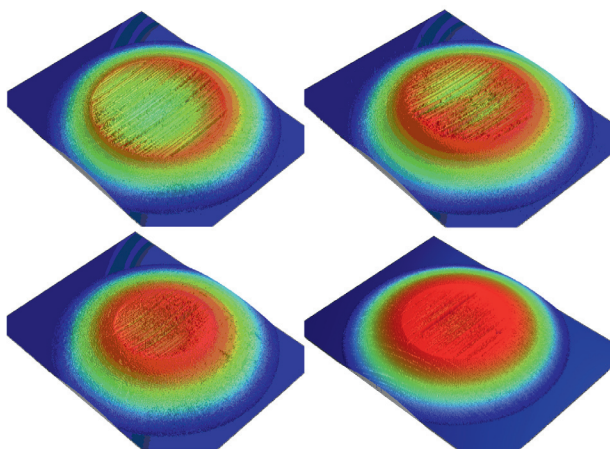


**Boron Compounds as Additives to Lubricants**  
*Synthesis, Characterization and Tribological  
Optimization*



Faiz Ullah Shah



# **Boron Compounds as Additives to Lubricants: Synthesis, Characterization and Tribological Optimization**

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*The most fundamental and lasting objective of synthesis is NOT production of new  
compounds but PRODUCTION OF NEW PROPERTIES*

*George S. Hammond. Norris Award lecture, 1968*



## SUMMARY

Developing new technological solutions, such as use of lightweight materials, less harmful fuels, controlled fuel combustion processes or more efficient exhaust gas after-treatment, are possible ways to reduce the environmental impact of machines. Both the reduction of wear and the friction control are key issues for decreasing of energy losses, improving efficiency and increasing of the life-span of an engine. Dialkyldithiophosphates (DTPs) of different metals have been extensively used as multifunctional additives in lubricants to control friction and reduce wear in mechanical systems. Among these DTP-compounds, zinc dialkyldithiophosphates (ZnDTPs) are the most common additives used for more than 60 years. These additives form protective films on steel surfaces and, thus, control friction and reduce wear. However, ZnDTPs contain zinc and large amounts of phosphorus and sulphur, which are human health hazards and cause environmental pollution by degrading catalytic converters in automobiles. Therefore, replacement of ZnDTPs by zinc free compounds with reduced amounts of sulphur and phosphorus are urgently needed.

Boron-containing compounds are known as corrosion inhibitors, antioxidants, friction modifiers and effective anti-wear additives either dissolved in oil or as an insoluble and inorganic borate salts dispersed in oil in the nanoparticulate form. These compounds are emerging as attractive replacements for the compounds already used as additives in lubricants. The focus of the present work is on the development and tribological investigations of new boron compounds as high performance additives in lubricants. These should be ashless with significantly reduced amounts sulphur and phosphorus, which is favourable for the environment protection.

The work was carried out in the following steps: (1) Synthesis of new additives; (2) Characterization of the additives with FTIR, ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{11}\text{B}$ ) NMR spectroscopy, elemental analysis and thermal analysis (TG/DTG, DTA and QMS); (3) Tribological evaluation using four ball Tribometer; (4) Surface analysis using an optical profiler and Scanning Electron Microscopy coupled with X-ray Energy Dispersive Spectroscopy (SEM/EDS). It was found that the novel boron compounds have considerably better antiwear performance and higher stability of the coefficient of friction with time as compared with ZnDTP. These novel compounds are ashless with reduced amounts of sulphur and phosphorus. They also have excellent tribological properties, high thermal stability, good miscibility with oils and positive environmental issues which make them an attractive alternative to ZnDTP.

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## List of papers

This thesis is based on the following three papers:

- (I) Synthesis, Physicochemical and Tribological Characterization of S-di-n-octoxyboron-*O,O'*-di-n-octyldithiophosphate.  
Faiz Ullah Shah, Sergei Glavatskih and Oleg N. Antzutkin  
(*ACS Applied Materials & Interfaces*, **2009**, In press)
- (II) A Novel Ashless Lubricant Additive, Alkylborate-dithiophosphate: Synthesis, Characterization and Antiwear performance  
Faiz Ullah Shah, Sergei Glavatskih, Mats Lindberg and Oleg N. Antzutkin  
(To be submitted to *ACS Applied Materials & Interfaces*)
- (III) Organoboron-dithiophosphates as Ashless Antiwear additives: Synthesis, Characterization and Tribological Evaluation  
Faiz Ullah Shah, Sergei Glavatskih, Erik Höglund and Oleg N. Antzutkin  
(To be submitted to *Tribology Letters*)

### Other publications by the Author, which are not included in this thesis

1. F. U. Shah, S. Glavatskih and O. N. Antzutkin. Novel Boron Compounds as High Efficient Antiwear Additives. Synthesis, Characterization and Tribological Studies. (Swedish patent application, 2009, in preparation).
2. F. U. Shah, J. Aslam, Z. Akhter and B. Mirza. Synthesis and Biological Activities of Some Schiff Bases and Their Metal Complexes including Ferrocene Based Schiff Bases, (Submitted to *J. Organometal. Chem.*, 2009).
3. F. U. Shah, T. Barri, J. Å. Jönsson and K. Skog. Determination of Heterocyclic Aromatic Amines in Human Urine by Using Hollow-Fibre Supported Liquid Membrane Extraction and Liquid Chromatography-Ultraviolet Detection System, *J. Chromatogr. B*, **870** (2008) 203-208.
4. F. U. Shah, Z. Akhter, H. M. Siddiqi, M. Parvez. Synthesis, Structure and Characterization of Some Schiff bases bearing phenylferrocene, *Appl. Organometal. Chem.*, **21** (2007) 758–762.

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Paper I

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## CHAPTER 1

### 1. INTRODUCTION

#### 1.2 Tribology

The word “Tribology” is derived from two Greek words: “Tribo” meaning rubbing and “Logos” meaning principle or logic. Tribology is defined as “the science and technology of interacting surfaces in relative motion”, and covers the fields of friction, wear and lubrication, including the interactions between solids, liquids and gases [1]. Tribology is an interdisciplinary science, based on the expertise of chemists, physicists, mechanical engineers, materials scientists and metallurgists. Lubricants and lubrication technology are essential components in the modern industry, reducing wear and controlling friction. New machine designs create special and sometimes extreme operating conditions, such as higher temperatures, loads and speeds. The lubricants must be able to meet the requirements at these operating conditions.

The field of tribology can be subdivided into two main branches, namely *tribotechnology* and *triboscience*. Tribotechnology covers the technical behaviour of certain basic units and sets, while triboscience is aimed at clarifying the fundamental processes occurring during friction and wearing processes and establishing universally valid laws. Triboscience regards *tribophysical* and *tribochemical* processes, that is, processes connected with the occurrence of friction, which take place under the influence of mechanical energy [2].

#### 1.2 Tribochemistry

Tribology is generally considered as a part of mechanical engineering. The tribological research is being conducted from mechanical engineering point of view. Recently, the role of surface chemistry in tribology has attracted more attention of researchers. In order to understand the origin of friction and wear in modern tribological contacts, the importance of surface chemistry can not be ignored. Tribochemistry deals with the chemical interactions, which occur between the lubricant/additives and the rubbing surfaces under boundary lubrication conditions.

#### 1.3 Tribochemical Challenges

The importance of tribology has motivated research in many practical and real life applications. A fundamental understanding of friction, wear, and lubrication has yet to satisfy the needs of technology development. Interesting issues are, for example, changes in material

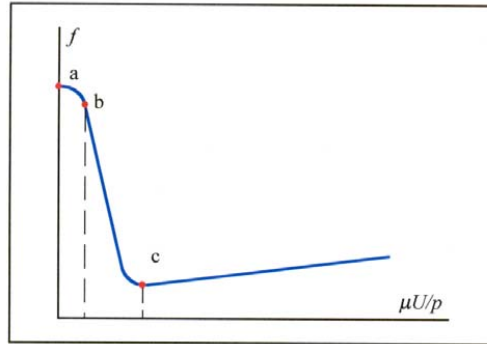
properties during friction; strengthening of engineering materials and surfaces; new methodologies to modify surfaces; and innovative methods to protect, repair, and maintain engineering surfaces. The importance of improving tribological surfaces cannot be underestimated as major issues related to surfaces from a practical application point of view but remain yet unexplored. Therefore, improving the chemical and mechanical properties of metal surfaces used in industrial applications is an important issue that must be dealt with. The use of additives in lubricants is one of the most practical methods for protecting surfaces against damage during sliding motion.

On the other hand, one of the current challenges in tribology is the development of high performance environmentally friendly lubricants for the modern tribological interfaces. The fuel economy, durability, and environmental issues all depend on the quality and effectiveness of the lubricants being used. Inefficient lubrication may result in high friction and wear losses, which can in turn adversely affect the fuel economy and durability. From an environmental point of view, lower fuel economy also means higher environmental pollution. To cope with these challenges, there is a need for high efficient lubricants, as well as fundamental understanding of tribochemical interactions and surface properties.

#### **1.4 Lubrication Regimes**

Three different lubrication regimes can be distinguished for two surfaces sliding against each other in a lubricated system (Figure 1):

1. *Boundary lubrication*: the two solid surfaces are in direct contact and the load is carried by the asperities.
2. *Mixed lubrication*: a lubricant film is present between the contact surfaces but some asperities are in contact. The load is carried by both fluid and asperities.
3. *Hydrodynamic lubrication*: the lubricant film is thick enough to prevent contacts between the surfaces and load is carried by the lubricant. The physical properties of the lubricant play the dominating role in this regime. Friction is low while there is no wear in the hydrodynamic regime.



**Figure 1.** Schematic Stribeck curve representing lubrication regimes. Boundary (a-b), mixed (b-c) and hydrodynamic (c-) lubrication regimes. ( $f$ : Friction coefficient,  $\mu$ : viscosity,  $U$ : sliding speed and  $p$ : pressure)

### 1.5 Chemical Aspects of Tribofilm Formation

In boundary or mixed lubrication, lubricant additives undergo decomposition under high load and elevated temperature forming a protective layer called tribofilm through chemical reactions or adsorption processes. The reactivity of the additive with surfaces is crucial. If an additive is not sufficiently reactive, then no adequate film can be formed before the parts become severely damaged. If the additive is too reactive, then the additive may lead to a corrosive attack on the surface resulting in excessive wear. Not only do the additive's properties define its reactivity in real applications, the reactivity also depends on the base oil, presence of other additives and the nature of surfaces.

A tribochemical reaction of an additive with a surface is generally catalyzed by the contact asperity temperature and the nascent metal surface. The contact temperature, also called “flash temperature”, is usually very high but short-lived. The nascent surface possesses very high surface energy and active sites. A raise in contact temperature is caused by the heat produced due to friction between the sliding asperities [3]. A variety of chemical reactions may occur due to the combined effect of heat and the active surface. These reactions mainly include oxidation of surfaces, oxidation and degradation of the lubricant, surface catalysis, polymerization, and the formation of inorganic and organometallic products [4]. The nature of these products formed on the surface depends on the reactivity, structure and composition of the additive. A high rate at which films form may also point to pressure-induced bulk effect. It

has been shown with a nanometer resolution that the tribofilms formed on top of asperities, which experience higher pressure, are harder than those between asperities [5].

## **1.6 Chemistry of Lubricant Additives**

Hydrocarbon base oils (lubricants) are classified in two groups: mineral and synthetic oils. Mineral oils are manufactured directly from crude oil. Their composition is very complex and consists of hydrocarbons, including more than a hundred of different aliphatic and aromatic compounds. The lubrication properties and oxidation stability vary with their composition. Mineral oils are the most commonly used because of their low price in comparison to synthetic oils.

It is well known that pure mineral/synthetic base oils do not meet all the requirements for lubricating materials used in modern engines or in other applications [6]. Organic or organometallic compounds containing tribologically active elements (P, S, N, C1, Zn, Mo and B) or combinations of compounds with these elements are added to base oils at low concentrations. Additives enhance the tribological performance of the base oils by adding new properties to the lubricant. Lubricant additives can be classified into two categories: chemically-inert and chemically-active. Chemically-inert additives such as viscosity modifiers, foam inhibitors, and pour point depressants modify the physical properties of the base oil. While the chemically-active additives such as antiwear, extreme pressure and corrosion inhibitors enhance the tribochemical properties of metal surfaces.

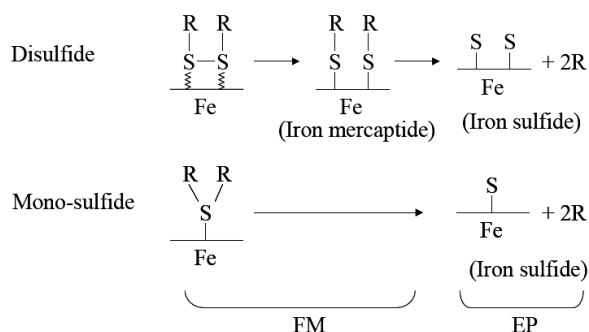
In general, lubricant additives are classified into the following types based on their chemical compositions: sulfur compounds, ashless phosphorus compounds, heterocyclic compounds, dialkyldithiophosphate complexes of metals (MDTPs), dialkyldithiocarbamate complexes of metals (MDTCs), chlorine compounds, boron compounds and ionic liquids.

### **1.6.1 Sulphur Compounds**

Sulfur-containing additives include organic mono and polysulfides, elemental sulfur as well as a wide variety of sulfurized fats and hydrocarbons. The anti-wear (AW) and extreme pressure (EP) properties of a series of organic disulphides have been investigated by Allum and Forbes in late 1960s [7]. They found that EP properties depend on the ease of cleavage of the C-S and S-S bonds. Disulphide additive with the S-S bond gives good antiwear properties due to an easy cleavage of this bond at high pressures [8, 9]. AW and EP mechanisms of sulphur compounds as additives have also been proposed (Figure 2). First, a sulphur-based additive (disulfide or mono-sulfide) physically adsorbs on an iron surface. It reacts then with



Fe active sites forming iron sulfide films. A mono-sulfide additive may directly form an iron sulfide film after physisorption, whereas the disulfide may form iron sulfide films through formation of iron mercaptides [10, 11].



**Figure 2.** Tribochemical mechanisms of tribofilm formations at iron surfaces by sulphur compounds as FM (friction modifiers), AW and EP additives. Adopted from [10].

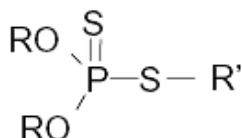
Elemental sulphur is an effective EP additive when dissolved in mineral oils [12, 13]. Its decomposition upon tribological stress on steel surfaces is well known and, as with organic sulfides, leads to the formation of iron sulfide films. The reactivity of elemental sulfur with nascent steel surfaces is known to be considerably higher than that of the organic sulfides [14, 15].

### 1.6.2 Ashless Phosphorus Compounds

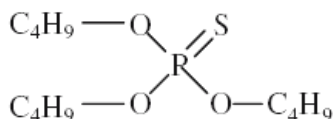
More than a hundred of different phosphorus compounds have been investigated for possible application in tribology, but only a small fraction of them are commonly used in industry [16]. These include ashless phosphorus compounds such as phosphates [17, 18] and dithiophosphates [19-22] (Figs. 3, 4). Ash consists of tiny, solid, metallic salt particles which originate from ZnDTP.

Schumacher and Zinke studied the antiwear behavior of several compounds based on the atomic structure of dithiophosphates, replacing sulfur by oxygen atoms and varying the length and branching of alkyl groups [23]. Similar wear and friction properties for both monothiophosphates and dithiophosphates were observed. A clear correlation was found between the presence of phosphorus in the antiwear film and lower wear rate. On the other

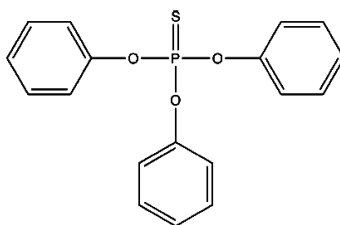
hand, there was no correlation between wear rate and sulphur content in additives. It was established that an increased thermal stability of phosphorus-containing compounds maintained good performance at high temperatures. Although some thermal instability is required to allow the compound to react and form protective antiwear tribofilms. Sarin *et al.* studied antiwear, extreme pressure and antioxidative performance of a series of *O,O'*-dialkylphosphorodithioic disulfides  $(RO)_2P(S)S-SP(S)(RO)_2$  as potential replacements of ZnDTP. They found that these additives provide antiwear properties, comparable to a commercial ZnDTP [24]. The antiwear performance of other dithiophosphate disulphide compounds was also investigated. It was shown that the disulphide group can provide superior EP properties compared with normal dithiophosphates.



**Figure 3.** General structure of an ashless dithiophosphate



**Figure 4.** Tributyl thiophosphate (TBT)



**Figure 5.** Triphenyl phosphorothionate (TPPT)

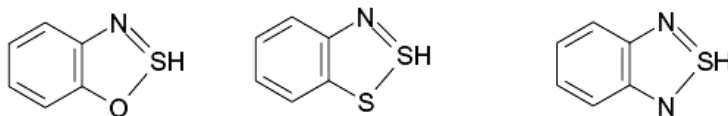
Heuberger *et al.* have investigated the reactivity of alkylated phosphorothionates, such as triphenyl phosphorothionate (TPPT, Fig. 5) with steel surfaces [25]. They found that the

cleavage of P=S double bonds in adsorbed molecules takes place under impact of a high contact pressure and a frictional heat, and sulphur reacts with iron forming iron sulphide.

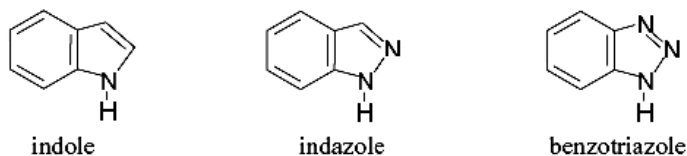
### 1.6.3 Heterocyclic Compounds

In the last few decades, the tribological performance of N, S and O heterocyclic compounds (Fig. 6) as lubricant additives was in the research focus, because of their promising friction and antiwear properties [26-34]. *N*-heterocyclic compounds have a high affinity to free iron and they readily adsorb on steel surfaces forming antiwear tribofilms.

Ren *et al.* studied antiwear properties of a series of N-heterocyclic compounds with one, two and three nitrogen atoms [35]. They found that antiwear properties of these compounds increase with the number of nitrogen atoms in heterocycles: The benzotriazole and its derivatives are the most effective antiwear additives in this class of compounds, because of an increase in coordinating ability to Fe atoms with a number of basic nitrogen atoms in the molecule (Fig. 7). XPS analysis of these N-heterocyclic compounds showed the same spectra for surfaces rubbed in solution and immersed in solution without rubbing. Therefore, these N-compounds were not chemically changed during rubbing.



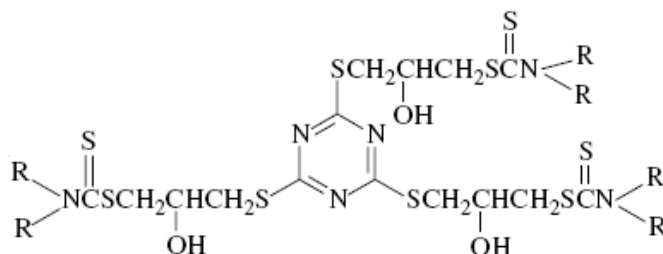
**Figure 6.** Molecular structures of S, N-heterocyclic compounds. Adapted from [34].



**Figure 7.** Molecular structures of N-heterocyclic compounds. Adapted from [35].

Dialkyldithiocarbamate derivatives of heterocyclic compounds have also been used as multifunctional additives in both mineral and vegetable base oils [36-40]. It was found that when the above mentioned *N*-heterocyclic compounds are bound in a single molecule with

dithiocarbamates, their antiwear ability is further improved. It is not for all types of base oils: For example, triazine derivatives of dithiocarbamates (Fig. 8) added in small concentrations to mineral oils decrease wear of steel-steel contacts [41], while the same additives may increase wear in the vegetable (rapeseed) oil [42, 43].



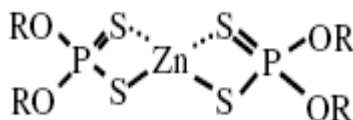
**Figure 8.** General structure of triazine derivatives of dithiocarbamate. Adopted from [43].

Organic compounds are thought to adsorb to metal surfaces via either negatively charged centers or by  $\pi$  electrons in double-bond or aromatic systems. A partial transfer of electrons occurs from polar (donor) groups to atoms on the metal surfaces. In the case of compounds with nitrogen heterocycles, coordinatively saturated or unsaturated covalent bonds can be formed in the process of such chemisorption, thus, providing antiwear and corrosion suppressing properties [44]. This is one of plausible reasons that nitrogen-carbon heterocyclic compounds are widely used by lubricant industries as both metal passivators and effective corrosion inhibitors [45]. The latter is due to their chelating action and their ability to form insoluble diffusion barriers on oxidized surfaces of metals, thus, preventing metal reaction and dissolution. Benzotriazole, benzimidazole, pyridazole, tetrazole, other nitrogen-containing heterocycles and their derivatives were found to be highly effective in inhibiting corrosion for copper, nickel, iron and other metals [46, 47].

#### 1.6.4 Dialkyldithiophosphate Complexes of Metals (MDTPs)

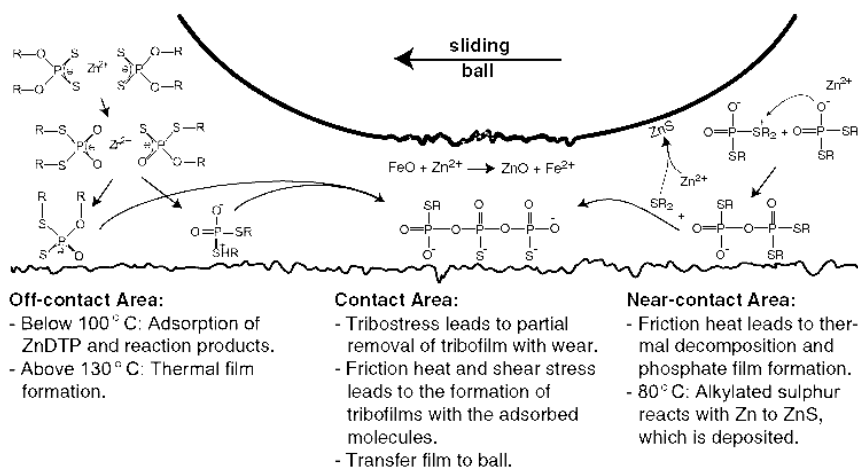
Dialkyldithiophosphate complexes (MDTPs) (Fig. 9) are being used in lubricating oil formulations for several decades due to their excellent antiwear, extreme pressure, friction reducing, antioxidant and corrosion resistance properties. Dialkyldithiophosphates of different metals such as molybdenum [48], cadmium [49], copper [50], titanium [51], gadolinium [52], iron, antimony and other metals [53-55] have been introduced and used as multifunctional

additives in lubricants. Among MDTPs, zinc dialkyldithiophosphates (ZnDTPs) are the most widely used for several decades [56-62].



**Figure 9.** General structure of a liquid mononuclear ZnDTP complex.

Heuberger *et al.* described effect of the contact pressure on formation of tribochemical films from ZnDTP [63]. These authors found that the tribological stress leads to formation of poly(thio)phosphate tribofilms at all temperatures investigated, while in the non-contact areas only very thin thermal films were formed at 30 °C and 80 °C (Fig. 10). It is assumed that the local frictional heating due to contact pressure accelerates the chemical reaction of the adsorbed additives. At 30 °C, iron phosphate was found in the reaction layer, which is an indication that nascent iron reacts with the phosphoryl groups.



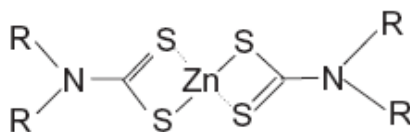
**Figure 10.** Schematic of reactions in the contact, near-contact and off-contact areas on samples tribostressed in the ZnDTP solution. Adapted from [63].

Willermet *et al.* have proposed a four-step process that describes the reaction mechanism of ZnDTP from solution, under mild wear conditions, to reaction products on steel surfaces [64]:

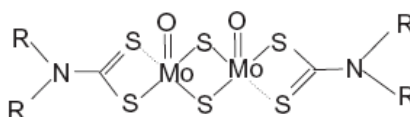
1. Adsorption of ZnDTP on steel surfaces.
2. Reaction of ZnDTP with the steel surface to form species of phosphates and phosphothionic moieties bound to the metal surface.
3. Formation of phosphate film precursors from antioxidant reactions of ZnDTP.
4. Condensation of the phosphates/phosphothionates species in polymeric chains, which are then terminated by zinc-containing compounds or other metal ions in the solution.

### 1.6.5 Dialkyldithiocarbamate Complexes of Metals (MDTCs)

Dialkyldithiocarbamate complexes of several metals have been widely investigated as antiwear additives in lubricant. The general structures of zinc and molybdenum dialkyldithiocarbamates are shown in Figures 11 and 12. Dithiocarbamates of several different metals and metalloids including zinc [65], molybdenum [66], cerium [67], copper [68], lead [69], antimony and bismuth [70, 71] have already been thoroughly studied.



**Figure 11.** General structure of zinc dialkyldithiocarbamate

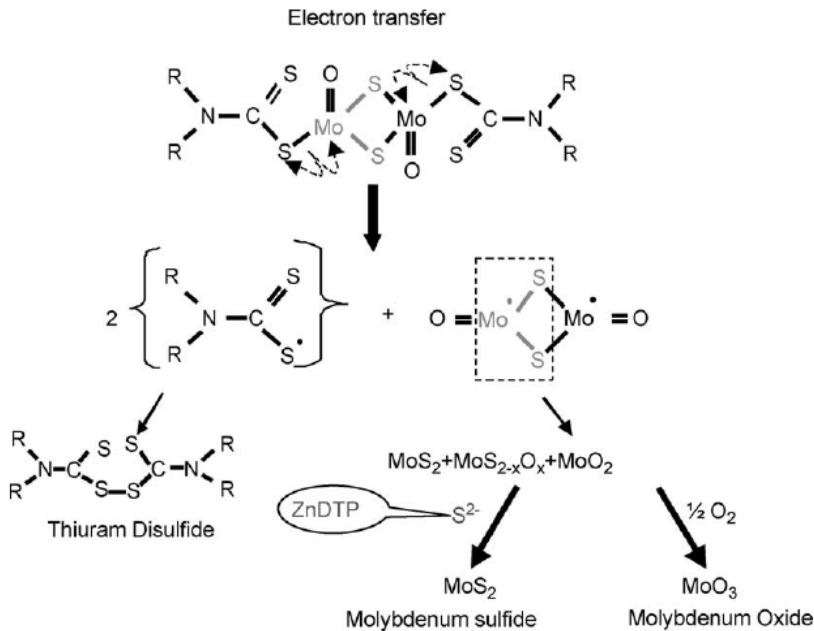


**Figure 12.** General structure of molybdenum dialkyldithiocarbamate

Molybdenum dialkyldithiocarbamates (MoDTC) were initially known as anti-oxidants and extreme pressure additives. They have also been widely used as friction modifier additives. The formation of low-friction tribofilms from MoDTC-containing lubricants was the main subject of several studies [72-74]. It is known that MoDTCs decompose in the sliding contact forming nanocrystals of MoS<sub>2</sub> [75].

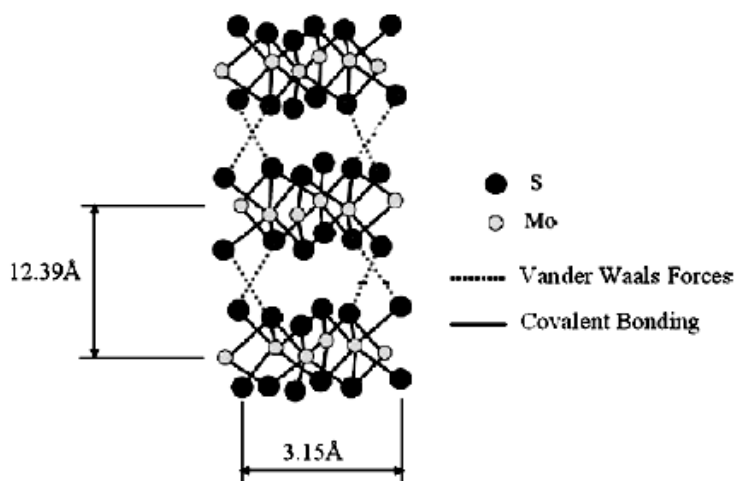
Further investigations by Barros *et al.* [76] on the tribochemistry of these additives on steel surfaces showed that ZnDTP additives also present in the lubricating oil which stimulate formation of  $\text{MoS}_2$ . The following mechanism of  $\text{MoS}_2$  formation in the presence of ZnDTP was proposed:

Electrons are transferred via Mo–S bonds in the MoDTC molecule leading to formation of free radicals during the rubbing processes. The chain-end radicals are recombined to form thiuram disulfide. The oxysulphide decomposes into  $\text{MoS}_2$ , which crystallizes into sheets and  $\text{MoO}_2$  (Fig. 13). The role of ZnDTP in these processes is to provide the sulphur atoms to complete the sulfuration of the oxysulphide. The amount of  $\text{MoS}_2$  formed depends on the concentration of ZnDTP present in the lubricant. These  $\text{MoS}_2$  units meet together forming a lamellar sheet, which covers asperity tips and efficiently reduces the friction.



**Figure 13.** Chemical processes leading to  $\text{MoS}_2$  formation from MoDTC. Adapted from [76].

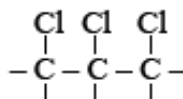
$\text{MoS}_2$  has a layer structure as shown in Figure 14. There is a strong covalent bonding between atomic species. There is only a very weak van der Waals interaction between lattice layers. These weak van der Waals forces between  $\text{MoS}_2$  layers are easy to shear within the molecule. They are responsible for low friction properties of lubricants based on this material [77].



**Figure 14.** Solid state structure of MoS<sub>2</sub>. Adapted from [77].

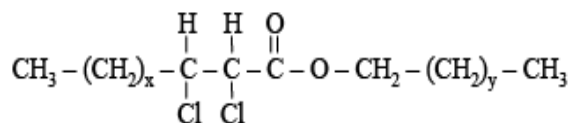
### 1.6.6 Halogens

Among halogen compounds, chlorine was one of the earliest AW and EP elements used by the lubricants industry. Chlorine compounds (Figs. 15 and 16) are known to possess extreme pressure and antiwear properties in lubricants [78, 79]. Kotvis *et al.* [80] and Crumer *et al.* [81] showed that some chlorine-containing compounds react with surface iron producing iron chloride. The main drawbacks of chlorine containing additives in their hazards to health and environment. Therefore, chlorine-containing additives are not considered as a viable option for modern lubricants.



