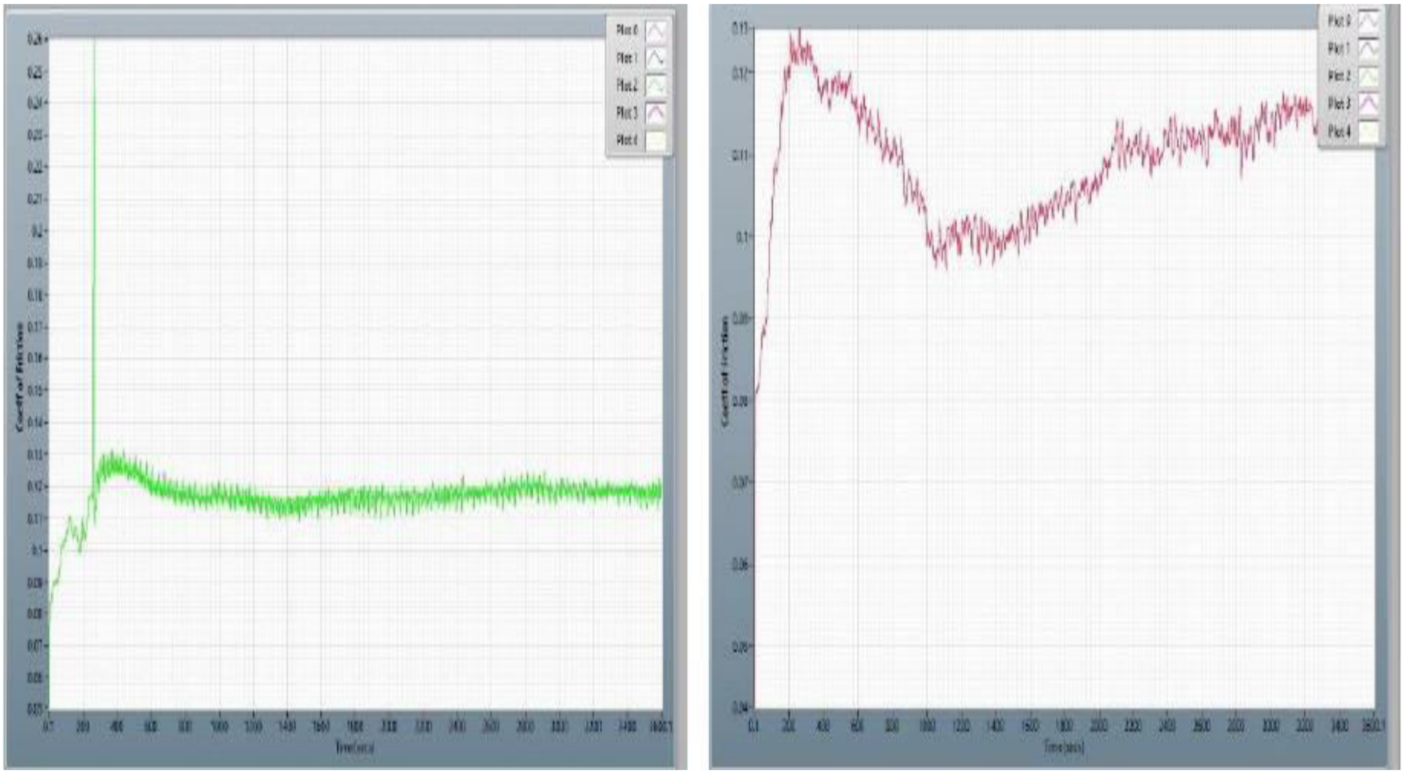


Fig. 11: Graph of CoF showing reduced intial friction with 2% treat rate (right side) of short chain alkyl dithiophosphate

4. CONCLUSION

The reaction for synthesis ashless Dithiophosphate-based additive for lubricant was explained. In a four-ball experiment, it was seen that ashless Dithiophosphate could reduce wear and friction substantially. Alkyl groups attached in the first step of synthesis of such ashless Dithiophosphate affect these additives' antiwear and antifriction performance. This study confirms that ashless Dithiophosphate have the potential to replace ZDDP in ashless lubricants and greases.

Detailed study can be conducted on other properties of ashless Dithiophosphate explained in this paper, such as hydrolytic and thermal stability, antioxidant property through peroxide decomposition and rust prevention properties in comparison with ZDDP.

The future study can also involve combining other ashless antiwear additive chemistry such as Amine phosphate or ashless Dithiocarbamate to get the synergistic effect to effectively replace ZDDP without compromising any performance attributes of the lubricants and greases.

Conflict of interest

None declared

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