**Figure 15.** Chlorinated paraffin





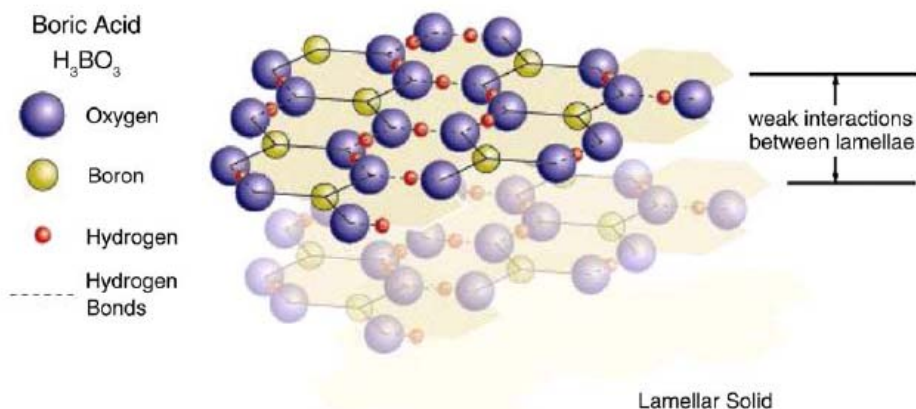
**Figure 16.** Chlorinated fatty oil

### 1.6.7 Boron Compounds

Boron compounds have unique combination of tribological properties. In addition, they are generally believed to have little if any detrimental effect on either the machine components or the environment [82]. Therefore, research on boron based additives has considerably increased within the last decade. Specifically, boron compounds have been extensively studied as boundary lubricating oil soluble additives, solid lubricants and surface coatings [83-86]. Oil soluble organoboron compounds are promising friction modifiers, corrosion inhibitors, antioxidants and effective antiwear additives [87-91].

Boron compounds are capable of forming glassy structures in a manner similar to ZnDTP but with different glass transition temperatures [92]. It is known that crystalline or amorphous boron, boron nitride and metal boride are very hard materials. Microindentation measurements on Rhenium boride ( $\text{ReB}_2$ ) indicated an average hardness of 48 GPa under the applied load of 0.49 N. Scratch marks left on a diamond surface confirmed its superhard nature [93]. Hard iron boride ( $\text{Fe}_2\text{B}$ ) can be formed on the steel surfaces improving their hardness [94, 95]. The hardness of crystalline boron is 30 GPa and amorphous boron thin films can also have hardness approaching that of crystalline boron [96].

In a moisture-containing environment, surface oxide of boron ( $\text{B}_2\text{O}_3$ ) is known to react with water forming boric acid ( $\text{H}_3\text{BO}_3$ ), which acts as a solid lubricant (Fig. 17). The lubricity of boric acid has been attributed to its tendency to form a triclinic crystal structure made up of atomic layers parallel to the basal plane. In each layer, the B, O and H atoms are closely packed and bonded to each other with covalent bonds, while the layers are held together with weak van der Waals forces. The latter facilitates the layers to easily slide with respect to each other providing lubricity in the system [97].



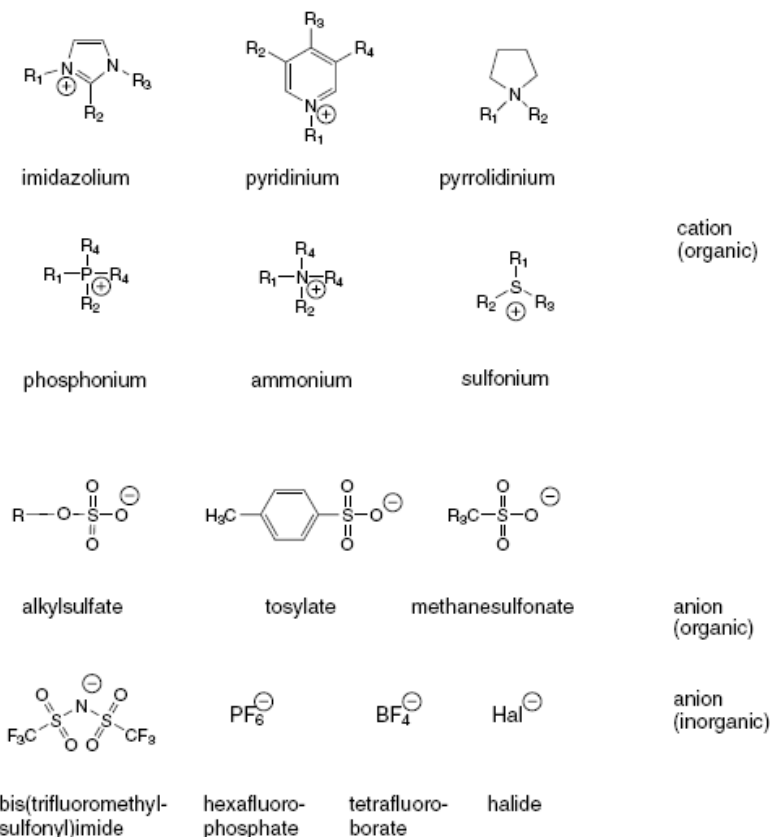
**Figure 17.** Lamellar structure of boric acid. Adapted from [97].

### 1.6.8 Ionic Liquids

Ionic liquids (IL) are a new class of purely ionic, salt-like materials that are liquid at unusually low temperatures. The definition of IL uses the boiling point of water as a point of reference: “Ionic liquids are ionic compounds which are liquid below 100°C.” Some IL have melting points below room temperature while some of them have melting points even below 0°C. They have a number of characteristics including negligible volatility, negligible flammability, high thermal and chemical stability, low melting point and control miscibility with organic compounds and base oils. During the past decade an explosive growth of studies on IL took place, thanks to their diverse applications as catalysts, liquid crystals, green solvents in organic synthesis, and in separations, electrochemistry, photochemistry, CO<sub>2</sub> storage devices, etc. Recently, it was found that IL act as versatile lubricants and lubricant additives for different sliding pairs providing excellent friction reduction, antiwear performance and high load-carrying capacity. IL have unique dipolar structures, which can be easily adsorbed on the sliding surfaces in frictional pairs. Subsequently, an effective boundary film would form reducing both friction and wear. These properties make them excellent lubricants and are highly desirable in tribology [98-104].

A choice of cations has a strong impact on IL properties and often defines their stability. Chemistry and functionality of IL are, in general, controlled by the anion choice. Different combinations of a broad variety of cations and anions lead to a theoretically possible number of  $10^{18}$ . Today only about 1000 IL are described in the literature, and approximately 300 of

them are commercially available. Typical IL combine organic cations with inorganic or organic anions (Fig. 18):



**Figure 18.** Typical structures of IL, which is a combination of an organic cation with an inorganic or organic anion.

IL could be used both as neat lubricants alone and lubricant additives in oil. IL with cations imidazolium [105-107], ammonium [108, 109] and phosphonium [110, 111] and anions tetrafluoroborates [112-114] and hexafluorophosphates [115-117] are the most commonly used in tribological applications.

Recently, it was found that alkylimidazolium IL could act as a versatile lubricant for different sliding pairs providing excellent friction reduction, antiwear performance and high load-carrying capacity. In particular, alkylimidazolium tetrafluoroborates and hexafluorophosphates have shown promising lubricating properties as base oils for a variety

of contacts [118]. Alkylimidazolium tetrafluoroborates could be used as a kind of novel versatile lubricant for the contact of steel–steel, steel–aluminium, steel–copper, steel–SiO<sub>2</sub>, Si<sub>3</sub>–SiO<sub>2</sub>, steel–Si(100), steel–sialon ceramics, and Si<sub>3</sub>N<sub>4</sub>–sialon ceramics: These IL exhibit excellent friction-reduction, anti-wear performance and high load-carrying capacity [119].

### 1.7 Research Objectives

Some of the most effective and widely used lubricant additives contain heavy metals or chlorine containing compounds. Due to environmental and human health considerations there is an increasing legislative pressure to reduce or eliminate harmful lubricant additives. Since 1940s, Zinc dialkyldithiophosphates (ZnDTPs) have been widely used as antiwear lubricant additives. This class of additives contains zinc and large amounts of both sulphur and phosphorus. These additives degrade the catalytic converters of automobiles and result in the emission of poisonous gases such as carbon monoxide (CO) and nitrogen oxides (NO<sub>x</sub>) which badly effect the environment and human health in an every day life.

A possible solution of this hidden disaster is the development and broad uses of new ashless lubricant additives, with reduced amounts of sulphur and phosphorus. Recently, interest in the use of boron compounds for challenging applications in tribology certainly appears to be increasing due to their unique tribochemical properties. Specifically, boron compounds have been extensively studied as boundary lubricating oil soluble additives, solid lubricants and surface coatings. Oil soluble organoboron compounds are promising friction modifiers, corrosion inhibitors, antioxidants and effective antiwear additives.

Based on literature review and current demands, the main goals of this work are:

1. To develop a new class of lubricant additives that contains borate and dialkyldithiophosphate groups in a single molecule. It is expected that such a class of ashless compounds i.e. without zinc and with reduced amounts of sulphur and phosphorus, would provide enhanced tribological and environmental performance.
2. To characterize chemical structures of these novel compounds.
3. To study the effect of temperature on their physicochemical properties such as thermal stability, weight loss, and a pathway of fragmentation of these compounds as a result of thermal decomposition.
4. To perform tribological evaluations of these new additives in comparison with commercial ZnDTP.

## CHAPTER 2

**2 EXPERIMENTAL SECTION****2.1 Chemicals**

Phosphorus pentasulphide,  $P_2S_5$  (Aldrich, 99 % purity), pentanol (Prolabo, 98% purity), octanol (Prolabo, 97 % purity), decanol (Merck, >99 % purity), 2-chloroethanol (Fluka, >99% purity), sodium sulphate (Merck, analytical grade), potassium hydroxide pellets (Merck, analytical grade), boric acid (Merck, analytical grade) and toluene (Fluka, > 99.7 % purity) were used as received.

**2.2 Chemical Synthesis****2.2.1 *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) (ZnDTP)**

The commercially available ZnDTP contains a mixture of 85 % *O,O'*-di-*iso*-butyl-dithiophosphato-zinc(II) and 15 % *O,O'*-di-*n*-octyl-dithiophosphato-zinc(II) [120]. In this study, we used ZnDTP (as a reference compound) with the same number of carbon atoms in alkyl chains as in the commercial ZnDTP additive but we selected *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) instead of Zn(II)-*i*BuDTP. *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) is a viscous liquid at room temperature. It is easily miscible with the base oil used in this study. On the contrary, Zn(II)-*i*BuDTP is a solid at room temperature that makes it difficult to fully dissolve it in the base oil. *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) was synthesized by a reported method [121]. The purity of the latter ZnDTP and its corresponding potassium salt were proven by  $^{31}P$  NMR: for ZnDTP (145.70 MHz,  $\delta$ ): 100.29 ppm [122] and for potassium salt (145.70 MHz, ethanol,  $\delta$ ) 112.72 ppm.

**2.2.2 *S*-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP)**

**Step 1:** Boric acid (10 mmol) and 1-octanol (30 mmol) were mixed in a flask with toluene (50 mL), equipped with a magnetic stirrer, a condenser and a water separator. The reaction mixture was refluxed for 3 h. Water formed during the reaction was removed continuously using a separator. Toluene was rotary evaporated and a product was distilled under reduced pressure (0.2 mm Hg) to remove toluene and residual octanol. A colourless liquid product of trioctyl borate (TOB) was obtained in 88 % yield.

**Step 2:** Phosphorus pentasulphide (11.28 g, 10 mmol) and trioctyl borate (45.15 g, 40 mmol) were mixed in toluene in a flask equipped with a magnetic stirrer and a condenser (pre-baked

on vacuum to exclude any moisture). The reaction mixture was refluxed for 3 h under nitrogen atmosphere. After cooling, the precipitate was filtered, the filtrate was rotary evaporated to remove toluene and distilled at 0.2 mm Hg, 120 °C for 30 minutes. A transparent liquid product was obtained in 52 % yield (7.30 g).

### 2.2.3 S-(di-*n*-pentylborate)-ethyl-*O,O'*-di-*n*-pentyldithiophosphate (DPB-EDTP)

**Step 1:** Phosphorus pentasulphide (4.44 g, 20 mmol) was suspended in toluene and pentanol (80 mmol) was added. The reaction mixture was stirred at 80-100 °C for 3 hours. The suspension was filtered to remove unreacted phosphorus pentasulphide (P<sub>2</sub>S<sub>5</sub>). An equivalent amount of potassium hydroxide was added in the form of 50% aqueous solution with continuous stirring at room temperature. Toluene and water were removed and the crude product was dried. The crude potassium *O,O'*-di-*n*-pentyldithiophosphate was washed with hexane (yield 75 %).

**Step 2:** 20 mmol (1.61 g) of chloroethanol was added to an aqueous suspension of potassium salt of *O,O'*-di-*n*-pentyldithiophosphate (20 mmol, 6.16 g) with constant stirring. The resulting reaction mixture was refluxed for 3 hours. Organic layer formed was extracted with toluene from aqueous phase, washed with water several times and dried over anhydrous sodium sulphate. Sodium sulphate was filtered, filtrate was rotary evaporated to get S-hydroxyethyl-*O,O'*-di-*n*-pentyldithiophosphate, (4.64 g, 74 % yield).

**Step 3:** A solution of 10 mmol (3.14 g) of S-hydroxyethyl-*O,O'*-di-*n*-pentyldithiophosphate (**2**) was put together with 10 mmol (0.618g) of boric acid, 20 mmol of 1-pentanol and 80 ml of toluene to a 250 ml round-bottom flask equipped with a magnetic stirrer, a condenser and a water separator (pre-baked on vacuum to exclude any moisture). The reaction mixture was refluxed for 6 hours under nitrogen atmosphere. Water was continuously removed from the reaction mixture. The reaction mixture was rotary evaporated to remove solvent. The product formed was distilled at 0.2 mm Hg, 120 °C for 30 minutes to remove traces of solvent and 1-pentanol. A transparent viscous liquid product, S-(di-*n*-pentylborate)-ethyl-*O,O'*-di-*n*-pentyldithiophosphate was obtained in 89 % yield (4.42 g). Anal. Calcd. for C<sub>22</sub>H<sub>48</sub>O<sub>5</sub>PS<sub>2</sub>B (MW 498.46): C, 53.0; H, 9.7; B, 2.2. Found: C, 52.3; H, 9.7; B, 2.6.

### 2.2.4 S-(di-*n*-octylborate)-ethyl-*O,O'*-di-*n*-octyldithiophosphate (DOB-EDTP)

DOB-EDTP was synthesized using the same procedure as for DPB-EDTP described above. A transparent viscous liquid, yield 90 %. Anal. Calcd. for C<sub>34</sub>H<sub>72</sub>O<sub>5</sub>PS<sub>2</sub>B (MW 666.75): C, 61.3; H, 10.9; B, 1.62. Found: C, 63.5; H, 11.3; B, 1.58.

### 2.2.5 S-(di-*n*-decylborate)-ethyl-*O,O'*-di-*n*-decyldithiophosphate (DDB-EDTP)

DDB-EDTP was synthesized using the same procedure as for DPB-EDTP and DOB-EDTP described above. A transparent viscous liquid, yield 92 %. Anal. Calcd. for  $C_{42}H_{88}O_5PS_2B$  (MW 779.02): C, 64.6; H, 11.4; B, 1.40. Found: C, 67.6; H, 11.8; B, 1.64.

## 2.3 Chemical Characterization

The elemental analysis for C and H was performed at Mikrokemi AB, Uppsala, according to procedures described on their homepage [123]. The elemental analysis of B was carried out at ALS laboratory group, Luleå using ICP-MS: Detailed procedure is described on their homepage [124].

FT-IR spectra were recorded on a Perkin-Elmer 2000 spectrometer in the range 4000–370  $cm^{-1}$ . Sampling was performed by placing a droplet of a compound onto a KBr pellet. Multinuclear NMR spectra were recorded on a Varian/Chemagnetics InfinityPlus CMX-360 (B=8.46 T) spectrometer in  $CDCl_3$  ( $^1H$ ,  $^{13}C$ ) or in toluene ( $^{31}P$ ,  $^{11}B$ ) using TMS as an internal reference for  $^1H$  (0 ppm), the 77.2 ppm resonance peak of  $CDCl_3$  for  $^{13}C$ ,  $Et_2O.BF_3$  as an external reference (0 ppm) for  $^{11}B$  and  $H_3PO_4$  (85%) as an external reference (0 ppm) for  $^{31}P$ .

## 2.4 Thermal Analysis

Thermal analysis of the synthesized compound was performed by Netzsch STA 409 instrument equipped with simultaneous thermogravimetric (TG), differential thermal analysis (DTA) coupled with a quadrupole mass spectrometer (QMS) at a rate of 20°C/min and with argon flow rate of 100 ml/min. The sensitivity of this STA instrument is  $\pm 1 \mu g$ .

## 2.5 Tribological Characterization

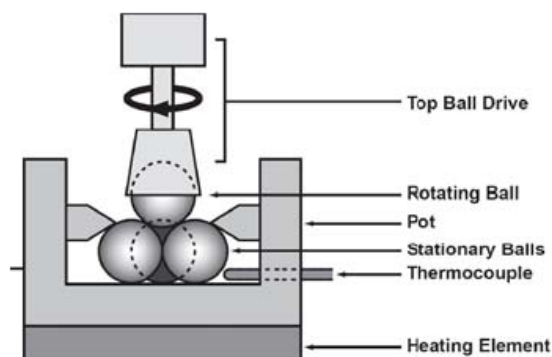
### 2.5.1 Antiwear and Friction Studies

Additives were admixed in mineral base oil at various concentrations: 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 weight % using an analytical balance. The physicochemical properties and the elemental analysis of the base oil used in this study are given in Table 1. Balls ( $\varnothing = 12.7$  mm) used in tribological tests are made of AISI 52100 steel with a composition of C, 0.95–1.10%; Si, 0.15–0.30%; Mn, <0.25%; P, <0.03%; S, <0.025%; Cr, 1.30–1.60%. Ball hardness is HRC 60–67.

**Table 1.** Physicochemical properties of the mineral base.

Density ( $\text{g.mL}^{-1}$ )	0.8135
Viscosity (m Pa.s) at 40 °C	17.5
Viscosity (m Pa.s) at 100 °C	4.9
Carbon (%)	$86.0 \pm 0.7$
Hydrogen (%)	$14.5 \pm 0.5$

The friction and wear properties of the synthesized boron compounds as additives in the base oil were evaluated with a four ball tribometer at a rotating speed of 1450 rpm, test duration time of 30 min, load 392 N and at room temperature (294 K). The schematic representation of the sample compartment of a four-ball tribometer is given in Figure 19. Wear scar diameters and the friction coefficient were measured at additive concentrations in the range of 0-1.0 wt %. An optical profiler (WYCO NT 1100) was used to determine the wear scar diameters of the three stationary balls. Then a mean value was calculated and reported here as the wear scar diameter (WSD). Before each test, the holder for the balls was washed with petroleum ether and the balls were cleaned ultrasonically in petroleum ether and thoroughly air-dried.

**Figure 19.** Schematics of the sample compartment of a four-ball tribometer.

### 2.5.2 Surface Analysis

The morphology of worn surfaces after tribological testing was studied using an optical profiler and SEM with EDS. 3D topography was obtained with WYCO NT 1100 optical profiler.



Philips XL 30 scanning electron microscope (SEM) equipped with LaB<sub>6</sub> emission source was used for surface studies. A link ISIS Ge energy dispersive X-ray detector (EDS) attached to the SEM was used to additionally probe the composition of the entire tribofilms on the ball surfaces. Prior to the analysis, the balls were cleaned ultrasonically for 5 min with petroleum ether, in order to eliminate the residual lubricant.

## CHAPTER 3

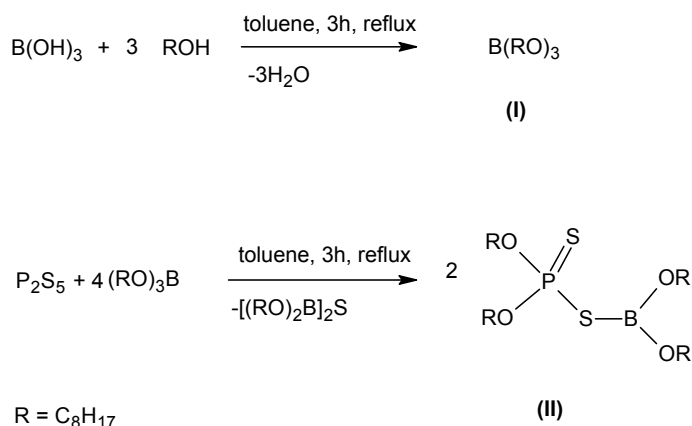
## 2. RESULTS AND DISCUSSION

## 2.1 Chemical Synthesis

2.1.1 S-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP)

Compounds containing P(S)SB structural fragments are of interest in synthetic chemistry due to their high reactivity and their use as synthetic intermediates in the preparation of organothiophosphorus, organometallic and organometalloid sulphur compounds.

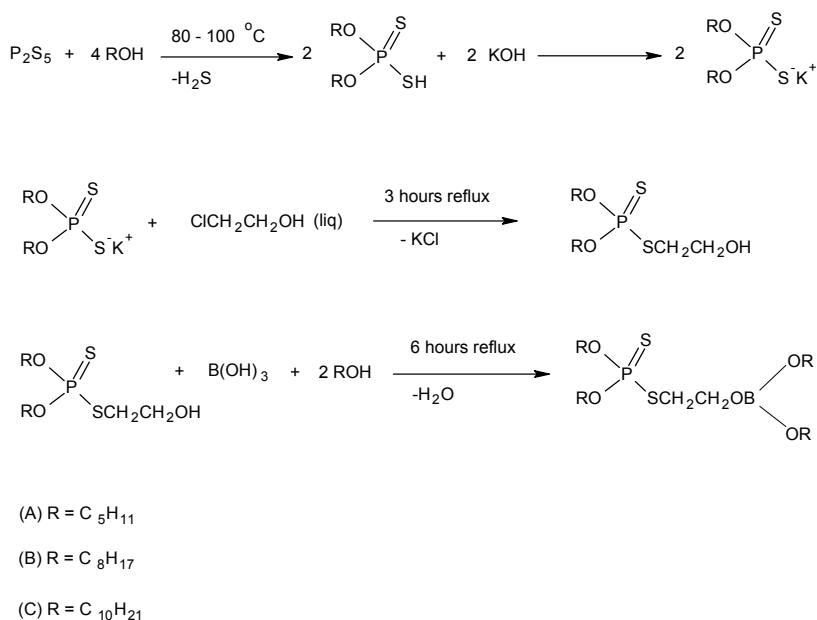
S-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP) was synthesized by a reaction in two steps (Scheme 1). In the first step, trioctyl borate, TOB (**I**) was synthesized by treating boric acid and octanol. This step was followed by the synthesis of DOB-DTP (**II**) using a reported method [125] by reacting phosphorus pentasulphide ( $P_2S_5$ ) with trioctyl borate in a 1:4 molar ratio. This method was used for shorter chains alkyl borates but we have modified this method for borate with longer alkyl chains, i.e. trioctyl borate. During this reaction, B-O bonds of borate were cleaved and new B-S bonds were formed simultaneously giving rise to the final product (**II**). A semi-solid by-product,  $[(RO)_2B]_2S$ , formed in the same reaction was removed by filtration.



**Scheme 1.** Synthesis of DOB-DTP

### 2.1.2 Organoboron Derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate

Organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate were synthesized following several steps (Scheme 2). The first step was followed by a common procedure reported previously [126]. *O,O'*-dialkyldithiophosphoric acid was the main product in the reaction of phosphorus pentasulphide ( $P_2S_5$ ) with primary pentanol mixed in a 1:4 molar ratio. No attempts were further made to isolate and purify this acid, because it is slowly oxidised by atmospheric oxygen. Instead, the crude product was used for the following preparation of potassium *O,O'*-dialkyldithiophosphates. In the second step, S-hydroxyethyl of *O,O'*-dialkyldithiophosphates were prepared by refluxing 2-chloroethanol with an aqueous suspension of potassium *O,O'*-dialkyldithiophosphates in a 1:1 molar ratio for 3 hours. In the third step, the final products were prepared by treating S-hydroxyethyl of *O,O'*-dialkyldithiophosphate with boric acid and a corresponding alcohol. Since boron-sulphur bond is susceptible to hydrolysis by atmospheric moisture, boron was bound to *O,O'*-dialkyldithiophosphates group through ethyl group in order to avoid hydrolysis during tribological applications.



**Scheme 2.** Synthesis of organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphates

## 2.2 FT-IR Analysis

FT-IR spectra of synthesized compounds show a few bands of characteristic peaks. Absorption frequencies of the aliphatic C-H vibrations in the alkyl groups of these compounds were mainly observed between 2960 and 2850  $\text{cm}^{-1}$ . Unambiguous assignment of P-S and P=S stretching frequencies in FT-IR spectra of dialkyldithiophosphate compounds encounters difficulties: For example, bands associated with the P-S stretching frequencies in the transition-metal complexes, which contain bidentate chelating dithiophosphate ligands appear in the same region as for free acids  $(\text{RO})_2\text{P}(=\text{S})\text{SH}$  and their esters  $(\text{RO})_2\text{P}(=\text{S})\text{SR}'$  [127].

### 2.2.1 S-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP)

FT-IR data for trioctylborate (TOB) and S-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP) are given in Table 2. These data present the characteristic absorption frequencies of the aliphatic C-H vibrations in the alkyl groups in the range of 2960-2850  $\text{cm}^{-1}$ . Strong bands were observed at 1337  $\text{cm}^{-1}$  and 1336  $\text{cm}^{-1}$  for TOB and DOB-DTP respectively, which are attributed to the  $\nu(\text{B-O})$  band in these compounds. Strong band at 992  $\text{cm}^{-1}$  and medium bands at 666  $\text{cm}^{-1}$  and 531  $\text{cm}^{-1}$  were observed in the FT-IR spectrum of DOB-DTP only and these are assigned to  $\nu(\text{P-OC})$ ,  $\nu(\text{P=S})$  and  $\nu(\text{P-S})$  bands, respectively. The latter is an additional proof that DOB-DTP is formed from the intermediate TOB.

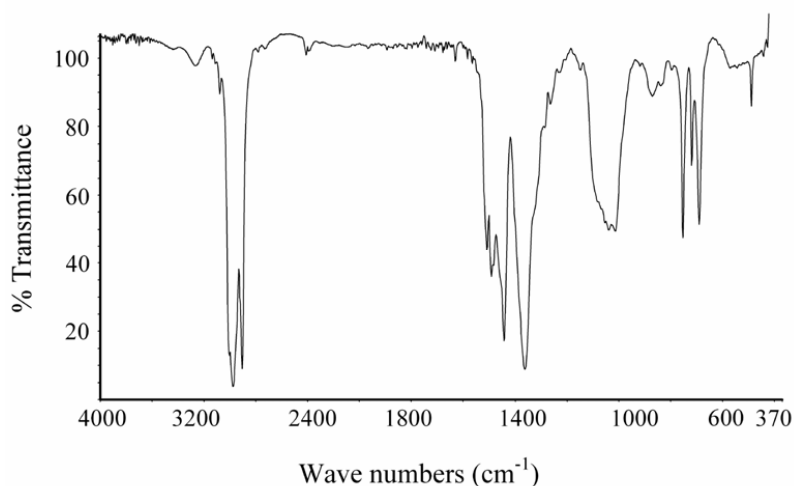
**Table 2.** FTIR (KBr,  $\text{cm}^{-1}$ ) of TOB and DOB-EDTP

Compound	$\text{cm}^{-1}$
TOB	2927, 2856 $\nu(\text{C-H, stretching})$ ; 1417 $\nu(\text{CH}_2 \text{ bending})$ ; 1337 $\nu(\text{B-O strong})$ .
DOB-DTP	2927, 2856 $\nu(\text{C-H, stretching})$ ; 1417 $\nu(\text{CH}_2 \text{ bending})$ ; 1336 $\nu(\text{B-O, strong})$ ; 992 $\nu(\text{P-OC, broad})$ ; 859 $\nu(\text{PO-C, medium})$ ; 666 $\nu(\text{P=S, medium})$ ; 531 $\nu(\text{P-S, medium})$ .

### 2.2.2 Organoboron Derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphates

FT-IR spectra of intermediates and the final products of organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphates show four bands with characteristic absorption peaks tabulated in Table 3. (As an example, Figure 20 shows a FT-IR spectrum of DDB-EDTP.) Absorption frequencies of the aliphatic C-H vibrations in the alkyl groups of these compounds were observed in the range of 2960-2850  $\text{cm}^{-1}$ . Medium and broad bands present in the FTIR spectra of all these compounds in the regions of 984-980  $\text{cm}^{-1}$  are assigned to  $\nu(\text{P-}$

OC). Bands in the region of  $730\text{--}708\text{ cm}^{-1}$  are assigned to  $\nu(\text{P}=\text{S})$  and bands around  $666\text{--}540\text{ cm}^{-1}$  are attributed to  $\nu(\text{P}-\text{S})$ . In the final products, strong bands were also observed at  $1337\text{ cm}^{-1}$  and assigned to  $\nu(\text{B}-\text{O})$ . This band is absent in the intermediate products. No shift in this band was observed for different chain lengths of alkyl groups in borates.



**Figure 20.** FT-IR spectrum of DDB-EDTP.

**Table 3.** FT-IR (KBr,  $\text{cm}^{-1}$ ) of organoboron derivatives of dialkyldithiophosphates.

Compound	$\text{cm}^{-1}$
K-DTP	2957, 2873 $\nu(\text{C-H, stretching})$ ; 1466 $\nu(\text{CH}_2 \text{ bending})$ ; 1379 $\nu(\text{CH}_3 \text{ bending})$ ; 983 $\nu(\text{P-OC, medium})$ ; 708 $\nu(\text{P}=\text{S, medium})$ ; 548 $\nu(\text{P-S, medium})$ .
DTP-EtOH	3427 $\nu(\text{O-H, broad})$ ; 2927, 2858 $\nu(\text{C-H, stretching})$ ; 1468 $\nu(\text{CH}_2 \text{ bending})$ ; 1381 $\nu(\text{CH}_3 \text{ bending})$ ; 980 $\nu(\text{P-OC, medium})$ ; 729 $\nu(\text{P}=\text{S, medium})$ ; 662 $\nu(\text{P-S, strong})$ .
DPB-EDTP	2957, 2932, 2873 $\nu(\text{C-H, stretching})$ ; 1467 $\nu(\text{CH}_2 \text{ bending})$ ; 1337 $\nu(\text{B-O, strong})$ ; 984 $\nu(\text{P-OC, medium})$ ; 730 $\nu(\text{P}=\text{S, medium})$ ; 666 $\nu(\text{P-S, medium})$ .
DOB-EDTP	2956, 2927, 2856 $\nu(\text{C-H, stretching})$ ; 1466 $\nu(\text{CH}_2 \text{ bending})$ ; 1337 $\nu(\text{B-O, strong})$ ; 987 $\nu(\text{P-OC, medium})$ ; 729 $\nu(\text{P}=\text{S, medium})$ ; 666 $\nu(\text{P-S, medium})$ .
DDB-EDTP	2955, 2926, 2855 $\nu(\text{C-H, stretching})$ ; 1466 $\nu(\text{CH}_2 \text{ bending})$ ; 1337 $\nu(\text{B-O, strong})$ ; 989 $\nu(\text{P-OC, medium})$ ; 729 $\nu(\text{P}=\text{S, medium})$ ; 666 $\nu(\text{P-S, medium})$ .

## 2.3 Multinuclear NMR Analysis

### 2.3.1 S-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP)

Data evaluated from  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR spectra of DOB-DTP are presented in Table 4.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of this compound exhibit J-multipletts assigned to alkyl protons and carbons in ligand moieties.

$^{31}\text{P}$  NMR of DOB-DTP measured in toluene reveals a singlet at 84.58 ppm that is expected for pure boron *O,O'*-dialkyldithiophosphate compounds [128].

$^{11}\text{B}$  NMR spectra of TOB and DOB-DTP were recorded in toluene and observed chemical shifts are 16.56 and 16.36 ppm for these two compounds, respectively. This is consistent with the presence of the three-coordinated B atoms in boron-*O,O'*-dialkyldithiophosphates [128]. The boron nucleus in DOB-DTP is more shielded (by 0.20 ppm) compared to B in TOB that is in accord with a formation of a  $\text{SBO}_2$  group instead of  $\text{BO}_3$ .

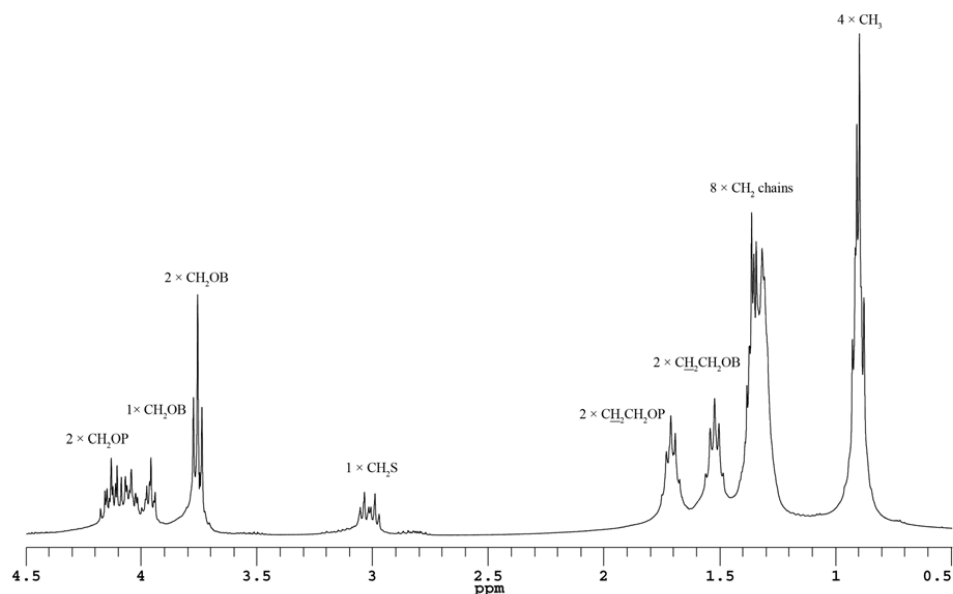
**Table 4.**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR data of TOB and DOB-DTP

Compound	NMR chemical shifts ( $\delta$ , ppm)			
	$^1\text{H}$ ( $\text{CDCl}_3$ )	$^{13}\text{C}$ ( $\text{CDCl}_3$ )	$^{31}\text{P}$ (toluene)	$^{11}\text{B}$ (toluene)
TOB	--	--	--	16.56
DOB-DTP	0.88 (12H, t, $^3J_{\text{HH}} = 6.7$ Hz, $\text{CH}_3$ ); 1.26-1.34 (40H, m, $-\text{CH}_2-$ chain); 1.48-1.60 (4H, m, $\text{CH}_2\text{CH}_2\text{OB}$ ); 1.69-1.76 (4H, m, $\text{CH}_2\text{CH}_2\text{OP}$ ); 3.76 (4H, t, $^3J_{\text{HH}} = 6.6$ Hz, $\text{CH}_2\text{OB}$ ); 4.15 (4H, dt, $^3J_{\text{HP}} = 9.47$ , $^3J_{\text{HH}} = 6.56$ , $\text{CH}_2\text{OP}$ ).	14.26 ( $4 \times \text{CH}_3$ ), 22.84 ( $4 \times \text{CH}_2\text{CH}_3$ ), 26.02, 29.34, 29.51, 30.14, 32.02 ( $20 \times -\text{CH}_2-$ chain), 63.41 ( $2 \times \text{CH}_2\text{OB}$ ); 68.62 ( $2 \times \text{CH}_2\text{OP}$ ).	84.58	16.36

### 2.3.2 Organoboron Derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphates

Multinuclear  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR data of organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphates are summarized in Tables 5 and 6. A  $^1\text{H}$  NMR spectrum of DPB-EDTP is given in Figure 21. Multipletts reveal three-bond J-couplings between  $\alpha$ -protons and phosphorus nuclei in alkyl groups at the  $\text{OP}(\text{S})\text{S}$  group. Similarly, three-bond  $^1\text{H}$ -C-S- $^{31}\text{P}$   $^3J_{\text{HP}}$ -couplings were observed between the  $\alpha$ -proton of the ethyl group directly bound

to the OP(S)S group. No interaction was observed between  $\alpha$ -protons and boron nuclei ( $^{11}\text{B}$  or  $^{10}\text{B}$ , which are both magnetic) in the borate parts of these compounds.



**Figure 21.**  $^1\text{H}$  NMR spectrum of 100 mM DPB-EDTP in  $\text{CDCl}_3$

The  $^{31}\text{P}$  chemical shift of phosphorus sites in potassium *O,O'*-di-*n*-pentyldithiophosphate measured in ethanol is 112.79 ppm. A  $^{31}\text{P}$  NMR spectrum of DTP-EtOH measured in  $\text{CDCl}_3$  revealed a singlet at 96.25 ppm. The 15.54 ppm upfield shift (shielding) in the latter compound indicates that hydroxyethyl group is bound to *O,O'*-di-*n*-pentyldithiophosphate through one of sulphur atoms in the P(S)S group [129]. A  $^{31}\text{P}$  NMR spectrum of 100 mM DPB-EDTP in  $\text{CDCl}_3$  shows a singlet at 95.91 ppm. The phosphorus site is more shielded (0.34 ppm) in the final product compared to its intermediate as expected. This is because of bonding of the alkyl group to the sulphur atom, which shields more the phosphorus nucleus as compared to the intermediate, DTP-EtOH.  $^{31}\text{P}$  NMR reveals no significant changes in  $^{31}\text{P}$  chemical shifts as a function of the length of alkyl chains in DPB-EDTP, DOB-EDTP and DDB-EDTP.

$^{11}\text{B}$  NMR spectra of the latter compounds in  $\text{CDCl}_3$  reveal a singlet at 17.59, 17.52 and 17.50 ppm for DPB-EDTP, DOB-EDTP and DDB-EDTP, respectively.

**Table 5.**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR data of DPB-EDTP and its intermediates in the synthesis

Compound	NMR chemical shifts ( $\text{CDCl}_3$ , $\delta$ , ppm)			
	$^1\text{H}$	$^{13}\text{C}$	$^{31}\text{P}$	$^{11}\text{B}$
K-DTP			112.79	
DTP-EtOH	0.91 (6H, t, $^3J_{\text{HH}} = 6.54$ Hz, $\text{CH}_3$ ); 1.32-1.40 (8H, m, $-\text{CH}_2-$ ); 1.68-1.76 (4H, m, $\text{CH}_2\text{CH}_2\text{OP}$ ); 2.21 (1H, s, OH); 3.09 (2H, dt, $^3J_{\text{HP}} = 18.65$ , $^3J_{\text{HH}} =$ 5.76, $\text{CH}_2\text{S}$ ); 3.85 (2H, t, $^3J_{\text{HH}} = 6.04$ Hz, $\text{CH}_2\text{OH}$ ); 4.04-4.18 (4H, m, $\text{CH}_2\text{OP}$ ).	14.05 ( $2 \times \text{CH}_3$ ); 22.30 ( $2 \times$ $\text{CH}_2-\text{CH}_3$ ); 27.82, 29.80, ( $4 \times -\text{CH}_2-$ ); 36.46 ( $1 \times \text{CH}_2-\text{S}$ ); 62.04 ( $1 \times \text{CH}_2-\text{O}-\text{B}$ ); 68.37 ( $2 \times \text{CH}_2-\text{O}-\text{P}$ ).	96.25	--
DPB-EDTP	0.91 (6H, t, $^3J_{\text{HH}} = 7.0$ Hz, $\text{CH}_3$ ); 0.90 (6H, t, $^3J_{\text{HH}} = 6.94$ Hz, $\text{CH}_3$ ); 1.30-1.40 (16H, m, $-\text{CH}_2-$ ); 1.49-1.57 (4H, m, $\text{CH}_2\text{CH}_2\text{OB}$ ); 1.68-1.75 (4H, m, $\text{CH}_2\text{CH}_2\text{OP}$ ); 3.01 (2H, dt, $^3J_{\text{HP}} = 16.37$ , $^3J_{\text{HH}} =$ 6.56, $\text{CH}_2\text{S}$ ); 3.76 (4H, t, $^3J_{\text{HH}} = 6.64$ Hz, $\text{CH}_2\text{OB}$ , pentyl chain); 3.96 (2H, t, $^3J_{\text{HH}} = 6.49$ Hz, $\text{CH}_2\text{OB}$ , ethyl); 4.02-4.18 (4H, m, $\text{CH}_2\text{OP}$ ).	14.20 ( $2 \times \text{CH}_3$ ); 14.06 ( $2 \times$ $\text{CH}_3$ ); 22.57 ( $2 \times \text{CH}_2-\text{CH}_3$ ); 22.36 ( $2$ $\times \text{CH}_2-\text{CH}_3$ ); 27.86, 28.15, 29.84, 31.37 ( $8 \times$ $\text{CH}_2$ , pentyl chains); 34.79 ( $1 \times \text{CH}_2-\text{S}$ ); 63.34 ( $3 \times \text{CH}_2-\text{O}-\text{B}$ ); 68.03 ( $2 \times \text{CH}_2-\text{O}-\text{P}$ ).	95.91	17.59



**Table 6.**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR data of organoboron derivatives of dialkyldithiophosphates

Compound	NMR chemical shifts ( $\text{CDCl}_3$ , $\delta$ , ppm)			
	$^1\text{H}$	$^{13}\text{C}$	$^{31}\text{P}$	$^{11}\text{B}$
DOB-EDTP	0.88 (12H, t, $^3J_{\text{HH}} = 6.37$ Hz, $\text{CH}_3$ ); 1.26-1.40 (40H, m, $-\text{CH}_2-$ ); 1.48-1.56 (4H, m, $\text{CH}_2\text{CH}_2\text{OB}$ ); 1.67-1.75 (4H, m, $\text{CH}_2\text{CH}_2\text{OP}$ ); 3.01 (2H, dt, $^3J_{\text{HP}} = 16.65$ , $^3J_{\text{HH}} = 6.37$ , $\text{CH}_2\text{S}$ ); 3.76 (4H, t, $^3J_{\text{HH}} = 6.50$ Hz, $\text{CH}_2\text{OB}$ , octyl chains); 3.96 (2H, t, $^3J_{\text{HH}} = 6.42$ Hz, $\text{CH}_2\text{OB}$ , ethyl); 4.01-4.18 (4H, m, $\text{CH}_2\text{OP}$ ).	14.26 ( $4 \times \text{CH}_3$ ); 22.84 ( $4 \times \text{CH}_2\text{-CH}_3$ ); 26.01, 28.15, 29.52, 30.70, 32.01, ( $20 \times \text{CH}_2$ , octyl chains); 34.85 ( $1 \times \text{CH}_2\text{-S}$ ); 63.41 ( $3 \times \text{CH}_2\text{-O-B}$ ); 68.09 ( $2 \times \text{CH}_2\text{-O-P}$ ).	95.88	17.52
DDB-EDTP	0.88 (12H, t, $^3J_{\text{HH}} = 6.51$ Hz, $\text{CH}_3$ ); 1.25-1.32 (56H, m, $-\text{CH}_2-$ ); 1.48-1.55 (4H, m, $\text{CH}_2\text{CH}_2\text{OB}$ ); 1.66-1.74 (4H, m, $\text{CH}_2\text{CH}_2\text{OP}$ ); 3.01 (2H, dt, $^3J_{\text{HP}} = 16.31$ , $^3J_{\text{HH}} = 6.28$ , $\text{CH}_2\text{S}$ ); 3.76 (4H, t, $^3J_{\text{HH}} = 6.45$ Hz, $\text{CH}_2\text{OB}$ , decyl chains); 3.96 (2H, t, $^3J_{\text{HH}} = 6.42$ Hz, $\text{CH}_2\text{OB}$ , ethyl); 4.02-4.18 (4H, m, $\text{CH}_2\text{OP}$ ).	14.26 ( $4 \times \text{CH}_3$ ); 22.88 ( $4 \times \text{CH}_2\text{-CH}_3$ ); 24.26, 26.01, 28.38, 29.83, 30.96, 31.19, 32.10, ( $28 \times \text{CH}_2$ , decyl chains); 33.54 ( $1 \times \text{CH}_2\text{-S}$ ); 63.38 ( $3 \times \text{CH}_2\text{-O-B}$ ); 68.01 ( $2 \times \text{CH}_2\text{-O-P}$ ).	95.90	17.50

## 2.4 Thermal Analysis

In many tribological systems, the contact temperature is high due to friction between the sliding surfaces. This high temperature may cause evaporation and decomposition of additives. Therefore, it is important to study the effect of temperature on the physicochemical properties of the lubricant additives such as their thermal stability, weight loss, and the nature of compounds in the course of thermal decomposition. Differential thermal analysis is usually represented as “exothermic” or “endothermic” peaks at elevated temperatures. Generally, exothermic peaks are the result of a chemical decomposition or oxidation, which are

accompanied by exothermic processes. In turn, endothermic peaks are due to physical processes such as melting, boiling or other phase transitions of a compound [130]. The thermal decomposition temperature of dialkyldithiophosphates of different metal ions is strongly dependent on the type of alkyl groups and molecular structures of these compounds; i.e. (i) aryl dialkyldithiophosphates of zinc(II) are more stable than alkyl derivatives of ZnDTPs; (ii) primary alkyl are more stable than secondary alkyl ZnDTPs. The differential thermal analysis of these compounds has shown that, with the primary alkyl ZnDTP, the hydrogen atom bound to a  $\beta$ -carbon atom of the alkyl group is more stable than those in the secondary alkyl ZnDTP [131, 132]. Therefore, formation of olefins may only occur at relatively high temperatures.

During a thermal decomposition of the synthesized boron compounds, two categories of decomposition products were obtained. The residual product with a melting point above 500 °C was solid and no attempts were made to characterize its composition. The volatile products were characterized by quadrupole mass spectrometer attached to the thermal analysis instrument. Thermal properties of the synthesized compounds are summarized in Table 7.

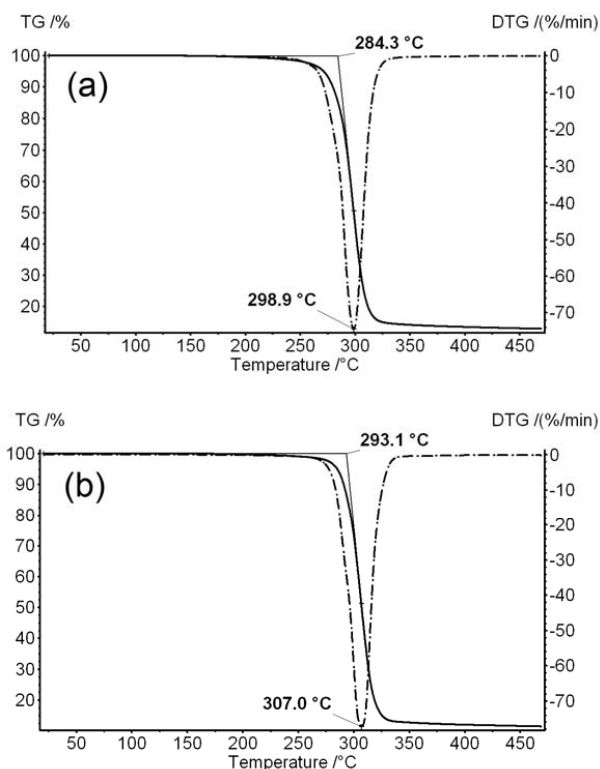
**Table 7.** Thermal properties of synthesized boron compounds

Compound	TG (°C)	Weight loss (%)	DTG (°C)	DTA (°C)	
				Exothermic	Endothermic
DOB-DTP	267.7	86	273.6	274.7	-
DPB-EDTP	256.8	62	269.4	266.5	273.8
DOB-EDTP	284.3	87	298.9	284.0	317.1
DDB-EDTP	293.1	89	307.0	297.0	323.4

#### 2.4.1 Thermogravimetric Analysis

The thermal decomposition of these boron compounds involves only one major step in the range of 256.8-293.1 °C. It indicates the complete decomposition of the molecules in a single step, which is initiated most probably, with breakage of PS and PO bonds in the thiophosphate group and followed by the decomposition of long alkyl chains. The total weight losses during these tests are from 62 to 89 wt% indicating that the tested compounds are to a large degree decomposed into volatile products. The patterns of the weight loss for DOB-EDTP and DDB-EDTP are shown in Figures 22 a and 22 b, respectively.

The highest rate of the weight loss during the thermal decomposition of these compounds appears in the range of 269.4-307.0 °C. It is found that the boron compounds with longer alkyl chains are thermally more stable than these with shorter alkyl chains. Furthermore, it is found that DOB-EDTP, in which boron is covalently bound to sulphur through the ethoxy group, is more stable than another compound with the direct boron-sulphur bond (DOB-DTP).

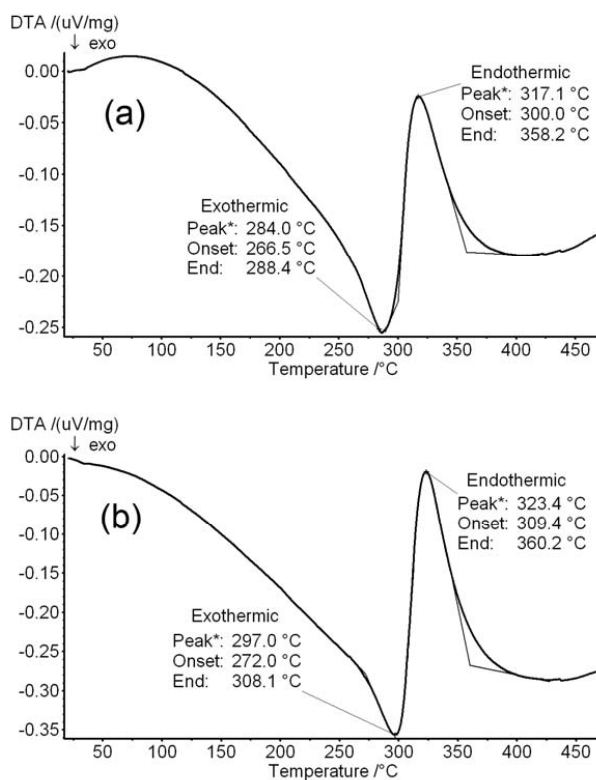


**Figure 22.** TG/DTG curves of organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate at a heating rate of 20° C/min and argon flow rate of 100 ml/min: (a) DOB-EDTP, (b) DDB-EDTP

#### 2.4.2 Differential Thermogravimetric Analysis

Figure 23 shows the differential thermal analysis (DTA) curves for DOB-EDTP and DDB-EDTP: Similar thermal events take place for organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate. These events are different for S-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP). Both the exothermic and endothermic peaks are observed in the DTA curves of DPB-EDTP, DOB-EDTP and DOB-EDTP while only one exothermic

peak is observed in DOB-DTP (in which boron is directly attached to sulphur). The exothermic peaks represent the thermal decomposition of these compounds. These exothermic peaks are followed by endothermic peaks only in the case of organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate, probably representing the physical processes of the decomposed products such as melting, boiling or other phase transitions. The DTA curves are in accordance with the TG/DTG curves and they do confirm that the decomposition of both these compounds takes place in a single step.



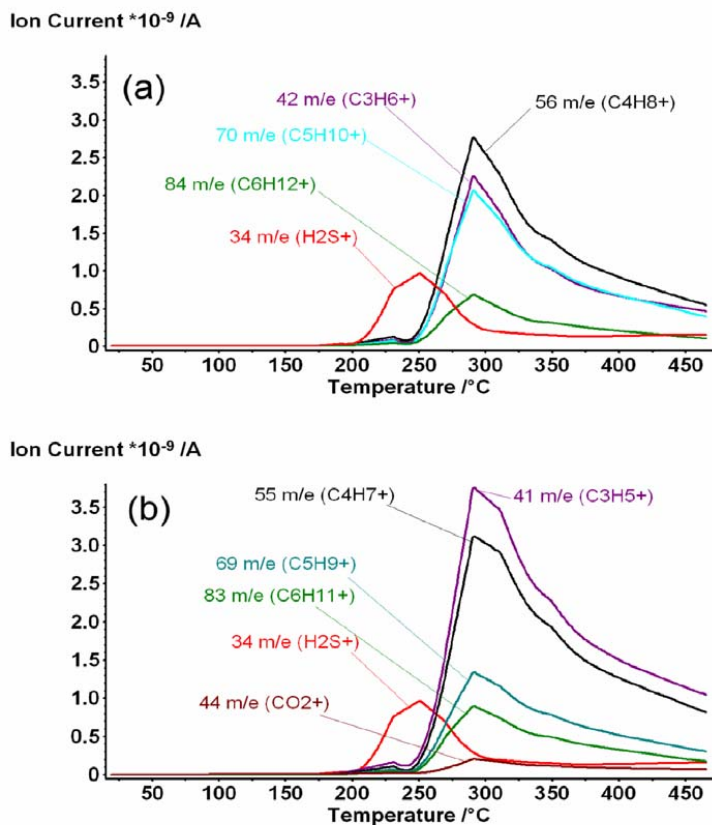
**Figure 23.** DTA curves of organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate at a heating rate of 20° C/min and argon flow rate of 100 mL/min: (a) DOB-EDTP, (b) DDB-EDTP.

#### 2.4.3 Quadrupole Mass Spectrometric Analysis

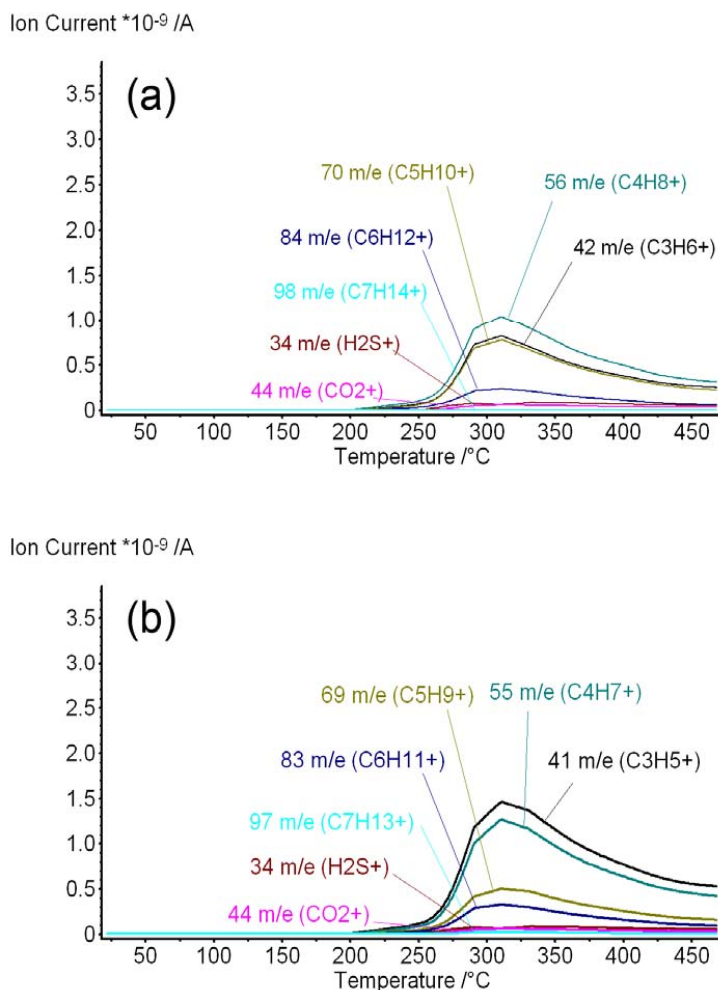
The thermal decomposition of parent compounds and formation of volatile products as a function of temperature under constant flow of argon gas were analyzed by quadrupole mass

spectrometry (QMS). Many volatile products were evolved in the 20-500 °C temperature range. Evolution of some selected products in the course of decomposition of DOB-DTP (Figure 5) and DOB-EDTP (Figure 6) are shown. The main volatile decomposition products of dialkyldithiophosphates are hydrogen sulphide and olefins [133]. Formation of hydrogen sulphide ( $\text{H}_2\text{S}^+$ ) with  $m/e=34$  is observed for all these compounds. Ion fragments with different number of carbons are formed in the course of cracking of parent alkyl chains at different positions. Relative intensities for peaks of the ion fragments are shown in comparison with the  $\text{H}_2\text{S}^+$  peak. Olefin cations have a similar evolution pattern. Among these cations, a propenyl cations ( $\text{C}_3\text{H}_5^+$  with  $m/e=41$  and  $\text{C}_3\text{H}_6^+$  with  $m/e=42$ ) and butenyl cations ( $\text{C}_4\text{H}_7^+$  with  $m/e=55$  and  $\text{C}_4\text{H}_8^+$  with  $m/e=56$ ) are the principle components in the mixture of volatile products of decomposition of these compounds. Peaks for decomposition products of the hydrocarbon chains with higher molecular weights have smaller intensities as compared with lower molecular weights.

DOB-EDTP is thermally more stable as compared to DOB-DTP, in which boron is directly bonded to sulphur atom of dialkyldithiophosphate group. Interestingly, in the case of DOB-EDTP, the pyrolysis of alkyl chains takes place before the formation of  $\text{H}_2\text{S}^+$ . While the formation of  $\text{H}_2\text{S}^+$  occurred before pyrolysis of alkyl chains in DOB-DTP. It indicates that B-S bond is thermally less stable than C-S bond.



**Figure 24.** QMS profiles for DOB-DTP at a heating rate of 20°C/min and argon flow rate of 100 mL/min. (a) Even molecular weight fragments, (b) Odd molecular weight fragments.



**Figure 25.** QMS profiles of DOB-EDTP at a heating rate of  $20^{\circ}\text{C}/\text{min}$  and argon flow rate of  $100\text{ ml}/\text{min}$ . (a) Even molecular weight hydrocarbon fragments, (b) Odd molecular weight hydrocarbon fragments.

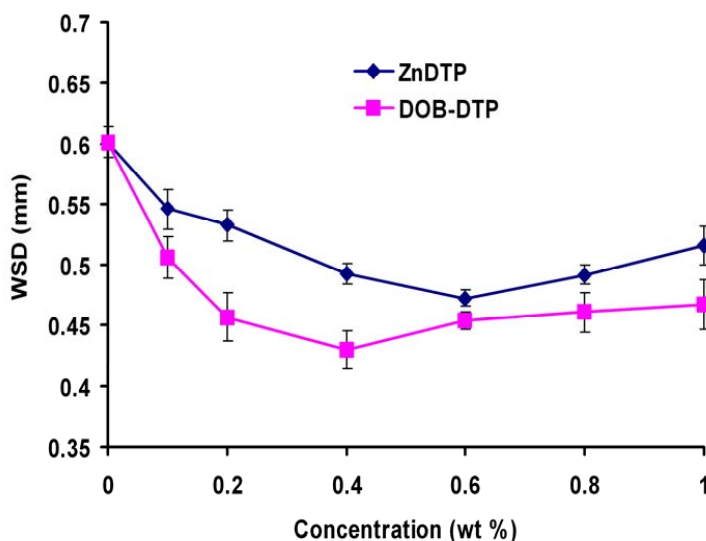
## 2.5 Tribological Characterization

### 2.5.1 Antiwear Performance

Antiwear performance of the novel additives was evaluated at different concentrations in the base oil. All these boron compounds reduce wear at lower concentrations as compared with ZnDTP. Generally, wear scar diameter decreases as a function of additive concentration, reaches its minimum and then increases slightly with an increase of concentration of additives.

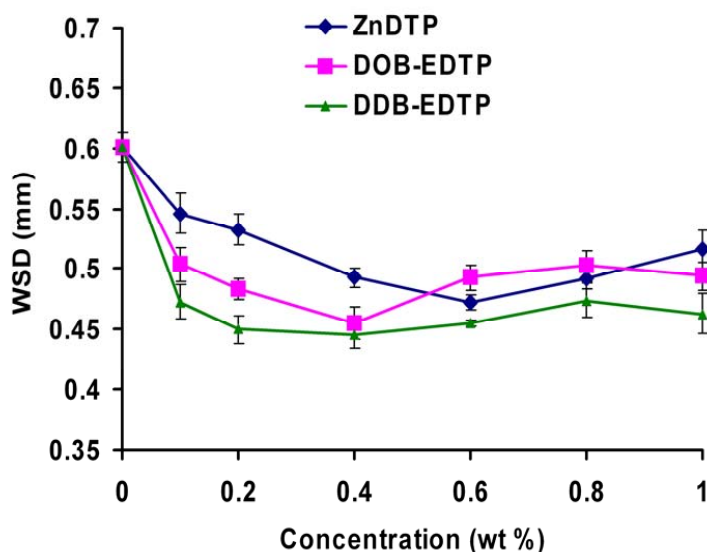
This increase in WSD may be attributed to a corrosive action of sulphur, which is present in molecules of all these additives. Note, that optimum concentrations for the wear reducing abilities of these boron compounds in the base oil (at chosen experimental conditions, i.e. load and temperature) were smaller as compared with ZnDTP.

Figure 26 shows variations of the wear scar diameter (WSD) measured on steel balls lubricated with the mineral base oil containing either DOB-DTP or ZnDTP additives. It was found that these additives are able to reduce wear scar diameters, when they were admixed into the mineral oil even at concentrations 0.4 to 0.6 wt%. A comparative antiwear performance of ZnDTP with DOB-EDTP and DDB-EDTP is shown in Figure 27.



**Figure 26.** Variations of the mean wear scar diameter (WSD, mm) on the lower steel balls with concentration (wt %) of additives in the base oil. Top (blue): ZnDTP, Bottom (pink): DOB-DTP.





**Figure 27.** Variations of the mean wear scar diameter (WSD, mm) on the lower steel balls with concentration (wt %) of additives in the base oil. Top (blue): ZnDTP, Middle (pink): DOB-EDTP; Bottom (green) DDB-EDTP.

A comparative analysis of the antiwear ability of an additive as a function of its concentration in the mineral base oil reveals that boron compounds forms a stable protective tribofilm even at a very low concentration (0.1 wt %, WSD = 0.43 – 0.46). The wear scar diameter is considerably larger for the reference additive, ZnDTP, at concentrations below 0.6 wt % in the base oil. Also, WSD increases considerably when concentration of ZnDTP is increased from 0.6-1.0 wt %.

The wear reducing ability of the additives can be explained by their affinities to and interactions with steel surfaces. More reactive additives are prone to reduce wear even at low concentrations by forming protective tribofilms on the contacting surfaces. On the other hand, an excess of sulphur in the lubricant causes a chemical corrosion, which limits the antiwear performance of S-based additives. Therefore, for each S-based additive there is an optimum concentration, at which WSD reaches its minimum. This minimum WSD is 0.473 mm for 0.6 wt % ZnDTP, 0.430 mm for 0.4 wt % DOB-DTP, 0.477 mm for 0.2 wt % DPB-EDTP, 0.456 mm for 0.4 wt % DOB-EDTP and 0.445 mm for 0.4 wt % DDB-EDTP.

**Table 8.** Variations of the mean wear scar diameter (mm) and the friction coefficient (an average over the last 10 min) with concentration (wt %) of novel DOB-DTP additive in comparison with the reference additive (Zn-*n*Bu-DTP)

Additive Concentration (wt %)	DOB-DTP		ZnDTP	
	WSD $\pm$ (SD) (mm)	Friction coefficient $\pm$ (Variation)	WSD $\pm$ (SD) (mm)	Friction coefficient $\pm$ (Variation)
0	0.602 (0.012)	0.042 (0.006)	0.602 (0.012)	0.042 (0.006)
0.1	0.506 (0.017)	0.062 (0.005)	0.546 (0.017)	0.082 (0.007)
0.2	0.457 (0.020)	0.060 (0.004)	0.533 (0.013)	0.074 (0.006)
0.4	0.430 (0.016)	0.060 (0.006)	0.493 (0.008)	0.065 (0.005)
0.6	0.454 (0.007)	0.063 (0.007)	0.473 (0.007)	0.072 (0.005)
0.8	0.461 (0.016)	0.060 (0.004)	0.492 (0.008)	0.066 (0.005)
1.0	0.467 (0.020)	0.062 (0.007)	0.516 (0.016)	0.066 (0.005)

There are two possible reasons for the efficient antiwear performance of the boron compounds as compared with ZnDTP. First, these boron compounds contain only two sulphur atoms while ZnDTP contains four sulphur atoms in the molecule. The excess of sulphur in additive or base oil may cause chemical corrosion of steel surfaces. Second, boron compounds contain the alkyl borate group in the molecule that enhances the antiwear ability of these additives and inhibits corrosive actions of sulphur even at higher concentrations of these additives in the base oil.

**Table 9.** Variations of the mean wear scar diameter (WSD, mm) and the friction coefficient (an average of the last 10 min) with concentration (wt %) of novel boron based additives.

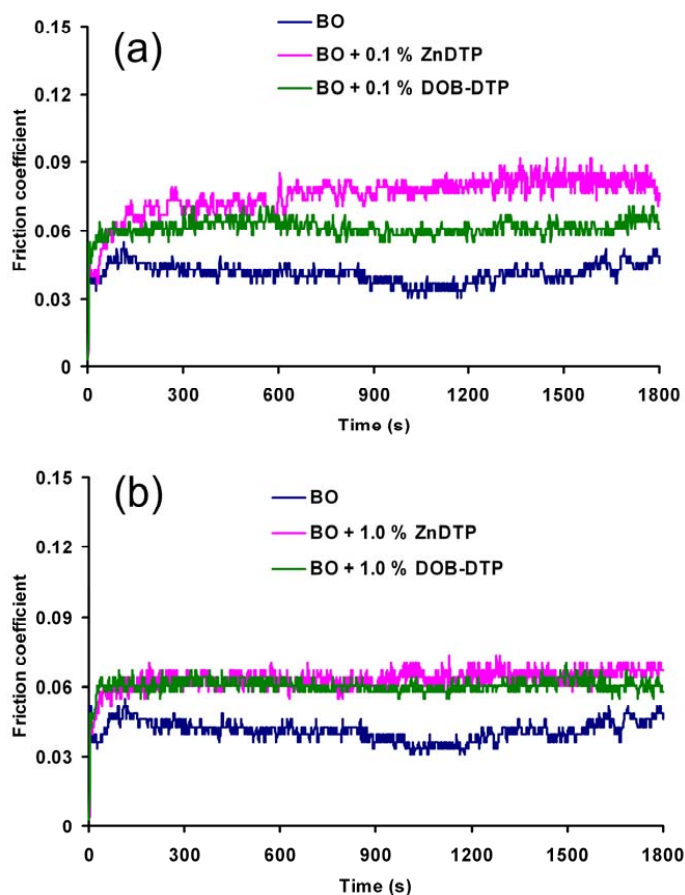
Additive concentration (%)	DOB-EDTP		DDB-EDTP	
	WSD $\pm$ (SD) mm	Friction coefficient $\pm$ (Variation)	WSD $\pm$ (SD) mm	Friction coefficient $\pm$ (Variation)
0	0.602 (0.012)	0.042 (0.006)	0.602 (0.012)	0.042 (0.006)
0.1	0.504 (0.014)	0.057 (0.004)	0.472 (0.014)	0.058 (0.005)
0.2	0.483 (0.008)	0.056 (0.006)	0.450 (0.011)	0.059 (0.004)
0.4	0.456 (0.013)	0.054 (0.006)	0.445 (0.010)	0.063 (0.007)
0.6	0.493 (0.010)	0.051 (0.006)	0.455 (0.003)	0.063 (0.006)
0.8	0.503 (0.012)	0.052 (0.005)	0.474 (0.014)	0.061 (0.005)
1.0	0.494 (0.012)	0.055 (0.005)	0.463 (0.016)	0.069 (0.006)

### 2.5.2 Friction Performance

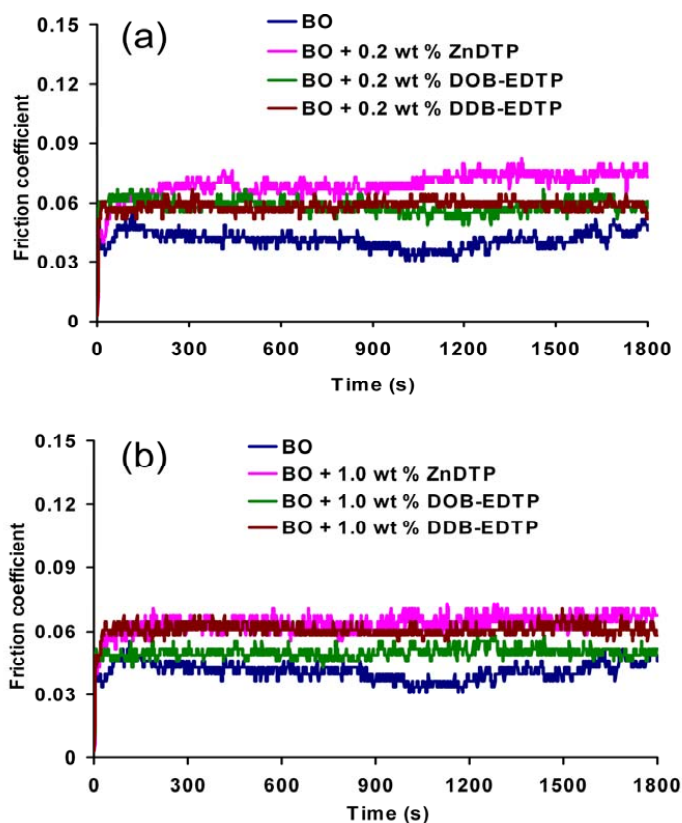
The friction performance of these boron compounds was also evaluated in comparison with ZnDTP using the same concentrations and tribological test conditions as described above.

Stability of the friction coefficient of these additives was studied as a function of time. The comparative results obtained for boron compounds and ZnDTP are shown in Figures 28 and 29. It is clear that when the base oil is formulated with either boron compounds or ZnDTP, the friction coefficient of the lubricant increases compared with those for the oil without these additives. Though the friction coefficient of the base oil is lower as compared to the oil with additives, it is not stable and varies considerably with time of the test. The friction coefficient of the base oil containing ZnDTP at low concentrations tested (0.1 - 0.2 wt %) increases slowly with time of the experiment (30 min, see Figs. 28 a and 29 a.) The friction coefficient is comparatively stable at higher concentrations (1.0 wt %) of ZnDTP (Fig. 19 b).

On the other hand, the friction coefficient of the oil containing boron compounds does not vary much with time at both low (0.1, 0.2 wt %) and higher (1.0 wt %) concentrations of these additives (Figs. 28 and 29). These test results suggest high stability of the tribofilms formed by boron compounds at both low and high concentrations.



**Figure 28.** Variations of the friction coefficient with time (s) for the base oil (BO), BO with ZnDTP and BO with DOB-DTP. (a) 0.1 wt % and (a) 1.0 wt % of the additives. Top (pink): ZnDTP, middle (green): DOB-DTP, bottom (blue): BO.

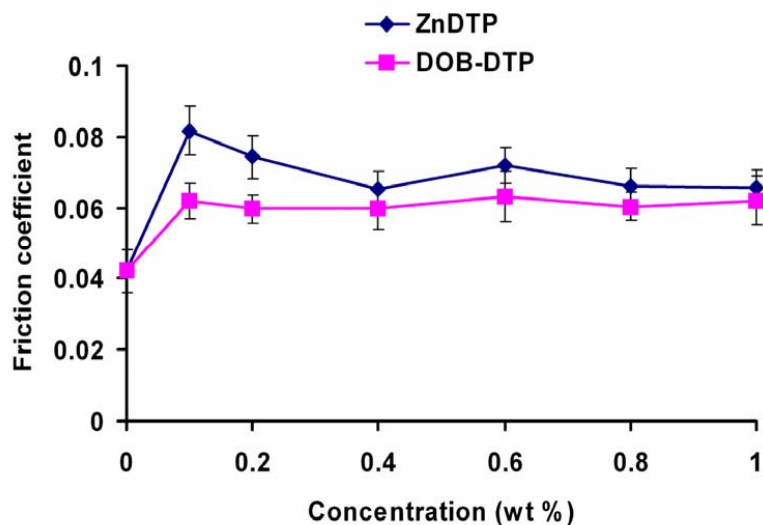


**Figure 29.** Variations of the friction coefficient with time (s) for the base oil (BO), base oil with ZnDTP, base oil with DOB-EDTP and base oil with DDB-EDTP. (a) 0.2 wt % and (B) 1.0 wt % of the additives. Top (pink): ZnDTP, upper middle (maroon): DDB-EDTP, lower middle (green): DOB-EDTP, bottom (blue): BO.

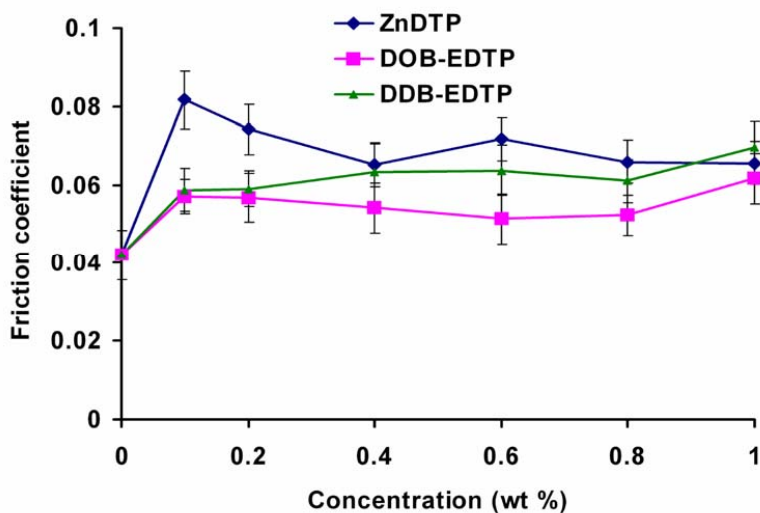
Variation of the friction coefficient with concentration (wt %) of these additives in the base oil is shown in Figures 30 and 31 (see Tables 8 and 9).

The coefficient of friction remains stable for the oil with boron compounds in the whole concentration range tested, 0.1-1.0 wt %. For ZnDTP, variations of the friction coefficient in the same concentration range of the additive are substantially larger. An increase in the coefficient of friction upon admixture of additives in the base oil is caused by the formation of tribofilms as a result of tribochemical reactions of the additives with steel surfaces during the wear process.

A comparison of the friction properties of boron compounds with ZnDTP reveals that boron compounds provide lower and more stable friction in a wider range of additive concentration in the base oil compared with ZnDTP.



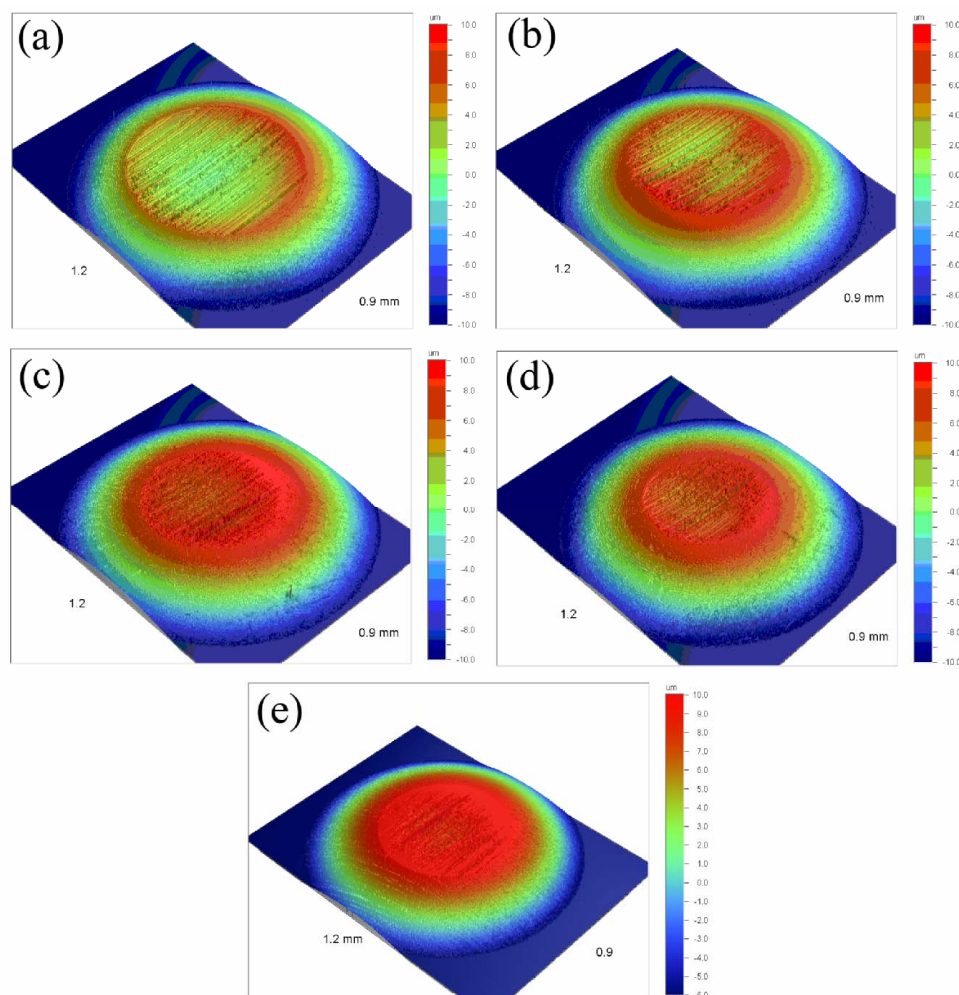
**Figure 30.** Variations of the friction coefficient with concentration (wt %) of additives (an average over the last 10 min). Top (blue): ZnDTP, bottom (red) DOB-DTP.



**Figure 31.** Variations of the friction coefficient with concentration (wt %) of additives (an average over the last 10 min). Top (blue): ZnDTP, Middle (green) DDB-EDTP; Bottom (pink): DOB-EDTP.

## 2.6 Surface Analysis

The surface topography of the wear scars on steel balls after tribological testing was studied by an optical profiler. Figure 32 shows 3D images of the worn surfaces lubricated with the base oil only and the base oil containing 1 wt % of either boron compounds or ZnDTP additives. These images clearly indicate the effect of additives incorporation in the base oil: The ball lubricated with the base oil only acquired significantly bigger wear scars (Fig. 32 a) as compared to the base oil containing ZnDTP (Fig. 32 b). The WSDs of the base oil containing DOB-EDTP (Fig. 32 c), DDB-EDTP (Fig. 32 d) or DOB-DTP (Fig. 32 e) are considerably smaller than these for the base oil only (Fig. 32 a) or the base oil containing ZnDTP (Fig. 32 b).

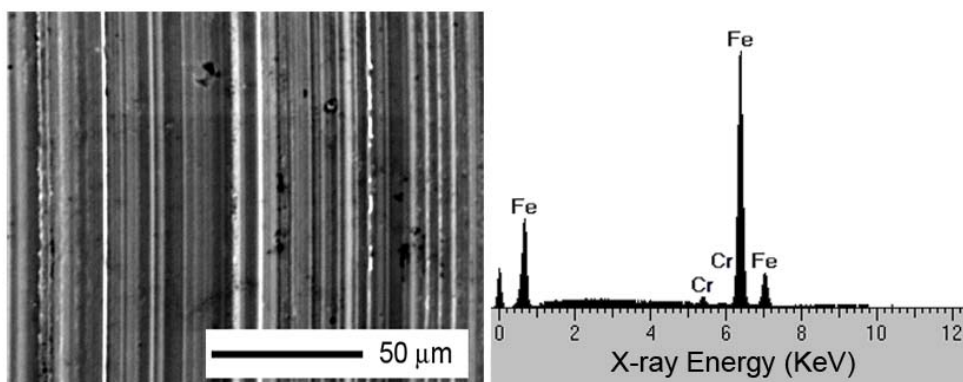


**Figure 32.** 3D images of worn ball surfaces lubricated with (a) base oil (b) base oil with 1.0 wt % ZnDTP, (c) base oil with 1.0 wt % DOB-EDTP, (d) base oil with 1.0 wt % DDB-EDTP and base oil with 1 wt % DOB-DTP.

Figures 33-38 show results of the surface analysis obtained using Scanning Electron Microscopic/Energy Dispersive X-ray Spectroscopy (SEM/EDS) techniques.

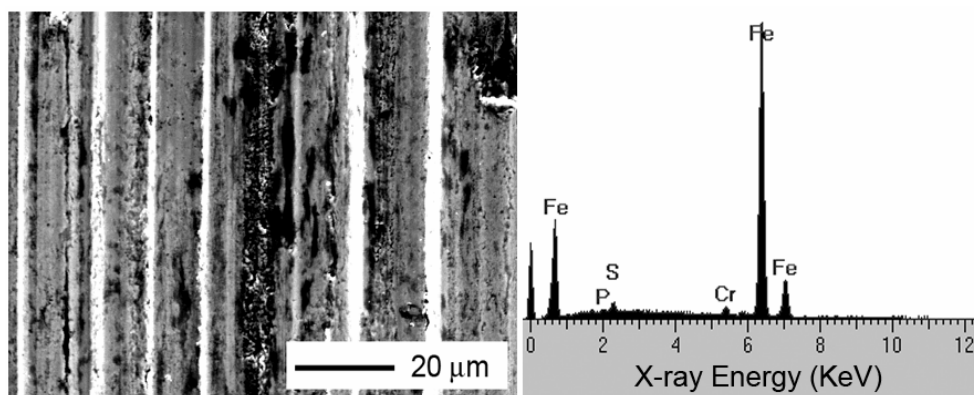
EDS spectra were obtained from the whole area of the SEM image showing the worn surfaces of balls lubricated with the base oil only (Fig. 33 left) and the base oil containing 1.0 wt % of the additives studied (Figs. 34 – 38, left images). In these figures one can compare both the morphology and a composition of the tribofilms formed from these additives.





**Figure 33.** SEM micrograph of the wear scar and the corresponding EDS spectrum of the worn surface of the steel ball lubricated with base oil alone. EDS spectrum was obtained from the whole area shown in the SEM micrograph.

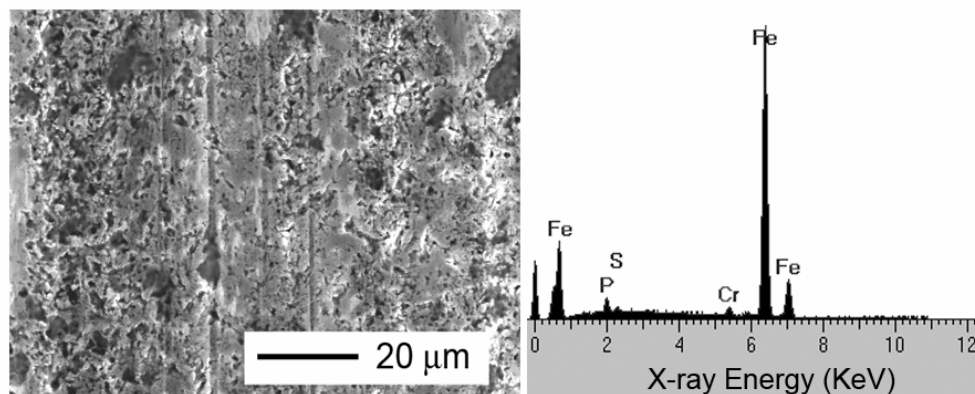
Figure 33 shows the SEM micrograph and the corresponding EDS analysis of the worn ball surface lubricated with the base oil alone. This micrograph shows wide grooves, which are the indication of a severe wear. When the additives were mixed into the base oil, the wear process slowed down. The surfaces are smoother (see Figs. 34 - 38) as compared to the surfaces lubricated with the mineral oil.



**Figure 34.** SEM micrograph of the wear scar and the corresponding EDS spectrum of the worn surface of the steel ball lubricated with base oil with 1.0 wt % ZnDTP. EDS spectrum was obtained from the whole area shown in the SEM micrograph.

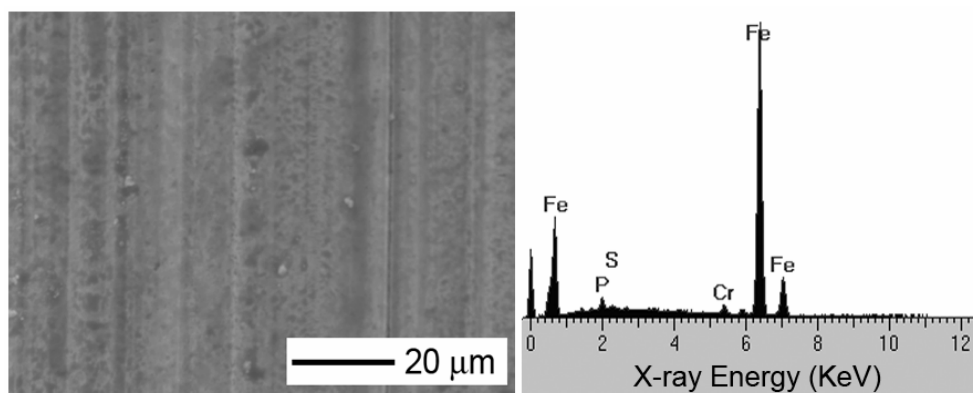
Let us compare the surfaces lubricated by the base oil containing ZnDTP and the novel boron compounds. The steel surfaces lubricated with the oil with the boron compounds appear to be

smoother than those lubricated with oil containing ZnDTP. The corrosive action of sulphur present in twice larger quantities in ZnDTP compared to the B-DTP additives causes rougher worn steel surfaces.

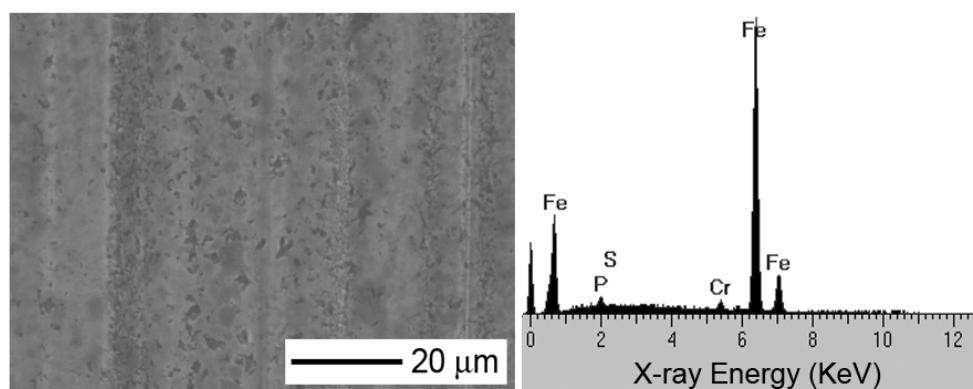


**Figure 35.** SEM micrograph of the wear scar and the corresponding EDS spectrum of the worn surface of the steel ball lubricated with base oil with 1.0 wt % DOB-DTP. EDS spectrum was obtained from the whole area shown in the SEM micrograph.

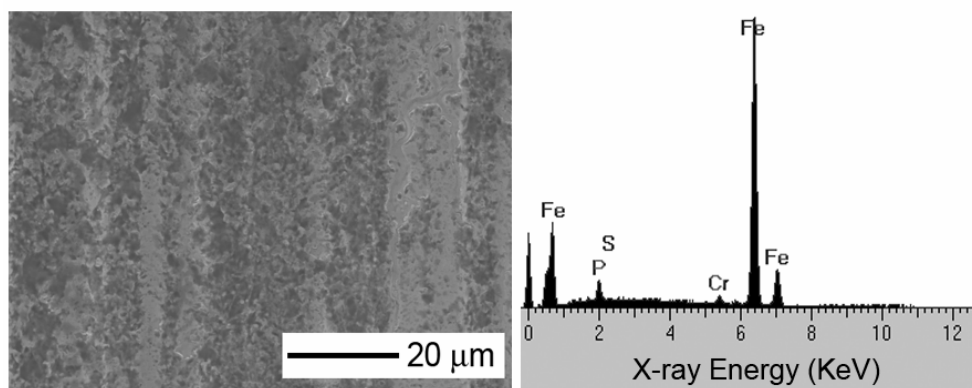
The EDS analysis of the worn surfaces reveals deposition of phosphorus and sulphur for all additives studied. In the case of boron compounds, boron was not detected on the surfaces, probably, because of a low sensitivity of the method to boron. Sulphur is the dominant element in the surface deposits from ZnDTP. At the same time, phosphorus, which dominates in deposits formed from boron compounds at the worn steel surfaces. It is quite clear that boron in the boron compounds (in combination with sulphur) acts as a good antiwear element. Thus, the corrosive action of sulphur with iron is, probably, suppressed by boron and resulting in less worn surfaces for B-DTPs compared with ZnDTP. Probably, the excess reactivity of sulphur with iron is inhibited by boron, but this hypothesis has to be tested further by additional surface sensitive experiments, such as XPS and TOF-SIMS.



**Figure 36.** SEM micrograph of the wear scar and the corresponding EDS spectrum of the worn surface of the steel ball lubricated with base oil with 1.0 wt % DPB-EDTP. EDS spectrum was obtained from the whole area shown in the SEM micrograph.



**Figure 37.** SEM micrograph of the wear scar and the corresponding EDS spectrum of the worn surface of the steel ball lubricated with base oil with 1.0 wt % DOB-EDTP. EDS spectrum was obtained from the whole area shown in the SEM micrograph.



**Figure 38.** SEM micrograph of the wear scar and the corresponding EDS spectrum of the worn surface of the steel ball lubricated with base oil with 1.0 wt % DDB-EDTP. EDS spectrum was obtained from the whole area shown in the SEM micrograph.

## Conclusions

Some boron derivatives of dialkyldithiophosphates with long primary alkyl groups (pentyl, octyl and decyl) were successfully synthesized using multi-steps reactions. The resulting products were purified and characterized by the elemental analysis, FT-IR and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR spectroscopy.

The thermal behaviour of these novel compounds was characterized by TG/DTG, DTA, and QMS analyses. These boron derivatives of dialkyldithiophosphates have shown good thermal stability under the conditions used in this study. Dihydrogen sulphide and olefins, which are typical products of decomposition of dialkyldithiophosphates complexes of metals, were formed upon heating of the compounds.

The tribological properties of these compounds admixed in the mineral oil were evaluated in comparison with *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) in a four ball tribometer. All these boron compounds have shown significantly better antiwear and friction properties at lower concentrations (0.2 – 0.4 wt %) compared with ZnDTP at condition of the tribological testing in this study. The friction coefficient was stable over time for the boron compounds at all concentrations used in this study. Predominantly phosphorus and less sulphur were detected by SEM/EDS analysis on the worn steel surfaces in the test with novel boron compounds, while for the ZnDTP sulphur was the dominant element in the films formed by on the steel surfaces.

These novel boron compounds are ashless with reduced amounts of sulphur and phosphorus. In addition, they have excellent tribological properties, high thermal stability, good miscibility with oils and positive environmental issues which make them an attractive alternative to ZnDTP.

### **Future Work**

The current trend in automotive industry is to replace heavy ferrous materials to lightweight non-ferrous materials in various components such as engines and other mechanical transmissions. As the commercial lubricants currently available are unable to form adequate tribofilms on non-ferrous materials, the risk is then a lack of suitable lubricants that can provide proper and efficient lubrication of these new materials.

A possible solution of this technical problem is to invoke boron based ionic liquids (IL) as lubricant additives for non-ferrous materials. IL may form stable tribofilms on non-ferrous materials, because of their unique chemical properties. IL have a number of important characteristics: negligibly low volatility, low flammability, high thermal and chemical stability, a low melting point and a good miscibility with both organic solvents and base oils. Recently, it was found that IL can act as versatile lubricant additives for different non-ferrous sliding pairs of surfaces and exhibit excellent friction-reducing and anti-wear performances, as well as a high load-carrying capacity. Molecules of IL have an intrinsic electric dipole moment and, therefore, they can be easily adsorbed on sliding surfaces in tribological contacts operating in a boundary or mixed lubrication regime. Subsequently, an effective boundary film would form reducing friction and wear. These properties are highly desirable in mechanical systems.

There is an ample future opportunity for developing of IL as additives in lubricants for non-ferrous materials. The key idea of the future work is, thus, to synthesize, characterize and tribologically optimize novel environmentally friendly IL additives for various industrial applications. We also aim at investigating of their tribochemical reaction mechanisms with solid-state NMR spectroscopy and various surface sensitive techniques.

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# Paper I

Synthesis, Physicochemical and Tribological Characterization of  
S-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate

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# Synthesis, Physicochemical, and Tribological Characterization of *S*-Di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate

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**ABSTRACT** Dialkyldithiophosphates (DTPs) of zinc(II), copper(II), and other metals have been extensively used as multifunctional additives in lubricants to control friction and reduce wear in mechanical systems. Among these DTP compounds, zinc dialkyldithiophosphates (ZnDTPs) are the most common additives extensively used for more than 60 years. These additives form a protective film on steel surfaces and, thus, control friction and reduce wear. However, ZnDTPs contain zinc and large amounts of phosphorus and sulfur, which impair the environment, both directly and indirectly, by adversely affecting the performance of catalytic converters of various automobiles. For this reason, environmental legislation imposes limitations on concentrations of phosphorus, sulfur, and zinc in the lubricants. In this work, we report on zinc-free *S*-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP) lubricant additive with amount of phosphorus and sulfur reduced by half in a molecule as compared with ZnDTPs. DOB-DTP was synthesized by a reaction in two steps under inert nitrogen atmosphere. The final product, a viscous liquid, was characterized by the elemental analysis, FT-IR, multinuclear <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>11</sup>B NMR spectroscopy and thermal analyses. Tribological performance of a mineral oil with this new additive was evaluated in comparison with *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) (ZnDTP) using a four-ball tribometer. The surface morphology and the elemental composition of the tribofilms were characterized using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS). The results show that DOB-DTP has a considerably better antiwear performance and higher stability of the coefficient of friction with time as compared with ZnDTP. Both phosphorus and sulfur were detected by the EDS on the worn steel surfaces at all concentrations of additives in the base oil.

**KEYWORDS:** *S*-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate • ZnDTP • lubricant additives • tribological characterization • thermal analysis • SEM/EDS

## 1. INTRODUCTION

Boron, sulfur, and phosphorus-containing additives are being used in lubricating oil formulations because of their excellent antiwear, extreme pressure, friction reducing, antioxidant, and corrosion resistance properties (1). These additives react with metal surfaces forming tribolayers, which provide low friction, low wear, and resist corrosion. The reactivity of these additives depends on their structure and concentration, applied load, sliding speed, contact temperature, time of the interaction, and surface materials.

Zinc dialkyldithiophosphates (ZnDTPs) are arguably the most successful lubricant additives ever invented. Since their introduction in the 1940s, ZnDTPs have been in continuous use over several decades and still being employed as excellent lubricant additives in practical applications (2–6). Over the past decade, demanding efforts were made by both companies developing new additives and researchers to replace ZnDTPs, which cause environmental pollution by poisoning exhaust catalysts (7). In addition to environmental

pollution, its health hazards include eye irritation, allergic contact dermatitis, and mutagenicity (8, 9). In a recent review on the history and action mechanism of ZnDTPs with metal surfaces (10), it is concluded that it has been so far proven impossible to identify any reasonably cost-effective compound having comparable antiwear properties to ZnDTPs lubricant additives. A survey of literature reveals that dialkyldithiophosphate esters (11), dialkyldithiophosphates of different metals such as molybdenum (12), cadmium (13), copper (14), titanium (15), gadolinium (16), iron, antimony, and other metals (17–19) have been introduced and used as multifunctional additives in lubricants. To the best of our knowledge, there are no open publications on boron dialkyldithiophosphates as additives in lubricants. One of the possible reason could be lack of suitable methods of synthesis for B-DTPs. Compounds with boron–sulfur bonds are reactive and they are usually used as intermediates for the synthesis of organometallic and organometalloid sulfur compounds (20, 21). However, the reactivity of such compounds toward metals and metalloids would help in reducing wear by the reaction of boron and sulfur with metal and metalloid surfaces via formation of superhard protective layers.

On the other hand, boron-containing compounds have been already widely studied as corrosion inhibitors, antioxidants, friction modifiers, and effective antiwear additives

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either dissolved in oil or as an insoluble and inorganic borate salts dispersed in oil in the nanoparticulate form (22–27). Tribofilms from oils containing boron based additives were recognized already in 1960s. However, it is only within the past decade that these compounds have received a proper attention. Boron-containing compounds may be an attractive alternative to commercial additives, with a similar antiwear performance in the absence (or a considerable reduction) of both phosphorus and sulfur in a lubricant. It is already well-understood that boron compounds are capable of forming glassy structures in a manner similar to ZnDTP but with different glass transition temperatures (28). It is also known that crystalline or amorphous boron, boron nitride and metal boride are very hard materials. Microindentation measurements on rhenium diboride ( $\text{ReB}_2$ ) indicated an average hardness of 48 GPa under the applied load of 0.49 N and scratch marks were left on a diamond surface by particles of this material confirming its superhard nature (29). Iron boride ( $\text{Fe}_2\text{B}$ ) can be formed on steel surfaces thus improving the hardness of machine elements made of steel (30, 31). The hardness of crystalline boron is 30 GPa and amorphous boron thin film can also have hardness approaching that of crystalline boron (32). A high hardness of surfaces could then be provided by boron or metal boride coatings. It would provide an additional benefit for antiwear tribofilm performances by protecting metal surfaces from damage during sliding in tribological contacts. In addition, in a moisture-containing environment, the surface oxide of boron ( $\text{B}_2\text{O}_3$ ) is known to react with water forming boric acid ( $\text{H}_3\text{BO}_3$ ), which acts as a solid lubricant. The lubricity of boric acid has been attributed to its tendency to form a triclinic crystal structure made up of atomic layers parallel to the basal plane. In each layer, the B, O, and H atoms are closely packed and bonded to each other with covalent bonds, whereas the layers are held together with weak van der Waals forces. The latter facilitates the layers to easily slide with respect to each other that provides lubricity in the system (33).

The combined effect of different borate and ZnDTP additives on tribological performance has been studied extensively during the past few years. Combinations of potassium triborate with ZnDTP (34), calcium borate with ZnDTP (35, 36), and a boric additive with tricresyl phosphate (TCP) and ZnDTP additives (37) have exhibited improved antiwear properties compared with commercial ZnDTPs alone. These results suggest that borate additives can be a possible partial replacement of ZnDTPs additives in lubricants.

In this work, we synthesized a novel compound *S*-di-*n*-octoxyboron-*O*,*O*'-di-*n*-octyldithiophosphate (DOB-DTP), with both boron and a dialkyldithiophosphate group bound in a single molecule. It can be expected that such a molecule, i.e., without zinc and with reduced amounts of sulfur and phosphorus, would provide a better tribological and environmental performance when used as the additive in mineral oils. We also report on physicochemical and tribological characterizations of DOB-DTP. Its tribological performance was evaluated in comparison with *O*,*O*'-di-*n*-butyl-dithio-

phosphato-zinc(II), (ZnDTP) at concentrations 0–1.0 wt % in a mineral oil.

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** Phosphorus pentasulphide,  $\text{P}_2\text{S}_5$  (Aldrich, 99 % purity), 1-octanol (Prolabo, 97 % purity), boric acid (Merck, analytical grade), and toluene (Fluka, > 99.7 % purity) were used as received. The commercially available ZnDTP contains a mixture of 85 % *O*,*O*'-di-*iso*-butyl-dithiophosphato-zinc(II) and 15 % *O*,*O*'-di-*n*-octyl-dithiophosphato-zinc(II) (38). In this study, we used ZnDTP (as a reference compound) with the same number of carbon atoms in alkyl chains as in the commercial ZnDTP additive but we selected *O*,*O*'-di-*n*-butyl-dithiophosphato-zinc(II) instead of Zn(II)-*i*BuDTP. *O*,*O*'-Di-*n*-butyl-dithiophosphato-zinc(II) is a viscous liquid at room temperature and it is easily miscible with the base oil used in this study. On the contrary, Zn(II)-*i*BuDTP is a solid at room temperature that makes it difficult to fully dissolve it in the base oil, if the ZnDTP ligand complex with a longer alkyl chain is not used in the same package of additives. *O*,*O*'-Di-*n*-butyl-dithiophosphato-zinc(II) was synthesized using a reported method (39). The purity of the latter ZnDTP and its corresponding potassium salt was checked by  $^{31}\text{P}$  NMR for ZnDTP (145.70 MHz,  $\delta$ : 100.29 ppm (40) and  $^{31}\text{P}$  NMR for potassium salt (145.70 MHz, ethanol,  $\delta$ ) 112.72 ppm (see the Supporting Information).

**2.2. Synthesis of *S*-Di-*n*-octoxyboron-*O*,*O*'-di-*n*-octyldithiophosphate (DOB-DTP). Step 1.** Boric acid (10 mmol) and 1-octanol (30 mmol) were added to a flask with toluene (50 mL), equipped with a magnetic stirrer, a condenser, and a water separator. The reaction mixture was refluxed for 3 h. Water formed during the reaction was removed continuously using a separator. Toluene was rotary evaporated and a product was distilled under reduced pressure (0.2 mmHg) to remove toluene and residual octanol. A colorless liquid product of trioctyl borate (I) was obtained in 88 % yield. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2927, 2856  $\nu(\text{C}-\text{H}$ , stretching); 1417  $\nu(\text{CH}_2$  bending); 1337  $\nu(\text{B}-\text{O}$  strong).  $^{11}\text{B}$  NMR (115 MHz, toluene,  $\delta$ ) 16.56 ppm (see SI).

**Step 2.** Phosphorus pentasulphide (11.28 g, 10 mmol) and trioctyl borate (45.15 g, 40 mmol) were added together with toluene to a flask equipped with a magnetic stirrer and a condenser (prebaked on vacuum to exclude any moisture). The reaction mixture was refluxed for 3 h under nitrogen atmosphere. After cooling the precipitate was filtered, the filtrate was rotary evaporated to remove toluene and distilled at 0.2 mmHg, 120 °C for 30 min. A transparent liquid product (II) was obtained in 52 % yield (7.30 g). Anal. Calcd. for  $\text{C}_{32}\text{H}_{68}\text{O}_4\text{P}_2\text{S}_2\text{B}$  (MW 622.76 g/mol): C, 61.71; H, 11.0; B, 1.73. Found: C, 64.7; H, 11.7; B, 2.2. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2927, 2856  $\nu(\text{C}-\text{H}$ , stretching); 1417  $\nu(\text{CH}_2$  bending); 1336  $\nu(\text{B}-\text{O}$ , strong); 992  $\nu(\text{P}-\text{O}-\text{C}$ , broad); 666  $\nu(\text{P}=\text{S}$ , medium); 531  $\nu(\text{P}-\text{S}$ , medium).  $^1\text{H}$  NMR (359.93 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.88 (12H, t,  $^3J_{\text{HH}} = 6.7$  Hz,  $\text{CH}_3$ ); 1.26–1.34 (40H, m,  $-\text{CH}_2$ -chain); 1.48–1.60 (4H, m,  $\text{CH}_2\text{CH}_2\text{OB}$ ); 1.69–1.76 (4H, m,  $\text{CH}_2\text{CH}_2\text{OP}$ ); 3.76 (4H, t,  $^3J_{\text{HH}} = 6.6$  Hz,  $\text{CH}_2\text{OB}$ ); 4.15 (4H, dt,  $^3J_{\text{HP}} = 9.47$ ,  $^3J_{\text{HH}} = 6.56$ ,  $\text{CH}_2\text{OP}$ ).  $^{13}\text{C}$  NMR (90.51 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 14.26 (4  $\times$   $\text{CH}_3$ ), 22.84 (4  $\times$   $\text{CH}_2\text{CH}_3$ ), 26.02, 29.34, 29.51, 30.14, 32.02 (20  $\times$   $-\text{CH}_2$ -chain), 63.41 (2  $\times$   $\text{CH}_2\text{OB}$ ), 68.62 (2  $\times$   $\text{CH}_2\text{OP}$ ) ppm.  $^{31}\text{P}$  NMR (145.70 MHz, toluene,  $\delta$ ): 84.58 ppm.  $^{11}\text{B}$  NMR (115.48 MHz, toluene,  $\delta$ ): 16.36 ppm (see the Supporting Information).

**2.3. Spectroscopic Characterization.** FT-IR spectra were recorded on a Perkin-Elmer 2000 spectrometer in the range 4000–370  $\text{cm}^{-1}$ . Sampling was performed by placing a droplet of a compound onto a KBr pellet. Multinuclear NMR spectra were recorded on a Varian/Chemagnetics InfinityPlus CMX-360 ( $B = 8.46$  T) spectrometer in  $\text{CDCl}_3$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or in toluene ( $^{31}\text{P}$ ,  $^{11}\text{B}$ ) using TMS as an internal reference for  $^1\text{H}$  (0 ppm), the 77.2 ppm resonance peak of  $\text{CDCl}_3$  for  $^{13}\text{C}$ ,  $\text{Et}_2\text{O} \cdot \text{BF}_3$  as an external

**Table 1. Physicochemical Properties of the Mineral Base Oil Used in This Study**

density (g mL <sup>-1</sup> )	0.8135
viscosity (m Pa s) at 40 °C	17.5
viscosity (m Pa s) at 100 °C	4.9
carbon (%)	86.0 ± 0.7
hydrogen (%)	14.5 ± 0.5

reference (0 ppm) for <sup>11</sup>B and H<sub>3</sub>PO<sub>4</sub> (85%) as an external reference (0 ppm) for <sup>31</sup>P.

**2.4. Thermal Analysis.** Thermal analysis of the synthesized compound was performed by Netzsch STA 409 instrument equipped with simultaneous thermogravimetric (TG), differential thermal analysis (DTA) coupled with a quadrupole mass spectrometer (QMS) at a rate of 20 °C/min and with argon flow rate of 100 mL/min. The sensitivity of this STA Instruments is ±1 μg.

**2.5. Tribological Characterization.** The additives were mixed with mineral oil at fixed weight (%) concentrations of 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0% using an analytical balance. The physicochemical properties and the elemental analysis of the base oil used in this study are given in Table 1. The balls used in the tests were 12.7 mm diameter and made of AISI 52100 steel with a composition of C, 0.95–1.10%; Si, 0.15–0.30%; Mn, <0.25%; P, <0.03%; S, <0.025%; Cr, 1.30–1.60%, and with a hardness HRC 60–67.

The friction and antiwear properties of these compounds as additives in the base oil were evaluated with a four ball Tribometer at a rotating speed of 1450 rpm, test duration time of 30 min, load 392 N, and at room temperature (294 K). Wear scar diameters and friction coefficients were measured at additive concentrations in the range of 0–1.0 wt %. An optical profiler (WYCO NT 1100) was used to determine the wear scar diameters of the three stationary balls. Then a mean value was calculated and reported here as the wear scar diameter (WSD). Before each test, the holder for the balls was washed with petroleum ether and the balls were cleaned ultrasonically in petroleum ether and thoroughly air-dried.

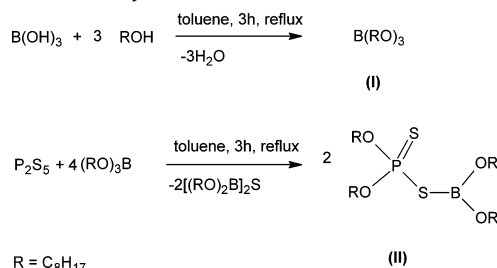
**2.6. Surface Analysis.** Philips XL 30 scanning electron microscope (SEM) equipped with LaB<sub>6</sub> emission source was used for surface studies. A link ISIS Ge energy dispersive X-ray detector (EDS) attached to the SEM was used to additionally probe the composition of the entire tribofilms on the ball surfaces. Prior to the analysis, the balls were cleaned ultrasonically for 5 min with petroleum ether, in order to eliminate the residual lubricant.

### 3. RESULTS AND DISCUSSION

**3.1. Syntheses and Chemical Analyses.** *S*-Di-*n*-octoxyboron-*O*,*O'*-di-*n*-octyldithiophosphate (DOB-DTP) was synthesized by a reaction in two steps (Scheme 1). In the first step, trioctyl borate (**I**) was synthesized by treating boric acid and octanol. This step was followed by the synthesis of DOB-DTP (**II**) using a reported method (41) by reacting phosphorus pentasulphide (P<sub>2</sub>S<sub>5</sub>) with trioctyl borate in a 1:4 molar ratio. During this reaction, B–O bonds of borate were cleaved and new B–S bonds were formed simultaneously giving rise to the final product (**II**). A semisolid byproduct, [(RO)<sub>2</sub>B]<sub>2</sub>S, formed in the same reaction was removed by filtration.

FTIR, <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>11</sup>B NMR spectroscopy were used to characterize the synthesized compounds. FTIR spectra of compounds **I** and **II** show the characteristic peaks with absorption frequencies of the aliphatic C–H vibrations in the

### Scheme 1. Synthesis of DOB-DTP



alkyl groups of compounds (**I**) and (**II**) in the range of 2856–2956 cm<sup>-1</sup>. Strong bands were observed at 1337 and 1336 cm<sup>-1</sup> for **I** and **II**, respectively, which are attributed to the ν(B–O) band in both these compounds. Strong band at 992 cm<sup>-1</sup> and medium bands at 666 and 531 cm<sup>-1</sup> were observed in the FTIR spectrum of compound **II** only and are assigned to ν(P–OC), ν(P=S), and ν(P–S) bands, respectively. The latter was an additional proof that compound **II** was formed from the intermediate compound **I**.

<sup>31</sup>P NMR of DOB-DTP (**II**) in toluene reveals a singlet at 84.58 ppm that is expected for pure boron *O*,*O'*-dialkyldithiophosphate compounds (41, 42).

<sup>11</sup>B NMR spectra of **I** and **II** were recorded in toluene and the observed chemical shifts are 16.56 and 16.36 ppm respectively, that also is consistent with the presence of the three-coordinated boron in boron *O*,*O'*-dialkyldithiophosphates (42). The boron nucleus in **II** is more shielded (by 0.20 ppm) than in **I**, which is in accord with a formation of a SBO<sub>2</sub> group instead of BO<sub>3</sub>.

**3.2. Thermal Analysis.** Because most tribological contacts operate at elevated temperatures, it is important to study the effect of temperature on the physicochemical properties of the lubricant additives such as thermal stability, weight loss, and the nature of compounds in the course of thermal decomposition. Differential thermal analysis is usually represented as “exothermic” or “endothermic” peaks at elevated temperatures. Generally, exothermic peaks are the result of chemical decomposition or oxidation, which is accompanied by exothermic processes, while endothermic peaks are due to physical processes such as melting, boiling, or other phase transitions of a compound (43). The thermal decomposition temperature of dialkyldithiophosphates of different metal ions is strongly dependent on the type of alkyl groups and molecular structures of these compounds: (i) aryl dialkyldithiophosphates of zinc(II) are more stable than alkyl derivatives of ZnDTPs; (ii) primary alkyls are more stable than secondary alkyls in ZnDTPs. The differential thermal analysis of these compounds have shown that within the primary alkyl groups of ZnDTP, the hydrogen atom bound to a β-carbon atom of the *n*-alkyl group is more stable than those in the secondary alkyl groups of ZnDTP (44, 45). Therefore, the formation of olefins may occur only at relatively high temperatures.

As a result of thermal decomposition of DOB-DTP, two categories of decomposition products were obtained, both

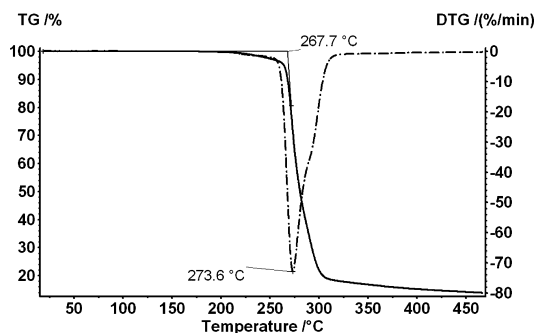


FIGURE 1. TG/DTG curves of DOB-DTP at a heating rate of 20 °C/min and argon flow rate of 100 mL/min.

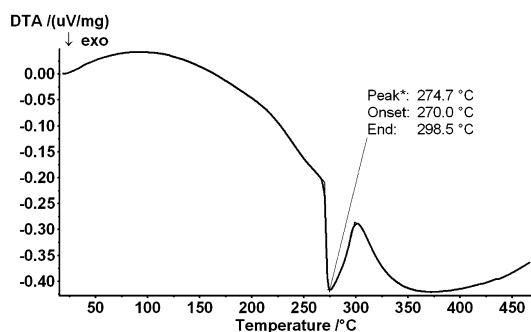


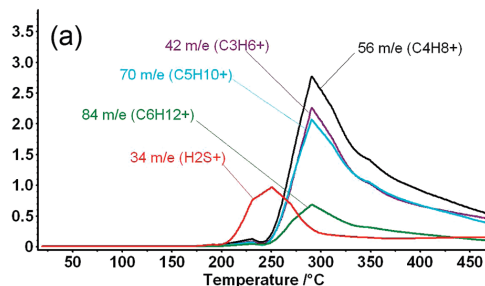
FIGURE 2. DTA curve of DOB-DTP at a heating rate of 20 °C/min and argon flow rate of 100 mL/min.

solid and volatile species. The residual product with a melting point above 500 °C was solid material. Because 200 mg of the liquid sample was used for thermal analysis, the amount of solid residue was not enough to further analyze it. The volatile products were additionally investigated by quadrupole mass spectrometer attached to the thermal analysis instrument.

Thermogravimetric/derivative thermogravimetric (TG/DTG) curves obtained for DOB-DTP are shown in Figure 1. The thermal decomposition of DOB-DTP involves only one major step, the onset of which is at 267.7 °C. This temperature indicates the complete decomposition of the molecule, which is initiated, most probably, with the breakage of the B–S bond and followed by the decomposition of *n*-octyl chains. The total weight loss during this test is 86 wt %, so much of the compound is decomposed into volatile products, whereas 14 wt % remains as a solid residue. The DTG curve represents the highest rate of the weight loss (75 %/min) at 273.6 °C. The TG and DTG analyses revealed that both the decomposition and the weight loss of this compound occur in one single step.

Differential thermal analysis (DTA) curve of DOB-DTP is shown in Figure 2. There is only one exothermic peak, representing the thermal decomposition of the compound. The exothermic peak appears in the temperature range 274–298 °C with a midpoint at 270 °C. This peak is in accord with the TG/DTG curves as discussed above. DOB-

Ion Current \*10<sup>-9</sup> /A



Ion Current \*10<sup>-9</sup> /A

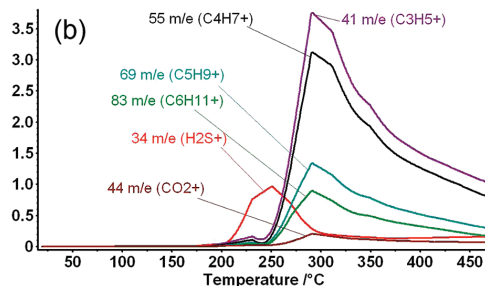


FIGURE 3. QMS profiles of DOB-DTP at a heating rate of 20 °C/min and argon flow rate of 100 mL/min. (a) Even number molecular weight fragments; (b) odd number molecular weight fragments.

DTP is almost completely decomposed into volatile products in this temperature range.

The formation of volatile products as a function of temperature under constant flow of argon gas was analyzed by QMS. Different compounds were evolved in the 20–500 °C temperature range. Evolution of some selected products by decomposition of DOB-DTP is shown in figure 3. The main volatile decomposition products of dialkyl dithiophosphates are dihydrogen sulphide and olefins (46). The type of olefins formed depends on the nature of an alkyl group attached to the dithiophosphate group. For DOB-DTP the formation of dihydrogen sulphide ( $\text{H}_2\text{S}^+$ ) with  $m/e = 34$  was observed when the temperature exceeded 200 °C. Olefin cations with different number of carbons are formed when the parent octyl chains break down at different positions. Their relative intensities are given in comparison with  $\text{H}_2\text{S}^+$  (see Figure 3). Relative intensities of fragments with odd number of carbons in olefin chains (Figure 3b) are higher than their corresponding species with even number of carbon atoms (Figure 3a). A propenyl cation ( $\text{C}_3\text{H}_5^+$ ) with  $m/e = 41$  and a butenyl cation ( $\text{C}_4\text{H}_7^+$ ) with  $m/e = 55$  have similar evolution patterns and they are the principle components in the mixture of volatile products of decomposition of DOB-DTP. The decomposition products with higher molecular weights have smaller relative intensities compared to these of both propenyl and butenyl cations.

**3.3. Tribological Characterization.** It is known that the antiwear ability of a specific additive depends on its concentration in the base oil. Figure 4 shows variations



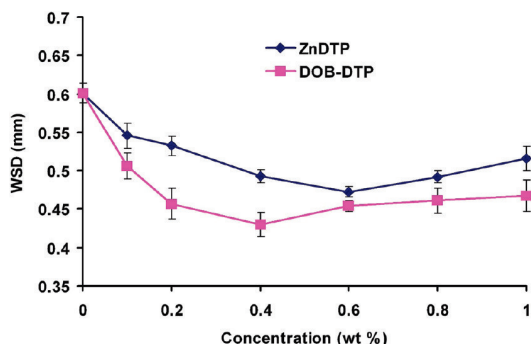


FIGURE 4. Variations of the wear scar diameter (mm) on the lower steel balls with concentration (wt %) of additives under 392 N load for 30 min at room temperature. Top (blue), ZnDTP; bottom (pink), DOB-DTP.

of the wear scar diameter (WSD) measured on steel balls lubricated with the mineral base oil containing either DOB-DTP or ZnDTP additives at different concentrations.

It was found that both DOB-DTP and ZnDTP are prone to reduce wear as measured here via mean wear scar diameters on the steel balls, when these additives were admixed into the mineral oil even at very small concentrations. In case of DOB-DTP, wear scar diameter decreases up to an additive concentration of 0.4 wt %. Then, WSD increases slightly with an increase of concentration of DOB-DTP. A similar trend was also found for ZnDTP. WSD decreases up to a 0.6 wt % concentration of this additive and then increases with the following increase of concentration of ZnDTP in the base oil. Thus, the optimum concentrations for the wear reducing ability of these additives in the base oil in the steel–steel contact under 392 N load during 30 min at room temperature were 0.4 and 0.6 wt % for DOB-DTP and ZnDTP additives, respectively.

We suggest that the concentration dependence of the wear reducing ability of the additives can be explained by their affinities to and interactions with steel surfaces. More reactive additives are prone to reduce wear even at low concentrations by forming protective tribofilms on the contacting interfaces. An excess of sulfur in the lubricant causes a chemical corrosion of steel surfaces (47, 48), which limits the antiwear performance of S-based additives at higher concentrations in the base oil. A comparative analysis of the antiwear ability of an additive as a function of its concentration in the mineral base oil reveals that DOB-DTP forms a stable tribofilm even at a very low concentration (0.1 wt %). Moreover, for this additive at concentrations 0.4–1.0 wt %, WSD increases by only 0.037 mm, i.e., 8.5% (see Figure 4 and Table 2). On the contrary, the wear scar diameter is considerably larger for ZnDTP at concentrations higher than 0.6 wt % in the base oil. Also, WSD increases sharply when concentration of ZnDTP is increased from 0.6 to 1.0 wt %.

There might be two reasons for the outstanding antiwear performance of the novel DOB-DTP additive. First, DOB-DTP contains only two sulfur atoms, whereas ZnDTP contains

Table 2. Variations of the Wear Scar Diameter (mm) and the Friction Coefficient (an average over last 10 min of the test) with Concentration (wt %) of Additives under 392 N load for 30 min at Room Temperature

additive concentration (wt %)	DOB-DTP		ZnDTP	
	WSD $\pm$ (SD) (mm)	friction coefficient	WSD $\pm$ (SD) (mm)	friction coefficient
0	0.602 (0.012)	0.042 (0.006)	0.602 (0.012)	0.042 (0.006)
0.1	0.506 (0.017)	0.062 (0.005)	0.546 (0.017)	0.082 (0.007)
0.2	0.457 (0.020)	0.060 (0.004)	0.533 (0.013)	0.074 (0.006)
0.4	0.430 (0.016)	0.060 (0.006)	0.493 (0.008)	0.065 (0.005)
0.6	0.454 (0.007)	0.063 (0.007)	0.473 (0.007)	0.072 (0.005)
0.8	0.461 (0.016)	0.060 (0.004)	0.492 (0.008)	0.066 (0.005)
1.0	0.467 (0.020)	0.062 (0.007)	0.516 (0.016)	0.066 (0.005)

four sulfur atoms in the molecule. As mentioned above, an excess of sulfur in an additive or a base oil may cause chemical corrosion of steel surfaces. Second, DOB-DTP contains the alkyl borate group in the molecule that enhances the antiwear ability and inhibits corrosive actions of sulfur even at higher concentrations of this additive in the base oil. In this case, the corrosive action of sulfur and antiwear performance of boron occur simultaneously. This results in a smooth increase in WSDs when concentration is increased (49).

Figure 5 shows variations in the friction coefficient with concentration (wt %) of the two additives in the base oil. It is evident from these measurements that incorporation of either DOB-DTP or ZnDTP additives in the base oil increases the friction coefficient. Even at a very low concentration (0.1 wt %) of each additive in the base oil, the coefficient of friction increases considerably from  $\mu = 0.04$  to ca. 0.06 (for DOB-DTP) or ca. 0.075 (for ZnDTP). The coefficient of friction remains quite stable ( $\mu = 0.060$ – $0.063$ ) for the oil with DOB-DTP in the whole concentration range tested, 0.1–1.0 wt %. Variations in friction coefficient with concentration of ZnDTP from 0.1 to 1.0 wt % are substantially larger,  $\mu = 0.065$ – $0.083$  (see Figure 5 and Table 2). An increase in the coefficient of friction upon admixture of

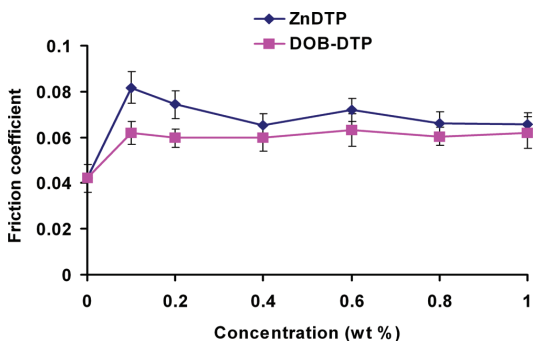


FIGURE 5. Variations of the friction coefficient with concentration (wt %) of additives under a 392 N load for 30 min at room temperature (an average over last 10 min of the test). Top (blue), ZnDTP; bottom (red), DOB-DTP.

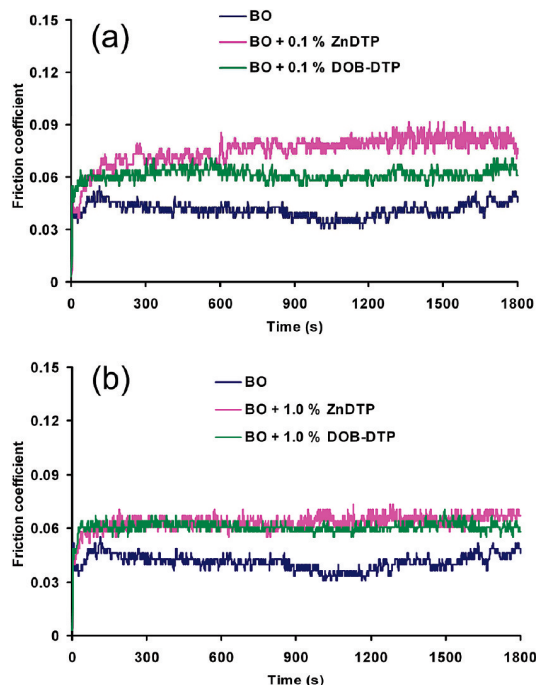


FIGURE 6. Variations of the friction coefficient with time (s) for the base oil (BO), BO with ZnDTP and BO with DOB-DTP. (a) 0.1 wt % of the additives. Top (pink), ZnDTP; middle (green), DOB-DTP; bottom (blue), BO.

additives in the base oil is caused by the formation of stable tribofilms as a result of tribochemical reactions of the additives with steel surfaces during the wear process. It is already known that the tribofilms formed by ZnDTP increase friction coefficient, which is probably due to the higher shear strength of the films formed by ZnDTP (50–52). DOB-DTP also increases friction coefficient but it is stable with time compared to ZnDTP. Here, it is suggested that both DOB-DTP and ZnDTP additives in the base oil at as low concentration as 0.1 wt % do form tribofilms on the steel surfaces.

However, a comparison of the friction properties of these two additives reveals that DOB-DTP provides lower and more stable friction in a wider range of additive concentrations in the base oil compared with ZnDTP.

Thus, both antiwear and friction properties of DOB-DTP are considerably better than those of the commercial additive, ZnDTP (compare data in Figures 4 and 5 and Table 2). We suggest that these properties depend strongly on a difference in compositions of the tribofilms formed on the steel surfaces, when either DOB-DTP or ZnDTP were tested. We will discuss these issues later in this article.

A variation of the friction coefficient with time is shown in plots a and b in Figure 6 for the base oil only and oil containing either DOB-DTP or ZnDTP additives (mean values of the friction coefficients over last 10 min of the test, when the friction coefficients have stabilized, are given in Figure 5 and Table 2). It can be seen that when the base oil is

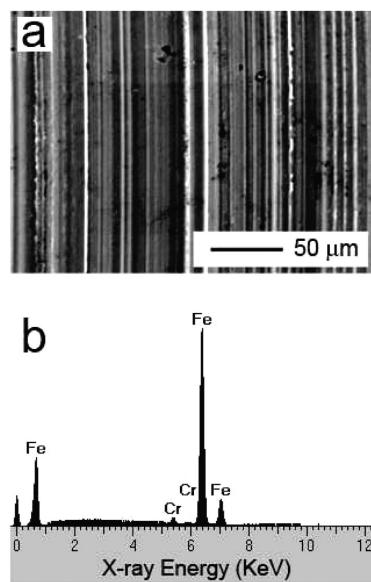


FIGURE 7. (a) SEM micrograph and (b) EDS spectrum of worn ball surface lubricated with the mineral base oil only.

formulated with either DOB-DTP or ZnDTP additives, the friction coefficient of the lubricant increases compared with the oil without additives. Though the friction coefficient of the base oil is lower than for the oil with additives, it is not stable and varies considerably with time of the test. The friction coefficient of the base oil containing ZnDTP at a low concentration (0.1 wt %) increases slowly with time (Figure 6a). The friction coefficient is stable at higher concentrations (0.8 wt %) of ZnDTP. On the other hand, the friction coefficient of the oil containing DOB-DTP does not vary much with time at both low (0.1 wt %) and high (1.0 wt %) concentrations of the additive (plots a and b in Figure 6). This test confirms the stability of the tribofilm formed by DOB-DTP at both low and high concentrations. Note that the stability of the friction coefficient with time is a very important property in mechanical systems needed for their functionality during the service life.

**3.4. Surface Analysis.** Figures 7–10 show results of the surface analysis obtained using Scanning Electron Microscopic/Energy Dispersive X-ray Spectroscopy (SEM/EDS) techniques. The worn surfaces of balls lubricated with the base oil containing 0.1, 0.4, and 1.0 wt % additives were studied by these methods in order to compare both the morphology and a composition of the tribofilms formed from these two additives at different concentrations. These data suggest a formation of tribofilms containing both sulfur and phosphorus at various compositions depending on the type of additive and their concentrations used in the tribological tests.

Figure 7 shows the SEM micrograph of the worn ball surface lubricated with the base oil under the load of 392 N. This micrograph shows wide grooves, which indicate a severe wear. When the additives are mixed with the base

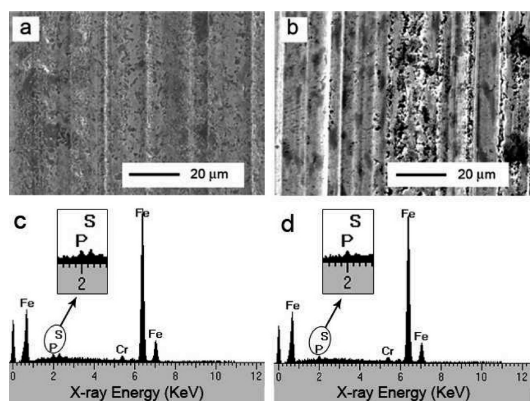


FIGURE 8. SEM micrographs of worn ball surfaces lubricated with the mineral base oil containing (a) 0.1% DOB-DTP and (b) 0.1% ZnDTP. (c, d) EDS spectra of tribofilms in a and b, respectively (the EDS spectra are the average of the whole area shown in the corresponding micrographs).

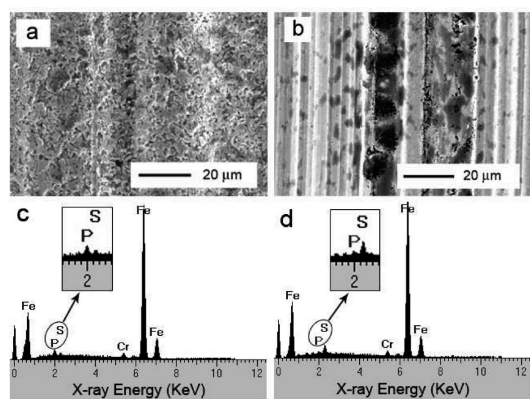


FIGURE 9. SEM micrographs of worn ball surfaces lubricated with the mineral base oil containing (a) 0.4% DOB-DTP and (b) 0.4% ZnDTP. (c, d) EDS spectra of tribofilms in a and b, respectively (the EDS spectra are the average of the whole area shown in the corresponding micrographs).

oil at very low concentration (0.1 wt %), the wear process slows down (see images a and b in Figure 8). The surfaces are smoother (see Figure 8a) as compared to the surfaces lubricated with the mineral oil. When the additive concentrations are increased to 0.4 wt %, WSDs remain close to their minimum values (images a and b in Figure 9) and the wear process further decreases, as discussed earlier (see Figure 4 and Table 2). Beyond this optimum concentration, the surfaces seem to become rougher again (see images a and b in Figure 10). Most probably, this roughness is increased by a corrosive action of sulfur. The worn ball surfaces lubricated with the mineral oil containing DOB-DTP are smoother for all the concentrations studied by SEM, as compared to those lubricated by oil with ZnDTP.

For additive concentrations of 0.1 wt % (see panels c and d in Figure 8), 0.4 wt % (panels c and d in Figure 9) and 1.0 wt % (panels c and d in Figure 10), active elements from the additives are transferred/adsorbed to the steel surfaces.

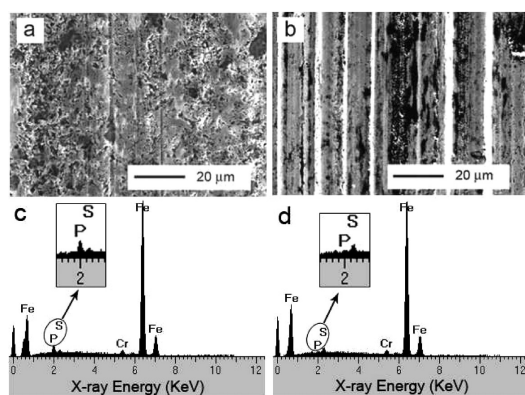


FIGURE 10. SEM micrographs of worn ball surfaces lubricated with the mineral base oil containing (a) 1.0% DOB-DTP and (b) 1.0% ZnDTP. (c, d) EDS spectra of tribofilms in a and b, respectively (the EDS spectra are the average of the whole area shown in the corresponding micrographs).

EDS analysis (Figures 8–10) shows deposition of phosphorus and sulfur on the worn surfaces for both DOB-DTP and ZnDTP additives. In the case of DOB-DTP additive, boron is not detected on the surfaces, probably because of the low sensitivity of the method.

The DOB-DTP additive is a polydentate ligand with a strong coordination capacity in terms of its molecular structure. It is expected to easily interact with the iron surfaces, forming stable protective layers that can reduce wear and inhibit corrosion of iron. We suggest the following mechanism of action of DOB-DTP with steel surfaces: Sulfur atoms present in the dialkyldithiophosphate group of this compound will interact with iron, forming iron sulfide layers on the steel surfaces. The B–S bond has a high reactivity toward metal ions including iron. Therefore, the whole molecule will then decompose and inorganic layers containing phosphorus, sulfur, oxygen, and boron will deposit on the steel surfaces, enhancing performance of the tribological contacts.

#### 4. CONCLUSIONS

S-Di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP) was successfully synthesized and characterized by the elemental analysis, FT-IR, and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , and  $^{11}\text{B}$  NMR spectroscopy. The thermal behavior was characterized by TG/DTG, DTA, and QMS analyses. The tribological properties of this novel additive admixed in the mineral base oil were evaluated in comparison with *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) in a four ball tribometer. DOB-DTP has a good thermal stability up to ca. 268 °C under the conditions used in this study. Dihydrogen sulfide and olefins, which are typical products of decomposition of metals dialkyldithiophosphates, were formed upon heating of the compound above this temperature. The extent of wear was significantly reduced when both DOB-DTP and ZnDTP were admixed into the base oil, whereas the friction coefficient increased in both cases. DOB-DTP showed better antiwear and friction properties compared with ZnDTP in the concentration range (0.1–1.0 wt %) studied. The friction coefficient was stable

over time for all these concentrations of DOB-DTP in the base oil, whereas it was unstable at low concentrations of ZnDTP in the base oil. Phosphorus and sulfur were detected by SEM/EDS analysis on the worn steel surfaces at concentrations studied, 0.1, 0.4, and 1.0 wt %, for both DOB-DTP and ZnDTP additives. However, phosphorus was the predominant element in depositions from DOB-DTP, whereas it was sulfur and not phosphorus in the surface layers formed by products of decomposition of ZnDTP on steel surfaces.

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**Supporting Information Available:**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , and  $^{11}\text{B}$  liquid-state NMR spectra of DOB-DTP, ZnDTP, and triethylborate (compound I) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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# Paper II

A Novel Ashless Antiwear Additive, Alkylborate-dithiophosphate: Synthesis, Characterization and Antiwear performance

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# A Novel ashless lubricant Additive, Alkylborate-dithiophosphate: Synthesis, Characterization and Antiwear performance

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## Abstract

Boron compounds have become of interest in tribology due to their unique tribochemical and tribological properties. At the same time, dialkyldithiophosphates (DTPs) of transition metals have been extensively used as multifunctional additives in lubricants to control friction and reduce wear in mechanical systems. Due to the environmental pollution and health hazards, ashless compounds and reduced amounts of sulphur and phosphorus in lubricants are desirable. In this work we report on the synthesis, characterization and tribological properties of a compound that contains borate and dialkyldithiophosphate in a single molecule bridged by an ethyl group. S-(di-*n*-pentyl borate)-ethyl-*O,O'*-di-*n*-pentyldithiophosphate (DPB-EDTP) was synthesized by a reaction in three steps. The final product, a viscous liquid, was characterized by the elemental analysis, FT-IR, multinuclear <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>11</sup>B NMR spectroscopy and thermal analyses. Antiwear and friction properties of a mineral base oil with this novel additive in comparison with *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II), ZnDTP, were evaluated in a four-ball tribometer. The surface morphology and the elemental composition of the tribofilm were characterized using scanning electron microscopy with energy dispersive X-rays spectroscopy (SEM/EDS). The results show that the ashless DPB-EDTP, in which amounts of sulphur and phosphorus is reduced by half, has better antiwear and friction reducing performance as compared with ZnDTP.

**Keywords:** Alkylborate-dithiophosphate, ashless lubricant additive, ZnDTP, thermal analysis, antiwear and friction properties, SEM/EDS

## 1. INTRODUCTION

Organometallic compounds of different metals and organic compounds containing boron, phosphorus, sulphur and nitrogen have been used as additives in lubricants for several decades to minimize wear, control friction, improve efficiency and hence prolong machine life service. In boundary lubrication, these additives undergo decomposition under extreme conditions (high load and high temperature) forming protective tribofilms through chemical reactions or adsorption processes. The thin tribofilm prevents direct metal-to-metal contact, welding of surface asperities and, thus, reduces wear. Wear is undesirable in practical applications, because it adversely affects functionality and limits the life-span of many mechanical devices with moving parts. The efficiency of additives depends on the ability to form a sufficiently hard protective film on the sliding surfaces. This ability is related to their action mechanism, namely physical adsorption, chemisorption or chemical reactions with metals. The action mechanism of different additives changes for different metals and surface coating materials. Their performance depends on the polarity due to a functional group, quantity of chemically active elements, the activity of the decomposition products and the chemical activity of the metal surfaces (1-5).

A tribochemical reaction of additives with surfaces is generally catalyzed by the contact asperity temperature and the nascent metal surfaces. The contact temperature (also called “flash temperature”) is usually very high but short-lived and the nascent surfaces also possess very high surface energy and active sites. The raise in contact temperature is caused by the heat produced due to friction between the sliding asperities (6, 7). A variety of chemical reactions may occur due to the combined effect of heat and the active surface. These reactions mainly include oxidation of the surfaces, oxidation and degradation of the lubricant, surface catalysis, polymerization, and formation of inorganic and organometallic products (8). The nature of inorganic and organometallic products formed on the surface depends on the reactivity, structure and composition of the additive. A high rate, at which tribofilms are formed may be also explained by pressure-induced bulk effect. It has been shown with a nanometer resolution that the films on top of asperities, which experience high pressure, are harder than these between asperities (9).

Zinc dialkyldithiophosphates (ZnDTPs) have been the additives of choice to provide protection against wear and are the most widely used additives since 1940s (10-14). Recently, environmental implications of using ZnDTPs have been addressed and the desire to use more environmentally friendly oil additives has become ever more apparent. It has been observed that ZnDTPs may cause eye irritation, contact dermatitis and these compounds are mutagenic (15, 16). These additives contain zinc, and large amounts of sulphur and phosphorus, which impair the environment



indirectly by poisoning of emission-control catalysts and by blocking filters in car exhaust systems (17, 18). Due to important health, economic and environmental issues, significant efforts are being made to develop and implement in practice lubricants that contain smaller amounts of Zn, S and P. Replacement of ZnDTP by zinc-free, low-sulphur and low-phosphorus efficient and environmentally friendly additives, is a hot topic of tribochemical research.

Interest to boron compounds in various applications is increasing due to the unique combination of chemical and tribological properties of these compounds. Specifically, boron compounds have been extensively studied as soluble additives in lubricating oils, as solid lubricants and as surface coatings (19-22). Oil soluble organoboron compounds are promising friction modifiers, corrosion inhibitors, antioxidants and effective antiwear additives (23-28). To reduce the amounts of sulphur and phosphorus in lubricants and to enhance their tribological performance, ZnDTPs have been widely studied and being used in combination with different borate additives. Combinations of ZnDTP with potassium triborate (29), calcium borate (30, 31) or boric additive (32) have exhibited improved antiwear properties. Combinations of boron and sulphur in a single molecule such as borate with mercaptobenzothiozole (33) or dithiocarbamates (34, 35) have also shown improved antiwear performance.

In this paper we report on the synthesis, characterization and tribological study of S-(di-*n*-pentylborate)-ethyl-*O,O'*-di-*n*-pentyldithiophosphate (DPB-EDTP), which belongs to a new class of lubricant additives. The main goal of this study is to combine B, S and P atoms in one organic molecule aiming at improving of tribological and environmental performance of both dialkyldithiophosphates and borate esters. Its performance is evaluated in comparison with *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) (ZnDTP), at concentrations 0-1.0 wt% in mineral base oil.

## 2. EXPERIMENTAL SECTION

### 2.1 Chemicals

Phosphorus pentasulphide,  $P_2S_5$  (Aldrich, 99% purity), pentanol (Prolabo, 98% purity), 2-chloroethanol (Fluka, >99% purity), boric acid (Merck, analytical grade), sodium sulphate (Merck, analytical grade), potassium hydroxide pellets (Merck, analytical grade) and toluene (Fluka, > 99.7% purity) were used as received. The commercially available ZnDTP contains a mixture of 85 % *O,O'*-di-*iso*-butyl-dithiophosphato-zinc(II) and 15 % *O,O'*-di-*n*-octyl-dithiophosphato-zinc(II) (36). In this study, we used ZnDTP (as a reference compound) with the same number of carbon atoms in alkyl chains as in the principal component of the commercial ZnDTP additive but we preferred *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) for tribological studies instead of *O,O'*-di-*iso*-

butyl-dithiophosphato-zinc(II). *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) is a viscous liquid at room temperature and it is easily miscible with the base oil used in this study. *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) was synthesized by a reported method (37). The purity of the latter ZnDTP complex and its corresponding potassium salt was checked by  $^{31}\text{P}$  NMR. (145.70 MHz,  $\delta$ ): 100.29 ppm (38) and  $^{31}\text{P}$  NMR for potassium salt (145.70 MHz, ethanol,  $\delta$ ) 112.72 ppm.

## 2.2 Synthesis of S-(di-*n*-pentylborate)-ethyl-*O,O'*-di-*n*-pentyldithiophosphate

*Step 1*: Phosphorus pentasulphide (4.44 g, 20 mmol) was suspended in toluene and pentanol (80 mmol). The reaction mixture was stirred at 80-100 °C for 3 hours. The suspension was filtered to remove unreacted phosphorus pentasulphide ( $\text{P}_2\text{S}_5$ ). An equivalent amount of potassium hydroxide was added in the form of 50% aqueous solution with continuous stirring at room temperature. Toluene and water were removed and the crude product was dried. The crude potassium *O,O'*-di-*n*-pentyldithiophosphate (**1**) was washed with hexane (yield 75 %).

FT-IR (KBr,  $\text{cm}^{-1}$ , powder): 2957, 2873  $\nu(\text{C-H}$ , stretching); 983  $\nu(\text{P-OC}$ , medium); 708  $\nu(\text{P=S}$ , medium); 548  $\nu(\text{P-S}$ , medium).

$^{31}\text{P}$  NMR (145.70 MHz, ethanol,  $\delta$ ): 112.79 ppm.

*Step 2*: 20 mmol (1.61 g) of chloroethanol was added to an aqueous suspension of potassium salt of *O,O'*-di-*n*-pentyldithiophosphate (**1**) (20 mmol, 6.16g) with constant stirring. The resulting reaction mixture was refluxed for 3 hours. A new formed organic layer was extracted with toluene from the aqueous phase, washed with water several times, dried over anhydrous sodium sulphate and filtered. Traces of solvent and water were removed in a rotary evaporator to get S-hydroxyethyl-*O,O'*-di-*n*-pentyldithiophosphate (**2**), (4.64 g, 74 % yield).

FT-IR (KBr,  $\text{cm}^{-1}$ ): 3427  $\nu(\text{O-H}$ , broad); 2927, 2858  $\nu(\text{C-H}$ , stretching); 980  $\nu(\text{P-OC}$ , medium); 729  $\nu(\text{P=S}$ , medium); 662  $\nu(\text{P-S}$ , medium).

$^1\text{H}$  NMR (359.93 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.91 (6H, t,  $^3J_{\text{HH}} = 6.54$  Hz,  $\text{CH}_3$ ); 1.32-1.40 (8H, m,  $-\text{CH}_2-$ ); 1.68-1.76 (4H, m,  $\text{CH}_2\text{CH}_2\text{OP}$ ); 2.21 (1H, s, OH); 3.09 (2H, dt,  $^3J_{\text{HP}} = 18.65$ ,  $^3J_{\text{HH}} = 5.76$ ,  $\text{CH}_2\text{S}$ ); 3.85 (2H, t,  $^3J_{\text{HH}} = 6.04$  Hz,  $\text{CH}_2\text{OH}$ ); 4.04-4.18 (4H, m,  $\text{CH}_2\text{OP}$ ).

$^{13}\text{C}$  NMR (90.57 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 14.05 ( $2 \times \text{CH}_3$ ); 22.30 ( $2 \times \text{CH}_2\text{-CH}_3$ ); 27.82, 29.80, ( $4 \times -\text{CH}_2-$ ); 36.46 ( $1 \times \text{CH}_2\text{-S}$ ); 62.04 ( $1 \times \text{CH}_2\text{-O-B}$ ); 68.37 ( $2 \times \text{CH}_2\text{-O-P}$ ) ppm.

$^{31}\text{P}$  NMR (145.70 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 96.25 ppm.

*Step 3*: A solution of 10 mmol (3.14 g) of S-hydroxyethyl-*O,O'*-di-*n*-pentyldithiophosphate (**2**) in 80 ml of toluene was placed together with 10 mmol (0.618 g) of boric acid and 20 mmol of 1-pentanol in a 250 ml round-bottom flask equipped with a magnetic stirrer, a condenser and a water separator (pre-baked on vacuum to exclude any moisture). The reaction mixture was refluxed for 6

hours under nitrogen atmosphere; water was continuously removed from the reaction mixture. The reaction mixture was rotary evaporated to remove the solvent. The product formed was distilled at 0.2 mm Hg, 120 °C for 30 minutes to remove traces of the solvent and 1-pentanol. A transparent viscous liquid product, S-(di-*n*-pentylborate)-ethyl-*O,O'*-di-*n*-pentyldithiophosphate (**3**) was obtained in 89 % yield (4.42 g).

Anal. Calcd for C<sub>22</sub>H<sub>48</sub>O<sub>5</sub>PS<sub>2</sub>B (Mr. 498.46): C, 53.0; H, 9.7; B, 2.2. Found: C, 52.3; H, 9.7; B, 2.6. FT-IR (KBr, cm<sup>-1</sup>): 2957, 2932, 2873 ν(C-H, CH<sub>3</sub> stretching); 984 ν(P-OC, medium); 730 ν(P=S, medium); 666 ν(P-S, medium).

<sup>1</sup>H NMR (359.93 MHz, CDCl<sub>3</sub>, δ): 0.91 (6H, t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH<sub>3</sub>); 0.90 (6H, t, <sup>3</sup>J<sub>HH</sub> = 6.94 Hz, CH<sub>3</sub>); 1.30-1.40 (16H, m, -CH<sub>2</sub>-); 1.49-1.57 (4H, m, CH<sub>2</sub>CH<sub>2</sub>OB); 1.68-1.75 (4H, m, CH<sub>2</sub>CH<sub>2</sub>OP); 3.01 (2H, dt, <sup>3</sup>J<sub>HP</sub> = 16.37, <sup>3</sup>J<sub>HH</sub> = 6.56, CH<sub>2</sub>S); 3.76 (4H, t, <sup>3</sup>J<sub>HH</sub> = 6.64 Hz, CH<sub>2</sub>OB, pentyl chain); 3.96 (2H, t, <sup>3</sup>J<sub>HH</sub> = 6.49 Hz, CH<sub>2</sub>OB, ethyl); 4.02-4.18 (4H, m, CH<sub>2</sub>OP).

<sup>13</sup>C NMR (90.57 MHz, CDCl<sub>3</sub>, δ): 14.20 (2 × CH<sub>3</sub>); 14.06 (2 × CH<sub>3</sub>); 22.57 (2 × CH<sub>2</sub>-CH<sub>3</sub>); 22.36 (2 × CH<sub>2</sub>-CH<sub>3</sub>); 27.86, 28.15, 29.84, 31.37 (8 × CH<sub>2</sub>, pentyl chains); 34.79 (1 × CH<sub>2</sub>-S); 63.34 (3 × CH<sub>2</sub>-O-B); 68.03 (2 × CH<sub>2</sub>-O-P) ppm.

<sup>31</sup>P NMR (145.70 MHz, CDCl<sub>3</sub>, δ): 95.91 ppm.

<sup>11</sup>B NMR (115.48 MHz, CDCl<sub>3</sub>, δ): 17.59 ppm.

### 2.3 Physical, Thermal and Surface Characterization

The elemental analysis for C and H was performed at Mikrokemi AB, Uppsala, according to procedures described on their homepage [39]. The elemental analysis of B was carried out by ICP-MS at ALS laboratory group, Luleå; detailed procedure is described on their homepage [40].

FT-IR spectra were recorded on a Perkin-Elmer 2000 spectrometer in the range 4000-370 cm<sup>-1</sup>. Sampling was performed by placing a droplet of a compound onto a KBr pellet. Multinuclear NMR spectra of **1-3** and ZnDTP compounds in CDCl<sub>3</sub> (5-10 % concentration) were recorded on a Varian/Chemagnetics InfinityPlus CMX-360 (B=8.46 T) spectrometer using a 10 mm probe for liquids and tuned to resonance frequencies of <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P or <sup>11</sup>B. TMS as an internal reference for <sup>1</sup>H, 77.2 ppm resonance peak of CDCl<sub>3</sub> for <sup>13</sup>C, Et<sub>2</sub>O.BF<sub>3</sub> as an external reference (0 ppm) for <sup>11</sup>B and H<sub>3</sub>PO<sub>4</sub> (85%) as an external reference (0 ppm) for <sup>31</sup>P.

Thermal analyses were performed by Netzsch STA 409 instrument equipped with simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) at a rate of 20°C/min and argon flow rate of 100 ml/min. The sensitivity of this STA instrument is ±1 µg.

Philips XL 30 scanning electron microscope (SEM) equipped with LaB6 emission source was used for surface studies. A link ISIS Ge energy dispersive X-ray detector (EDS) attached to the SEM was

used to additionally probe the composition of the entire tribofilms on the ball surfaces. Prior to the analysis, the balls were cleaned ultrasonically for 5 min with petroleum ether, in order to eliminate the residual lubricant.

## 2.4 Tribological Performance

Additives were mixed with the mineral base oil at fixed weight (%) concentrations of 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 % using an analytical balance. The density of the base oil is  $0.8135 \text{ g.ml}^{-1}$ , and viscosity: 17.5 m Pa.s at  $40^\circ \text{C}$  and 4.9 m Pa.s at  $100^\circ \text{C}$ . The elemental analysis of the base oil used in this study is: carbon,  $86.0 \pm 0.7 \%$  and hydrogen,  $14.5 \pm 0.5 \%$ . The steel balls used in the tests were in 12.7 mm diameter with a surface hardness HRc 60-67. AISI 52100 steel composition: C, 0.95–1.10%; Si, 0.15–0.30%; Mn,  $<0.25\%$ ; P,  $<0.03\%$ ; S,  $<0.025\%$ ; Cr, 1.30–1.60%.

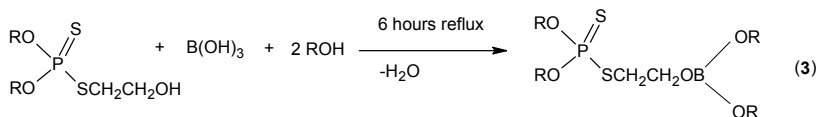
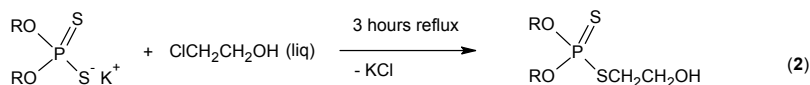
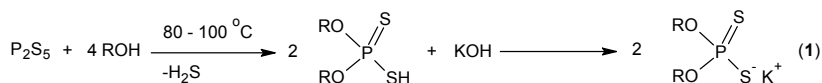
Friction and antiwear properties of these compounds as additives in the base oil were evaluated with a four ball Tribometer. Test conditions: rotational speed 1450 rpm, test duration time 30 min, load 392 N and ambient temperature (294 K). Dependence of wear scar diameter (WSD) and friction coefficient on additive concentration (wt %) was studied. An optical profiler (WYCO NT 1100) was used to measure the wear scar diameters for all three lower stationary balls. A mean of these three values was calculated and reported here as the wear scar diameter (WSD). Before each test, the ball holder was washed with petroleum ether while the balls were cleaned ultrasonically in petroleum ether and thoroughly air-dried.

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis and Spectroscopic Characterization

S-(di-*n*-pentylborate)-ethyl-*O,O'*-di-*n*-pentyldithiophosphate, (DPB-EDTP) (**3**) was synthesized following several steps (Scheme 1). The first step was followed by a procedure already reported for short alkyl chain compounds (41): Phosphorus pentasulphide ( $\text{P}_2\text{S}_5$ ) was reacted with primary pentanol in a 1:4 molar ratio giving rise to *O,O'*-di-*n*-pentyldithiophosphoric acid. No further attempts were made to isolate and purify this acid because it tends to be slowly oxidised by atmospheric oxygen. Instead, the crude product was directly used to prepare a potassium *O,O'*-di-*n*-pentyldithiophosphate salt (**1**), which is more stable at ambient conditions. In the second step, S-hydroxyethyl of *O,O'*-di-*n*-pentyldithiophosphate (**2**) was prepared by refluxing 2-chloroethanol with an aqueous suspension of (**1**) in a 1:1 molar ratio for 3 hours. In the third step, S-(di-*n*-pentylborate)-hydroxyethyl-*O,O'*-di-*n*-pentyldithiophosphate (**3**) was obtained by treating (**2**) with

boric acid and pentanol. Since boron-sulphur bonds are susceptible to hydrolysis by atmospheric moisture, boron was made covalently bound to the *O,O'*-di-*n*-pentyldithiophosphate group through the ethyl group, in order to avoid hydrolysis of this compound in lubricating oils used in tribological applications.



Scheme 1. Synthesis of DPB-EDTP

The stepwise progress in these reactions and intermediate products were identified by FT-IR and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{11}\text{B}$  NMR spectroscopic measurements. The combined spectroscopic information confirmed that **1**, **2** and **3** are the expected individual compounds.

All characteristic peaks in FTIR spectra of the intermediates **1**, **2** and the final product **3** were assigned. Figure 1 shows a representative molecular vibration spectrum of the end product (**3**), DPB-EDTP. The absorption frequencies of the aliphatic C-H vibrations in the alkyl groups of this compound (and also of **1** and **2**, FTIR spectra are not shown) were mainly observed in the range  $2957\text{--}2857 \text{ cm}^{-1}$ . The medium and broad bands present in the FTIR spectra of all these three compounds in the region  $984\text{--}980 \text{ cm}^{-1}$  are assigned to  $\nu(\text{P-OC})$  while bands in the region  $730\text{--}708$  and  $666\text{--}540 \text{ cm}^{-1}$  are attributed to  $\nu(\text{P-S})$  and  $\nu(\text{P=S})$ , respectively. However, it is difficult to distinguish with confidence between the P-S and P=S stretching frequencies. For example, vibration bands associated with the P-S stretching frequencies in the transition-metal complexes, which

contain bidentate chelating dithiophosphate ligands appear in the same region as for the free acids  $(\text{RO})_2\text{P}(=\text{S})\text{SH}$  and their thioesters  $(\text{RO})_2\text{P}(=\text{S})\text{SR}'$  (42). There seems no significant shifts in stretching frequencies of  $\text{P}=\text{S}$  for compounds (**2** and **3**) as compared with (**1**) that confirms the monodentate character of the thiophosphoryl group in all these three compounds. For bidentate complexes this band is shift to lower vibration frequencies compared with corresponding salts of dithiophosphoric acids (41). A strong and broad band at  $3427\text{ cm}^{-1}$ , observed in (**2**) only, is assigned here to  $\nu(\text{O-H})$ . In the final product (**3**), a strong band at  $1337\text{ cm}^{-1}$  is attributed to  $\nu(\text{B-O})$ : Obviously, it is absent in the intermediate products **1** and **2**.

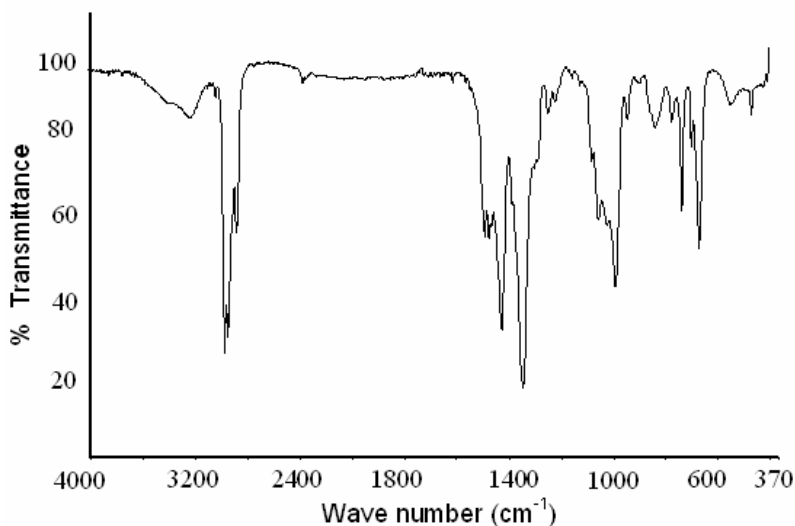


Figure 1. FTIR spectrum of DPB-EDTP.

A  $^1\text{H}$  NMR spectrum of 100 mM solution of compound (**3**) in  $\text{CDCl}_3$  is shown in Figure 2 together with assignment. Multipletts at ca 4.1 ppm are assigned to protons in  $\text{CH}_2\text{OP}$  molecular moieties: Apart from characteristic for this group large deshielding, and  $^3J_{\text{HH}}$ -coupling with a neighbour  $\text{CH}_2$  group, resonance lines are additionally split into a doublet by heteronuclear  $^3J_{\text{HP}}$ -coupling between  $\text{CH}_2$  protons and  $^{31}\text{P}$  nucleus (spin  $\frac{1}{2}$ , 100 % natural abundance). Similarly, a doublet of tripletts at ca 3 ppm is assigned to protons in the  $\text{CH}_2\text{-S-P}$  fragment of DPB-EDTP: Protons are J-coupled with phosphorus through a sulfur atom ( $^3J_{\text{HP}} = 16.37\text{ Hz}$ ). Interestingly, no three-bond J-couplings were observed between  $\text{CH}_2$ -protons and boron in the borate part of this molecule (tripletts at 3.76 and 3.96 ppm).  $^{10}\text{B}$  and  $^{11}\text{B}$  (spin  $> \frac{1}{2}$ ) have a large quadrupolar moment

and an asymmetric electric field gradient in the  $\text{BO}_3$  fragment of the molecule making  $^3J_{\text{HB}}$ -coupling difficult to be observed in isotropic liquids.

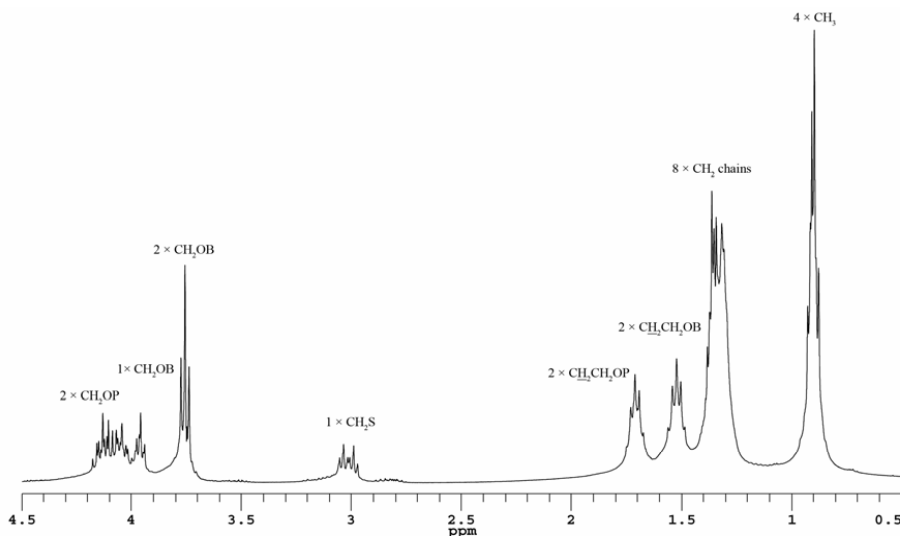


Figure 2. A 360 MHz  $^1\text{H}$  NMR spectrum of DPB-EDTP with assignment of multipletts.

Assignment of multipletts in the range of chemical shifts between 0.9 and 1.7 ppm to protons in different alkyl groups of DPB-EDTP (shown in Fig. 2 and tabulated in 2.2) is rather straightforward using isotropic chemical shifts, J-couplings and integrals of the multipletts.

The chemical shift of phosphorus nucleus of potassium *O,O'*-di-*n*-pentyldithiophosphate (**1**) in ethanol is 112.79 ppm, while  $\delta(^{31}\text{P})$  of (**2**) in  $\text{CDCl}_3$  is equal to 96.25 ppm. The 15.54 ppm upfield shift indicates the formation of a covalent P-S-C bond in (**2**) compared to the originally ionic fragment  $\text{P-S}^-\text{K}^+$  in (**1**) (44). The  $^{31}\text{P}$  NMR spectrum of 100 mM (**3**) in  $\text{CDCl}_3$  reveals a singlet at 95.91 ppm. The phosphorus site in DPB-EDTP is more shielded (by 0.34 ppm) compared to P in (**2**) because of an additional alkyl borate group in (**3**) covalently bound to P via the  $-\text{S-CH}_2\text{-CH}_2-$  molecular moiety. Thus,  $^{31}\text{P}$  NMR data additionally support the completion of the reaction shown in Scheme 1 with the formation of both intermediate (**2**) and the final product (**3**).

The  $^{11}\text{B}$  NMR spectrum of the final product (**3**) measured in  $\text{CDCl}_3$  reveals a singlet at 17.59 ppm, which suggests that the boron atom is coordinated to three oxygen atoms in the alkylborate groups (45).

### 3.2 Thermal Analysis

Thermogravimetric/Derivative thermogravimetric (TG/DTG) curves indicate that DPB-EDTP exhibit a good thermal stability in a wide temperature range up to 250 °C (Figure 3). The TG curve shows a weight loss during the thermal decomposition of the compound. The decomposition of compound (**3**) involves only one major step between 250 and 270 °C. The total weight loss of DPB-EDTP during the whole thermal process is *ca* 62 %, which corresponds to the formation of volatile products, while 38 % of the total weight has remained as a non-volatile solid with a melting point higher than 500 °C. The DTG curve shows a weight loss of (**3**) per minute with an increase in temperature. The rate of the weight loss is just a few % per min in the temperature interval 150-230 °C. Then it increases dramatically and at 269.4 °C reaches its maximum value of 80 %/min of the total weight of sample. Finally, the rate of the weight loss decreases abruptly to almost zero at the sample temperature larger than 290 °C.

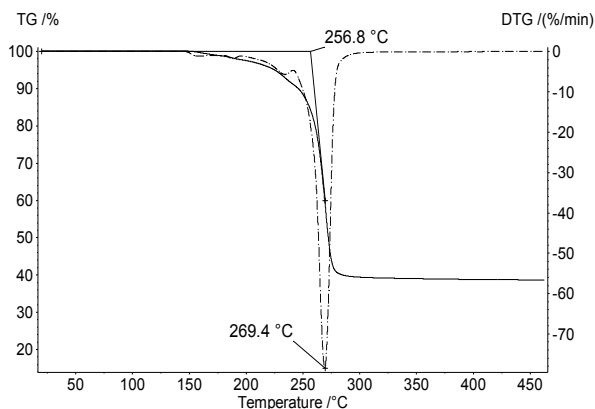


Figure 3. TG/DTG curves of DPB-EDTP at a heating rate of 20°C/min and argon flow rate of 100 mL/min.

A differential thermal analysis (DTA) curve of (**3**) is shown in Figure 4. An exothermic peak is observed at 266.5 °C, which is directly followed by an endothermic peak at 273.8 °C. The former exothermic peak represents the thermal decomposition of DPB-EDTP, while the latter endothermic



peak represents the physical processes of the decomposed products such as melting, boiling or other phase transitions (46).

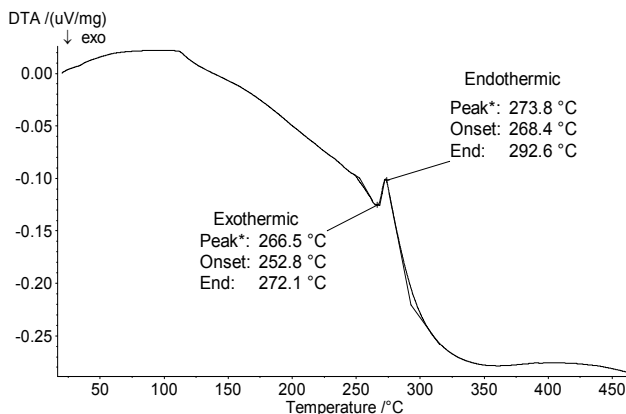


Figure 4. A DTA curve for DPB-EDTP at a heating rate of 20°C/min and argon flow rate of 100 mL/min.

### 3.3 Tribological Performance

Antiwear and friction performance of novel DPB-EDTP and ZnDTP was evaluated using the same base oil and test conditions. It is known that concentration of additives in base oils plays an important role in friction and wear performance. Therefore, tests were conducted in the concentration range from 0 to 1.0 wt % of either DPB-EDTP or ZnDTP. Both numerical values of the friction coefficient and mean wear scar diameters in this concentration range for the two additives in the mineral oil are given in Table 1.

Table 1. Mean values of WSDs and friction coefficients (an average over last 10 min) for DPB-EDTP and ZnDTP in the base mineral oil. Temperature (294 K), load 392 N and test duration 30 min.

Concentration (%)	DPB-EDTP		ZnDTP	
	WSD $\pm$ (SD) mm	Friction coefficient $\pm$ (variation)	WSD $\pm$ (SD) mm	Friction coefficient $\pm$ (variation)
0	0,603 (0,0122)	0,042 (0.006)	0,603 (0,0122)	0,042 (0.006)
0.1	0,485 (0,0105)	0,040 (0.006)	0,546 (0,0165)	0,082 (0.007)
0.2	0,477 (0,0133)	0,039 (0.004)	0,533 (0,0128)	0,074 (0.006)
0.4	0,493 (0,0079)	0,039 (0.004)	0,493 (0,0083)	0,065 (0.005)
0.6	0,496 (0,0123)	0,038 (0.004)	0,473 (0,0110)	0,072 (0.005)
0.8	0,508 (0,0098)	0,053 (0.009)	0,492 (0,0079)	0,066 (0.005)
1.0	0,515 (0,0035)	0,052 (0.005)	0,516 (0,0157)	0,066 (0.005)

Figure 5 shows variations of the mean WSD of the lower steel balls lubricated with the mineral base oil containing either DPB-EDTP or ZnDTP additives at different concentrations. Both DPB-EDTP and ZnDTP are found to reduce WSDs when added to the mineral base oil even at very small concentrations. A decrease in the WSD was detected upto 0.2 wt % of DPB-EDTP in the base oil. Then WSD gradually increases slightly with an increase of concentration of the additive. A similar trend was found for ZnDTP also. The WSD decreases upto 0.6 wt % and then increases with an increase in concentration of ZnDTP in the base oil. The optimum concentrations for the wear reducing ability of an additive in the base oil at steel-steel contacts were around 0.2 and 0.6 wt % for DPB-EDTP and ZnDTP additives, respectively.

In this concern a pertinent question is: Why this optimum concentration for DPB-EDTP is three-fold smaller compared with those for ZnDTP?

First of all, it is known that the increase in WSD at higher concentrations of additives (observed for both DPB-EDTP and Zn-DTP) is due to a corrosive action of sulphur present in these compounds (47-50). There might be at least two reasons for remarkably different antiwear behaviour of DPB-EDTP compared to ZnDTP. First, we anticipate that sulphur and phosphorus atoms present in DPB-EDTP are more reactive than P and S in ZnDTP. Thus, even a very small concentration of DPB-EDTP is sufficient for protective tribofilms on steel surfaces to be formed. Second, DPB-EDTP contains an alkyl borate group that may additionally enhance the antiwear ability of this additive and inhibit a part of the corrosive action of sulphur even at high concentrations of DPB-EDTP in the base oil (35).

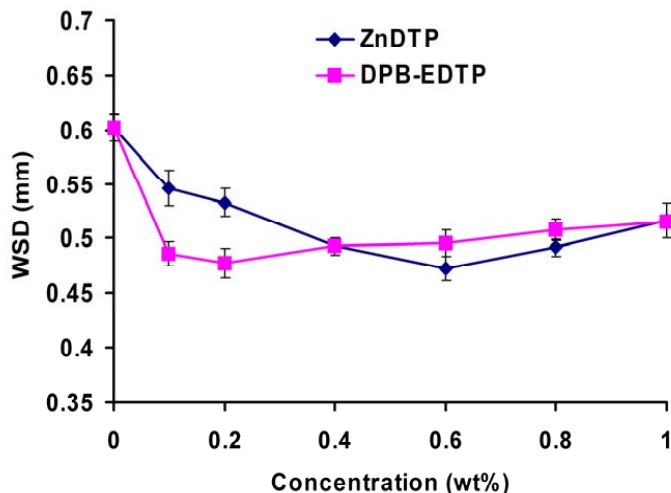


Figure 5. Mean WSD dependence on concentration of DPB-EDTP (squares) and ZnDTP (rhombs). Tests were performed in a four-ball tribometer at ambient temperature (294 K) and 392 N load during 30 min.

Figure 6 shows variations of the friction coefficient with concentration (wt %) for the two additives in the base oil under study. Incorporation of ZnDTP in the base oil does increase significantly (by more than 50 %) the friction coefficient of the resulting lubricant. In contrary, the friction coefficient of the lubricant with 0.1 – 0.6 wt % DPB-EDTP does increase insignificantly (less than by 10 %). What could be even more attractive for future tribological applications is the fact that the friction coefficient of the lubricant with DPB-EDTP does not vary significantly ( $\mu = 0.038 - 0.040$ ) in this concentration range of the novel additive, while friction coefficient varies considerably for ZnDTP ( $\mu = 0.066 - 0.074$ ) in the same concentration interval (see Fig. 6 and Table 1).

A putative mechanism explaining a dramatic increase in the friction coefficient for ZnDTP may involve a break down of the additive molecules as a result of their interactions with steel surfaces. Thus, tribofilms with a higher shear strength than those of the steel matrix itself are formed. The former is due to the stronger interfacial bonds in the new material formed on the surface that leads to an increase of the friction coefficient. It is already known that the tribofilms formed by ZnDTPs (51, 52) and S-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP) (53) increase friction coefficient. Here, it seems to be that tribofilm formed from DPB-EDTP have considerably lower shear strength and weaker interfacial bonds as compared with ZnDTP.

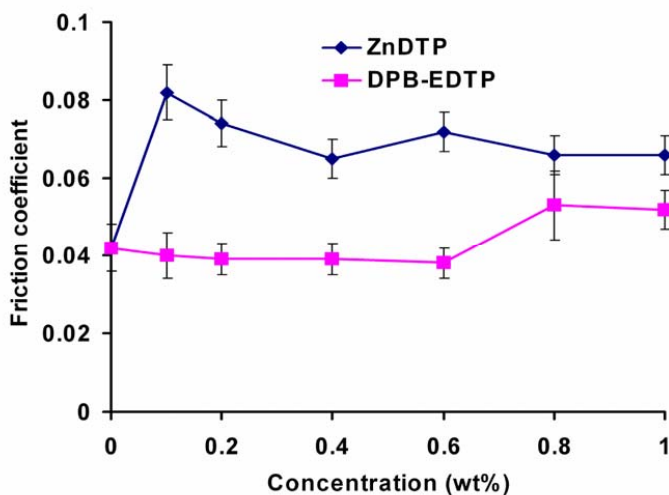


Figure 6 The friction coefficient (an average over last 10 min) as a function of concentration of additives in the mineral base oil: DPB-EDTP (pink squares) and ZnDTP (blue rhombs). Tests were performed in a four-ball tribometer at ambient temperature (294 K) and 392 N load during 30 min.

### 3.4 Surface Analysis

After tribological tests, the wear scars were analyzed using Scanning Electron Microscopic/Energy Dispersive X-ray Spectroscopy (SEM/EDS) techniques (Figures 7-9). The worn surfaces of balls lubricated with the base oil containing 0.2 and 1.0 wt % additives were studied to compare both morphology and composition of the tribofilms formed. Figure 7 shows a SEM micrograph and a corresponding EDS analysis of the worn ball surface lubricated with the base oil only. This micrograph shows wide grooves in the wear scars. The EDS spectrum shows only iron and traces of chromium on the worn surface.

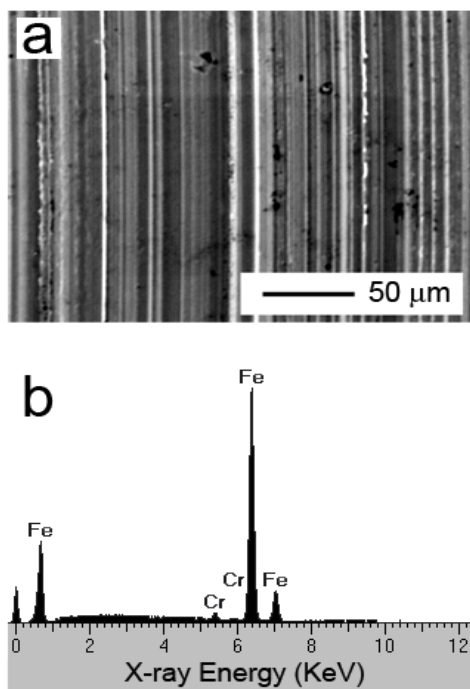


Figure 7. SEM micrograph and the corresponding EDS analysis of worn ball surface lubricated with the mineral base oil only.

The wear rate decreases when the additives were mixed into the base oil. Figure 8 shows the worn ball surfaces lubricated with the base oil containing 0.2 wt % of either DPB-EDTP or ZnDTP additives. The surfaces are smoother (see Figs. 8 a and 8 b) as compared to the surfaces lubricated with the base oil alone. At higher additive concentrations (1.0 wt %), the worn surfaces remained smooth although the WSDs are larger for both these additives at this concentration (see Figs. 9 a and 9 b). The worn ball surfaces lubricated with the mineral base oil containing DPB-EDTP are smoother for both concentrations studied by SEM, as compared to the base oil with ZnDTP.

The EDS analysis for additives at concentrations of 0.2 wt % (Fig. 8) and 1.0 wt % (Fig. 9) shows that active elements are transferred/adsorbed from the additives to the steel surfaces. The deposition of both phosphorus and sulphur were detected on the worn surfaces for DPB-EDTP and ZnDTP at concentrations studied with the EDS analysis (0.2 wt % and 1.0 wt %). Somewhat larger amounts of phosphorus were detected for 1 wt % DPB-EDTP compared with experiments at other concentrations of both additives. This feature is not fully understood yet and it would need additional studies using XPS and other surface sensitive methods. Unfortunately, for the novel

additive, DPB-EDTP, boron was not detected on the surfaces, probably, because of a low sensitivity of the EDS method to this element.

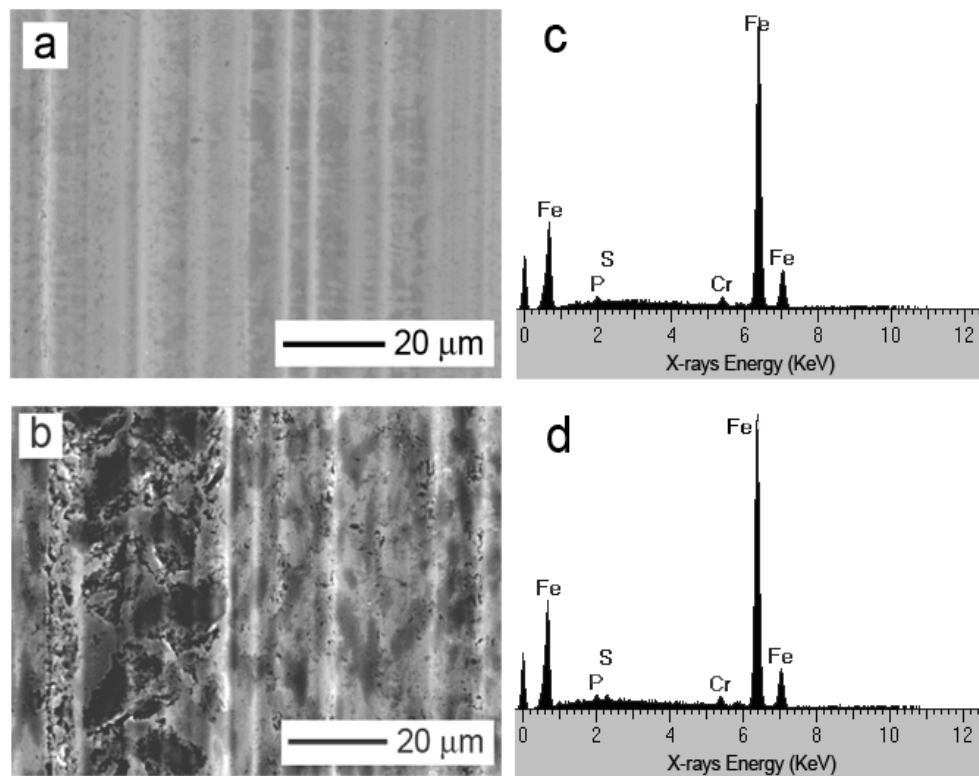


Figure 8. SEM micrographs of worn ball surfaces lubricated with the mineral base oil containing (a) 0.2 % DPB-EDTP and (b) 0.2 % ZnDTP. (c) and (d) are EDS spectra of tribofilms in (a) and (b), respectively (the EDS spectra are the average of the whole area shown area in the corresponding micrographs).

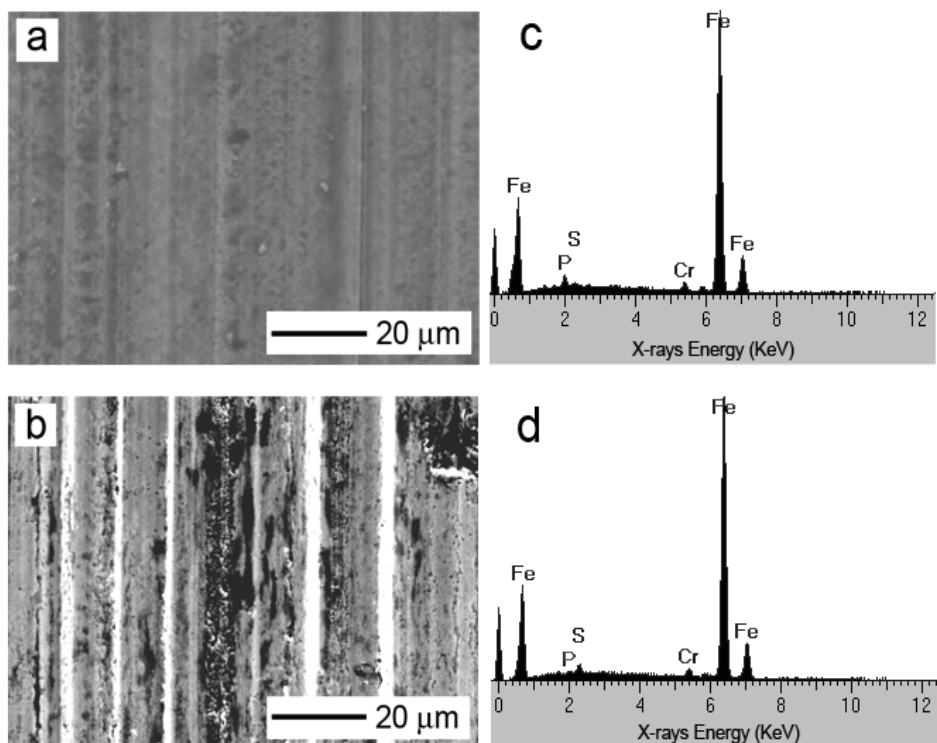


Figure 9. SEM micrographs of worn ball surfaces lubricated with the mineral base oil containing (a) 1.0 % DPB-EDTP and (b) 1.0 % ZnDTP. (c) and (d) are EDS spectra of tribofilms in (a) and (b), respectively (the EDS spectra are the average of the whole area shown area in the corresponding micrographs).

#### 4. CONCLUSIONS

A novel ashless additive to lubricating mineral oils, S-(di-*n*-pentylborate)-ethyl-*O,O'*-di-*n*-pentyldithiophosphate (DPB-EDTP) was synthesized by a multi step reaction and characterized by the elemental analysis, FT-IR and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR spectroscopy. The thermal behaviour of this compound was studied by TG/DTG and DTA analyses. DPB-EDTP showed a high thermal stability and a good miscibility with the mineral base oil. Friction and antiwear properties of DPB-EDTP as an additive in the mineral base oil were evaluated in comparison with *O,O'*-di-*n*-butyldithiophosphato-zinc(II), ZnDTP. Wear was significantly reduced for 0.1-0.6 wt % of DPB-EDTP in the base oil, while the friction coefficient has decreased by ca 10 % compared with those in the base oil alone. In the concentration range 0.1-0.6 wt %, DPB-EDTP showed improved antiwear and friction reducing properties compared with the base oil with ZnDTP. Both phosphorus and sulphur

were detected by SEM/EDS analysis on the worn steel surfaces at concentrations, 0.2 and 1.0 wt %, for both DPB-EDTP and ZnDTP.

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# Paper III

Organoboron-dithiophosphates as Ashless Antiwear additives: Synthesis, Characterization and Tribological Evaluation

Faiz Ullah Shah, Sergei Glavatskih, Erik Höglund and Oleg N. Antzutkin

To be submitted to *Tribology Letters*



# Organoboron-dithiophosphates as Ashless Antiwear additives: Synthesis, Characterization and Tribological Evaluation

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## Abstract

The most common and extensively used lubricant additives, zinc dialkyldithiophosphates (ZnDTPs), contain zinc and large amounts of phosphorus and sulphur. This adversely affects the environment and human health. The aim of this study is to develop ashless additives for partial or complete replacement of ZnDTPs by novel efficient and environmentally friendly additives in lubricants. In this work we report on zinc-free lubricant additives containing organoboron and dithiophosphate groups chemically bound in a single molecule. The amounts of phosphorus and sulphur are reduced by half as compared with ZnDTPs. These novel organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate were synthesized by a three-step reaction under inert nitrogen atmosphere. The final products were characterized by the elemental analysis, spectroscopic methods (FT-IR, multinuclear <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>11</sup>B NMR) and thermal analyses. Tribological performances of a mineral base oil with these new additives were evaluated in comparison with *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) (ZnDTP) using a four-ball tribometer. The morphology and the elemental composition of the tribofilms were characterized using an optical profiler and a scanning electron microscopy with energy dispersive X-rays Spectroscopy (SEM/EDS). The results show that these new ashless compounds with reduced amounts of sulphur and phosphorus have considerably better both antiwear performance and stability of the friction coefficient with time as compared with ZnDTP.

**Keywords:** organoboron-dithiophosphate, ashless lubricant additives, tribological evaluation, thermal analysis, SEM/EDS, NMR, ZnDTP.

## 1 Introduction

Both the chemical reactivity and adsorption of organic molecules on metal surfaces is of great importance in surface science and tribology. Formation of protective tribofilms can significantly change the properties of metal surfaces such as their chemical reactivity, corrosion inhibition and hardness of the surface layer. These protective films prevent wear of machine elements resulting in fuel economy and also extend the lifetime of the equipment in industrial applications. The use of lubricant additives is one of the most practical and widely used methods for providing such tribofilms during sliding motion. Among these lubricant additives, zinc dialkyldithiophosphates (ZnDTPs) are used for more than sixty years [1-7]. These additives contain both phosphorus and sulphur having affinity to iron and other metals. They interact with steel surfaces forming protective layers, which improve the tribological properties of machine elements.

Among limitations of ZnDTPs one can name high contents of zinc, phosphorus and sulphur. This poisons exhaust after-treatment catalytic systems in automobiles with petroleum driven engines during their operation. Brought with exhaust gases products of decomposition and pyrolysis of ZnDTPs in the engine enter the catalyst as metal phosphate particulates and phosphorus oxide vapours. They deposit on catalyst surfaces and inhibit their catalytic performance. Sulphur, in the form of  $\text{SO}_2$  in the exhaust gases, reacts with oxidation catalysts and decreases their action mechanism of CO conversion to  $\text{CO}_2$  (and  $\text{NO}_x$  to  $\text{N}_2$ ) in the exhaust gases. Zinc in ZnDTP contributes to ash that consists of tiny, solid zinc salt particles. Ash can also make the catalysts inactive and its main deleterious effect is in the blocking of filters in the mechanical systems [8]. In addition to the environmental pollution caused by ZnDTPs, their primary health hazards are known to concern with eye irritation and mutagenicity [9], and occupational allergic contact dermatitis [10, 11].

Due to the important health and environmental issues, research on ashless additives and compounds with reduced amounts of sulphur and phosphorus has considerably increased during the last decade [12-16]. For example, ashless thiophosphates can form phosphate films quite similar to these formed in lubricants with ZnDTP. However, a growth of the former films is limited by the initial lack of a suitable network-forming metal cation. To reduce the amounts of zinc, sulphur and phosphorus, and to enhance the tribological performance of lubricants, ZnDTPs have been mixed with different borate additives. These include the combination of ZnDTPs with potassium borate [17], calcium borate [18, 19], and other boric

additives [20]. It has been found that admixing of borate additives to ZnDTPs has improved tribological performances of lubricants.

Organoboron compounds as additives in lubricants possess a combination of good tribological properties, as were proven during last decade. These new class of compounds has already found its applications as friction modifiers, corrosion inhibitors, antioxidants and as promising antiwear additives in lubricants [21-26]. Boron-containing compounds are believed to be an attractive alternative for commercially available lubricant additives [27]. It is known that crystalline or amorphous boron, boron nitride and metal boride are very hard materials [28]. Recently it was found that Rhenium boride ( $\text{ReB}_2$ ) synthesized in mild chemical conditions has an average hardness of 48 GPa, which is even larger than this for boron nitride materials [29]. Therefore, hard iron boride phases ( $\text{Fe}_2\text{B}$ ) can also form on steel surfaces under mildly elevated local temperature (300 – 400°C) and pressure on surface nano-size asperities at the boundary lubrication conditions [30, 31]. A hard metal boride layer on steel surfaces is, probably, additionally supported by a glassy boron-phosphate coating, which is also formed in the tribofilm. Both layers provide an additional benefit for antiwear tribofilm performance by protecting metal surfaces from damage during sliding motion in tribological applications.

In this work, aiming at the specific properties of boron containing protective metal coatings, novel compounds, containing both the borate and the dialkyldithiophosphate groups chemically bound in a single molecule, were synthesized. Two novel organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate with long alkyl chains were characterized by the elemental analysis and spectroscopic techniques. Thermal characterizations of these new compounds were performed and the results were discussed in detail here. Tribological performances of these novel compounds were evaluated in comparison with *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II), ZnDTP, in the concentration range 0.1-1.0 wt % of additives in mineral base oil.

## 2 Experimental Section

### 2.1 Chemicals

Phosphorus pentasulphide,  $\text{P}_2\text{S}_5$  (Aldrich, 99 % purity), 1-octanol (Prolabo, 97 % purity), 1-decanol (Merck, >99 % purity), 2-chloroethanol (Fluka, >99 % purity), sodium sulphate (Merck, analytical grade), potassium hydroxide pellets (Merck, analytical grade), boric acid (Merck, analytical grade) and toluene (Fluka, > 99.7 % purity) were used as received. The

commercially available ZnDTP contains a mixture of 85 % *O,O'*-di-*iso*-butyl-dithiophosphato-zinc(II) and 15 % *O,O'*-di-*n*-octyl-dithiophosphato-zinc(II) [32]. In this study, we used ZnDTP (as a reference compound) with the same number of carbon atoms in alkyl chains as in the commercial ZnDTP additive but we selected *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) instead of Zn *iso*-BuDTP because of the following reasons: *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) is a viscous liquid at room temperature and it is easily miscible with the mineral base oil used in this study. In contrary, Zn-*iso*-BuDTP is a solid at room temperature poorly soluble in the base oil, if a liquid ZnDTP complex with larger alkyl chains is not used in the same package. *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) was synthesized as in ref. [33]. The purity of the latter ZnDTP and its corresponding potassium salt was controlled by  $^{31}\text{P}$  NMR: for *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) (145.70 MHz,  $\delta$ ): 100.29 ppm [34] and  $^{31}\text{P}$  NMR for potassium salt (145.70 MHz, ethanol,  $\delta$ ) 112.72 ppm.

## 2.2 General procedure for the synthesis of organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate

The desired organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate were synthesized by an approach, which we have reported previously [35]. In the first step, 20 mmol of phosphorus pentasulphide ( $\text{P}_2\text{S}_5$ ) was treated with 80 mmol of a corresponding alcohol and the reaction mixture was stirred at 80-100 °C for 3 hours. An equivalent amount of potassium hydroxide was added in the form of 50% aqueous solution with continuous stirring at room temperature. Potassium *O,O'*-dialkyldithiophosphates were obtained in a 70-75 % yield. In the second step, an aqueous suspension of potassium *O,O'*-dialkyldithiophosphates (20 mmol) were reacted with chloroethanol (20 mmol). The resulting reaction mixture was refluxed for 3 hours to get S-hydroxyethyl-*O,O'*-dialkyldithiophosphates (yield 75-80%). In the third step, a solution of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate (20 mmol) in 80 mL toluene was mixed with boric acid (20 mmol) and a corresponding alcohol (40 mmol) in a 250 mL round-bottom flask. The reaction mixture was refluxed for 6 hours under nitrogen atmosphere and water was continuously removed from the reaction mixture. The products formed were distilled at 0.2 mmHg, 120 °C for 30 minutes to remove traces of solvent or unreacted alcohol.

### 2.2.1 S-(di-*n*-octylborate)-ethyl-*O,O'*-di-*n*-octyldithiophosphate (DOB-EDTP)

A transparent viscous liquid, yield 90 %. Anal. Calcd for  $\text{C}_{34}\text{H}_{72}\text{O}_5\text{PS}_2\text{B}$  (MW. 666.75): C, 61.3; H, 10.9; B, 1.62. Found: C, 63.5; H, 11.3; B, 1.58.



FT-IR (KBr,  $\text{cm}^{-1}$ ): 2956, 2927, 2856  $\nu(\text{C-H, stretching})$ ; 1466  $\nu(\text{CH}_2, \text{bending})$ ; 1418  $\nu(\text{CH}_3, \text{bending})$ ; 1337  $\nu(\text{B-O, stretching})$ ; 987  $\nu(\text{P-OC, stretching})$ ; 729  $\nu(\text{P=S, stretching})$ ; 666  $\nu(\text{P-S, stretching})$ .

$^1\text{H}$  NMR (359.929 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.88 (12H, t,  $^3J_{\text{HH}} = 6.37$  Hz,  $\text{CH}_3$ ); 1.26-1.40 (40H, m,  $-\text{CH}_2-$ ); 1.48-1.56 (4H, m,  $\text{CH}_2\text{CH}_2\text{OB}$ ); 1.67-1.75 (4H, m,  $\text{CH}_2\text{CH}_2\text{OP}$ ); 3.01 (2H, dt,  $^3J_{\text{HP}} = 16.65$ ,  $^3J_{\text{HH}} = 6.37$ ,  $\text{CH}_2\text{S}$ ); 3.76 (4H, t,  $^3J_{\text{HH}} = 6.50$  Hz,  $\text{CH}_2\text{OB}$ , octyl chains); 3.96 (2H, t,  $^3J_{\text{HH}} = 6.42$  Hz,  $\text{CH}_2\text{OB}$ , ethyl); 4.01-4.18 (4H, m,  $\text{CH}_2\text{OP}$ ).

$^{13}\text{C}$  NMR (90.567 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 14.26 ( $4 \times \text{CH}_3$ ); 22.84 ( $4 \times \text{CH}_2-\text{CH}_3$ ); 26.01, 28.15, 29.52, 30.70, 32.01, ( $20 \times \text{CH}_2$ , octyl chains); 34.85 ( $1 \times \text{CH}_2-\text{S}$ ); 63.41 ( $3 \times \text{CH}_2-\text{O-B}$ ); 68.09 ( $2 \times \text{CH}_2-\text{O-P}$ ) ppm.

$^{31}\text{P}$  NMR (145.70 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 95.88 ppm.

$^{11}\text{B}$  NMR (115.48 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 17.52 ppm.

### 2.2.1 S-(di-*n*-decylborate)-ethyl-*O,O'*-di-*n*-decyldithiophosphate (DDB-EDTP)

A transparent viscous liquid, yield 92 %. Anal. Calcd for  $\text{C}_{42}\text{H}_{88}\text{O}_5\text{PS}_2\text{B}$  (MW. 779.02): C, 64.6; H, 11.4; B, 1.40. Found: C, 67.6; H, 11.8; B, 1.64.

FT-IR (KBr,  $\text{cm}^{-1}$ ): 2955, 2926, 2855  $\nu(\text{C-H, stretching})$ ; 1466  $\nu(\text{CH}_2, \text{bending})$ ; 1417  $\nu(\text{CH}_3, \text{bending})$ ; 1337  $\nu(\text{B-O, stretching})$ ; 989  $\nu(\text{P-OC, stretching})$ ; 729  $\nu(\text{P=S, stretching})$ ; 666  $\nu(\text{P-S, stretching})$ .

$^1\text{H}$  NMR (359.929 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.88 (12H, t,  $^3J_{\text{HH}} = 6.51$  Hz,  $\text{CH}_3$ ); 1.25-1.32 (56H, m,  $-\text{CH}_2-$ ); 1.48-1.55 (4H, m,  $\text{CH}_2\text{CH}_2\text{OB}$ ); 1.66-1.74 (4H, m,  $\text{CH}_2\text{CH}_2\text{OP}$ ); 3.01 (2H, dt,  $^3J_{\text{HP}} = 16.31$ ,  $^3J_{\text{HH}} = 6.28$ ,  $\text{CH}_2\text{S}$ ); 3.76 (4H, t,  $^3J_{\text{HH}} = 6.45$  Hz,  $\text{CH}_2\text{OB}$ , decyl chains); 3.96 (2H, t,  $^3J_{\text{HH}} = 6.42$  Hz,  $\text{CH}_2\text{OB}$ , ethyl); 4.02-4.18 (4H, m,  $\text{CH}_2\text{OP}$ ).

$^{13}\text{C}$  NMR (90.567 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 14.26 ( $4 \times \text{CH}_3$ ); 22.88 ( $4 \times \text{CH}_2-\text{CH}_3$ ); 24.26, 26.01, 28.38, 29.83, 30.96, 31.19, 32.10, ( $28 \times \text{CH}_2$ , decyl chains); 33.54 ( $1 \times \text{CH}_2-\text{S}$ ); 63.38 ( $3 \times \text{CH}_2-\text{O-B}$ ); 68.01 ( $2 \times \text{CH}_2-\text{O-P}$ ) ppm.

$^{31}\text{P}$  NMR (145.70 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 95.90 ppm.

$^{11}\text{B}$  NMR (115.48 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 17.50 ppm.

## 2.3 Physical Characterization

The elemental analysis for C and H was performed at Mikrokemi AB, Uppsala, according to procedures described on their homepage [36]. The elemental analysis of B (ICP-MS) was carried out at ALS laboratory group, Luleå; detailed procedure is described on their homepage [37].

FT-IR spectra were recorded on a Perkin-Elmer 2000 spectrometer in the range 4000-370  $\text{cm}^{-1}$ . Sampling was performed by placing a droplet of a compound onto a KBr pellet. Multinuclear NMR spectra were recorded on a Varian/Chemagnetics InfinityPlus CMX-360 ( $B=8.46$  T) spectrometer in  $\text{CDCl}_3$  (5-10 vol % concentration) in 10 mm glass tubes ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{11}\text{B}$ ) using TMS as an internal reference for  $^1\text{H}$  (0 ppm), the 77.2 ppm resonance peak of  $\text{CDCl}_3$  for  $^{13}\text{C}$ ,  $\text{H}_3\text{PO}_4$  (85%) as an external reference (0 ppm) for  $^{31}\text{P}$  and  $\text{Et}_2\text{O}.\text{BF}_3$  as an external reference (0 ppm) for  $^{11}\text{B}$ .

## 2.4 Thermal Analyses

Thermal analyses of the synthesized compounds were performed by Netzsch STA 409 instrument equipped with simultaneous thermogravimetric (TG), differential thermal analysis (DTA) coupled with a quadrupole mass spectrometer (QMS) at a rate of  $20^\circ\text{C}/\text{min}$  and with argon flow rate of  $100 \text{ mL}/\text{min}$ . The sensitivity of this STA instrument is  $\pm 1 \mu\text{g}$ .

## 2.5 Tribological Evaluation

Antiwear and friction characteristics of these compounds as additives in the base oil were evaluated with a four-ball tribometer. The additives were mixed with mineral base oil at fixed weight (%) concentrations of 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 % using an analytical balance. The physicochemical properties and the elemental analysis of the base oil used in this study are given in Table 1. Steel balls used in the standard four-ball tribometer tests were 12.7 mm diameter and made of AISI 52100 steel with a composition of C, 0.95–1.10%; Si, 0.15–0.30%; Mn, <0.25%; P, <0.03%; S, <0.025%; Cr, 1.30–1.60%, with a hardness HRC 60–67.

Table 1 Properties of the mineral base oil.

Density ( $\text{gml}^{-1}$ )	0.8135
Viscosity (m Pa.s) at $40^\circ\text{C}$	17.5
Viscosity (m Pa.s) at $100^\circ\text{C}$	4.9
Carbon (%)	$86.0 \pm 0.7$
Hydrogen (%)	$14.5 \pm 0.5$

Dependence of wear scar diameter (WSD) and friction coefficients on additive concentration (wt %) were measured at a rotating speed of 1450 rpm, test duration time of 30 min, load 392 N and at room temperature (294 K).

Wear scar diameters of the three lower balls were measured in an optical profiler (WYCO NT 1100). Then a mean of these three values was calculated and reported in the paper as the

WSD. Before each test, the ball holder was washed with petroleum ether and the balls were cleaned ultrasonically in petroleum ether and thoroughly air-dried.

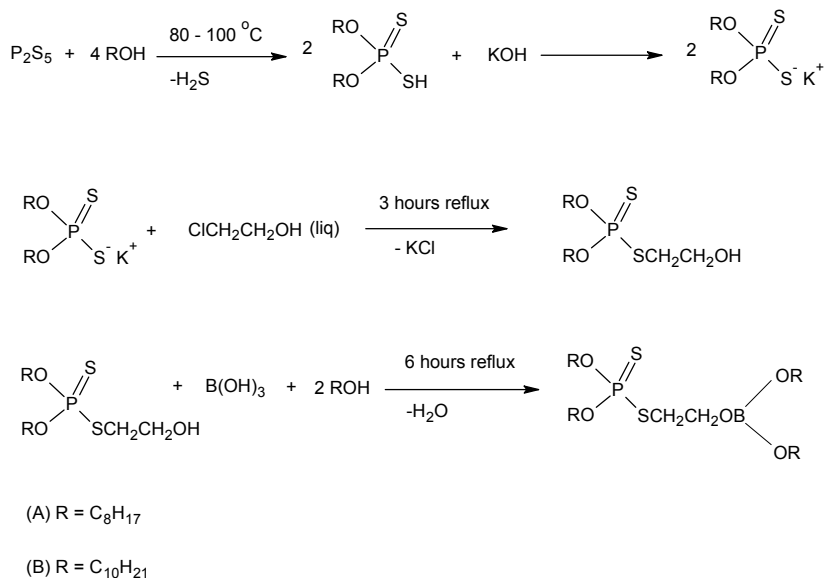
## 2.6 Surface Characterization

The morphology of the wear scars after tribological testing was studied using an optical profiler and SEM with EDS. 3D topography was obtained with WYCO NT 1100 optical profiler. Philips XL 30 scanning electron microscope (SEM) equipped with LaB6 emission source was used for surface analysis. A link ISIS Ge energy dispersive X-ray detector (EDS) attached to SEM was used to probe the elemental composition of tribofilms formed in the worn scar regions of the ball surfaces. Prior to the analysis, the balls were cleaned ultrasonically for 5 min with petroleum ether, in order to eliminate the residual lubricant.

## 3 Results and discussion

### 3.1 Spectroscopic characterization

Two novel compounds, organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate were synthesized using the reaction path way shown in Scheme 1.



Scheme 1. Synthesis of organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate

Figure 1 shows the molecular vibration spectrum of DDB-EDTP with a set of characteristic peaks. Absorption frequencies of the aliphatic C-H vibrations in the alkyl groups of these compounds were observed in the range of 2956-2855  $\text{cm}^{-1}$ . Broad bands present in the FTIR spectra of these two compounds in the regions of 989-987, at 729 and 666  $\text{cm}^{-1}$  are assigned to stretching modes  $\nu(\text{P-OC})$ ,  $\nu(\text{P=S})$  and  $\nu(\text{P-S})$ , respectively. High frequencies of these latter two characteristic bands, as compared with bidentate complexes suggest the monodentate nature of dithiophosphates in these compounds [38, 39]. No large differences in the latter two stretching frequencies of DOB-EDTP and DDP-EDTP were detected, because of similar structures of these two compounds. In both these compounds, a strong band was also observed at 1337  $\text{cm}^{-1}$ , which was assigned to the stretching frequency of the B-O bond.

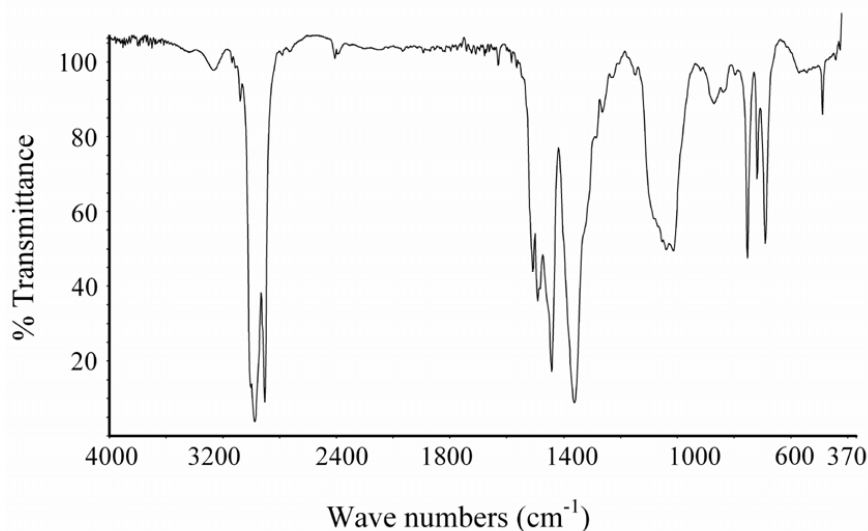


Figure 1. FTIR spectrum of DDB-EDTP.

$^{31}\text{P}$  NMR spectra of these compounds in  $\text{CDCl}_3$  gave singlets at 95.88 and 95.90 ppm, for DOB-EDTP and DDB-EDTP, respectively. These values for  $^{31}\text{P}$  chemical shifts are typical for the dithiophosphate,  $\text{P}(\text{O})_2(\text{S})(\text{S-C})$ , group that indirectly confirms binding of borate to dithiophosphate via the hydroxyethyl group in the named compounds [40].

$^{11}\text{B}$  NMR spectra of these compounds in  $\text{CDCl}_3$  also revealed singlets at 17.52 and 17.50 ppm for DOB-EDTP and DDB-EDTP, respectively, which are typical for borate and alkylborate compounds [41].

### 3.2 Thermal Analyses

For lubricant additives used in mechanical systems at elevated temperature, it is important to study the effect of temperature on their physicochemical properties, such as thermal stability, weight loss, and the nature of compounds in the course of their thermal decomposition. Two types of decomposition products were detected during the thermal decomposition of both DOB-EDTP and DDB-EDTP in argon atmosphere: solid residues with melting points more than  $500^\circ\text{C}$  and volatile products of pyrolysis of the alkyl and dithioalkyl groups (below  $500^\circ\text{C}$ ). The latter products were also analyzed by quadrupole mass spectrometry (QMS), which is discussed below.

#### 3.2.1 Thermogravimetric Analysis

Thermogravimetric/Derivative thermogravimetric (TG/DTG) curves for both DOB-EDTP and DDB-EDTP are shown in Figure 2. Thermal decompositions of both these compounds involve only one major step, the onset of which occurs at  $284.3$  and  $293.1^\circ\text{C}$  for DOB-EDTP (Fig. 2a) and DDB-EDTP (Fig. 2b), respectively. TG/DTG curves indicate the complete decomposition of the molecules in a single step, which involves both a breakage of PS and PO bonds in the dithiophosphate group and pyrolysis of long alkyl chains. The total weight losses during these tests are 87 and 89 wt % for DOB-EDTP and DDB-EDTP, respectively. It reveals that the compounds are decomposed mostly into volatile products and less than 13 wt % remains as solid residues. The highest rate of the weight loss during the tests (at  $298.9$  and  $307.0^\circ\text{C}$  for DOB-EDTP and DDB-EDTP, respectively) can be read out from DTG curves in Fig. 2: 74 %/min for DOB-EDTP and 77 %/min for DDB-EDTP. The TG and DTG curves revealed that both decompositions and weight losses of these compounds occur in a single step.

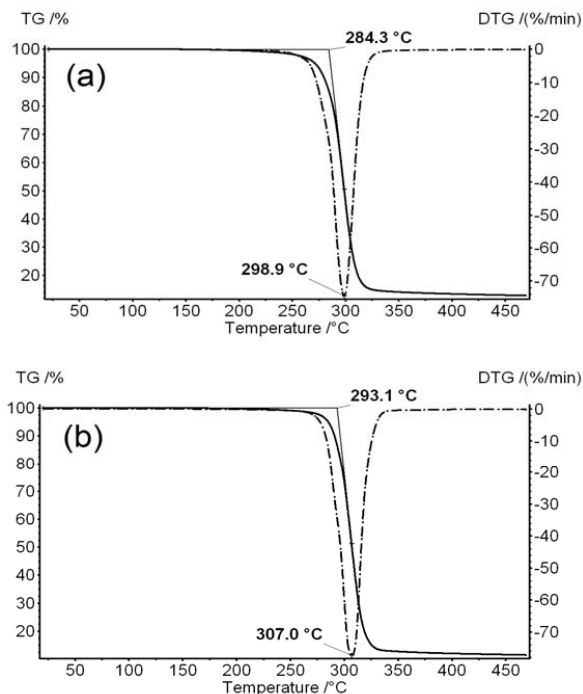


Figure 2. TG/DTG curves for DOB-EDTP (a) and DDB-EDTP (b), at a heating rate of 20°C/min and argon flow rate of 100 mL/min.

### 3.2.2 Differential Thermogravimetric Analysis

Differential thermal analysis (DTA) curves of organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkylidithiophosphate compounds under study are shown in Figure 3. Similar thermal events were observed for both DOB-EDTP and DDB-EDTP with characteristic exothermic and endothermic peaks. The exothermic peaks at 284.0 and 297.0 °C for DOB-EDTP and DDB-EDTP, respectively, represent the thermal decomposition of these compounds. The exothermic peaks are followed by endothermic ones at 317.1 and 323.4 °C for DOB-EDTP and DDB-EDTP, respectively, most probably representing phase transitions, such as melting and boiling, in the products of decomposition of the boron compounds under study [40].

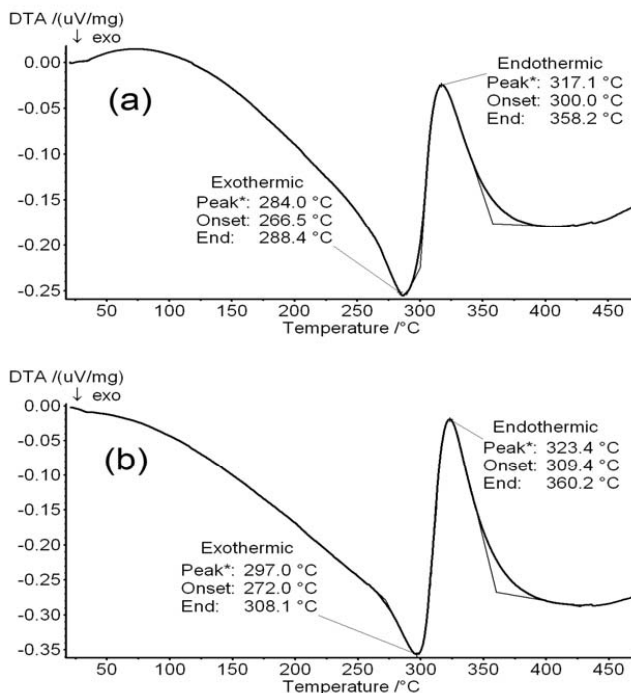


Figure 3. DTA curves for DOB-EDTP (a) and DDB-EDTP (b), at a heating rate of 20°C/min and argon flow rate of 100 mL/min.

### 3.2.3 Quadrupole Mass Spectrometric Analysis

It is known that the main volatile decomposition products of dialkyldithiophosphates are hydrogen sulphide and olefins [43, 44]. Therefore, the decomposition of the parent DOB-EDTP and DDB-EDTP compounds and the formation of volatile products as a function of temperature under a constant flow of argon gas were also analyzed by quadrupole mass spectrometry (QMS). A number of volatile products are formed and evolved in the temperature range from 20 to 500 °C in this study. Evolution curves for some selected products formed in the course of the thermal decomposition of both DOB-EDTP and DDB-EDTP are shown in Figure 4 and 5, respectively. The formation of hydrogen sulphide ( $\text{H}_2\text{S}^+$ ) with  $m/e=34$  is observed during pyrolysis of both DOB-EDTP and DDB-EDTP. Olefins with a different number of carbon atoms are formed under pyrolysis of parent alkyl chains in boron compounds under study. Relative intensities of hydrocarbon fragments in comparison with  $\text{H}_2\text{S}^+$  are plotted for both parent compounds (see Fig. 4 and 5). The propenyl cations ( $\text{C}_3\text{H}_5^+$  with  $m/e=41$  and  $\text{C}_3\text{H}_6^+$  with  $m/e=42$ ) and butenyl cations ( $\text{C}_4\text{H}_7^+$  with  $m/e=55$  and  $\text{C}_4\text{H}_8^+$

with  $m/e=56$ ) have rather similar evolution patterns and they are the principle components in the mixture of volatile products of decomposition of these compounds. Olefin cations with larger molecular weights ( $C_5H_9^+$ ,  $C_5H_{10}^+$ ,  $C_6H_{11}^+$ ,  $C_6H_{12}^+$ ,  $C_7H_{13}^+$  and  $C_7H_{14}^+$ ) have smaller intensities in the QMS profiles as compared with cations with three and four carbon atoms in the chain.

These two compounds are thermally more stable as compared to S-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate [45], in which boron is directly bonded to sulphur atom of dialkyldithiophosphate. The thermal behaviour of this compound was carried out under the same experimental conditions as used in this study. Interestingly, in DOB-EDTP and DDB-EDTP, the pyrolysis of alkyl chains takes place before the formation of  $H_2S^+$ , while the formation of  $H_2S^+$  occurred before pyrolysis of alkyl chains for above mentioned compound. It indicates that B-S bond is thermally less stable than C-S bond.



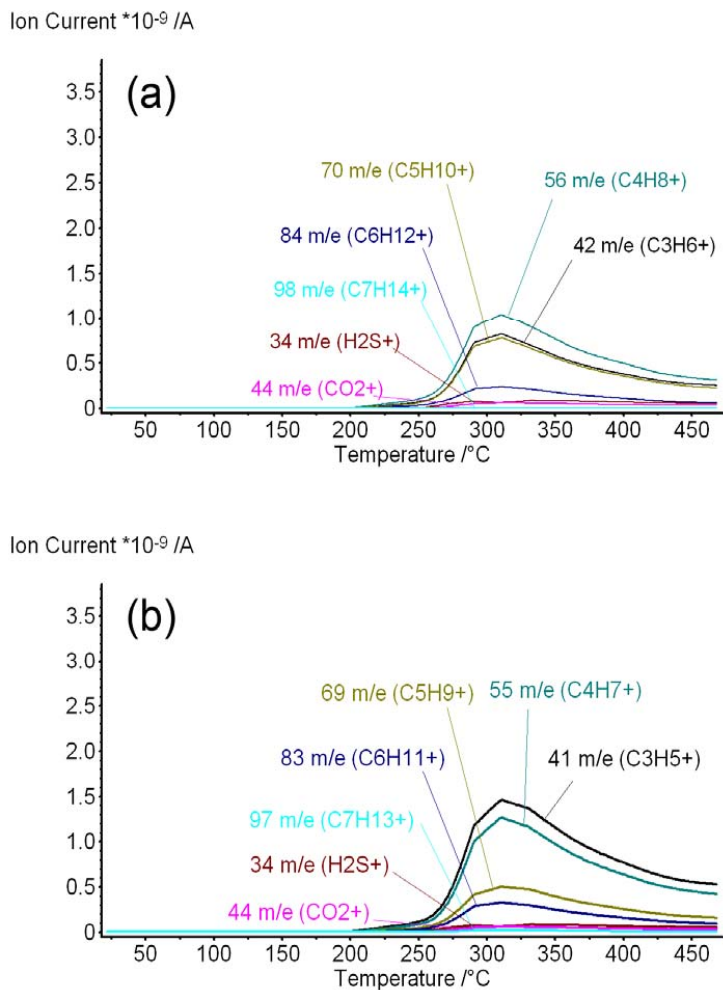


Figure 4. QMS profiles of DOB-EDTP at a heating rate of 20°C/min and argon flow rate of 100 ml/min. (a) Even molecular weight hydrocarbon fragments, (b) Odd molecular weight hydrocarbon fragments.

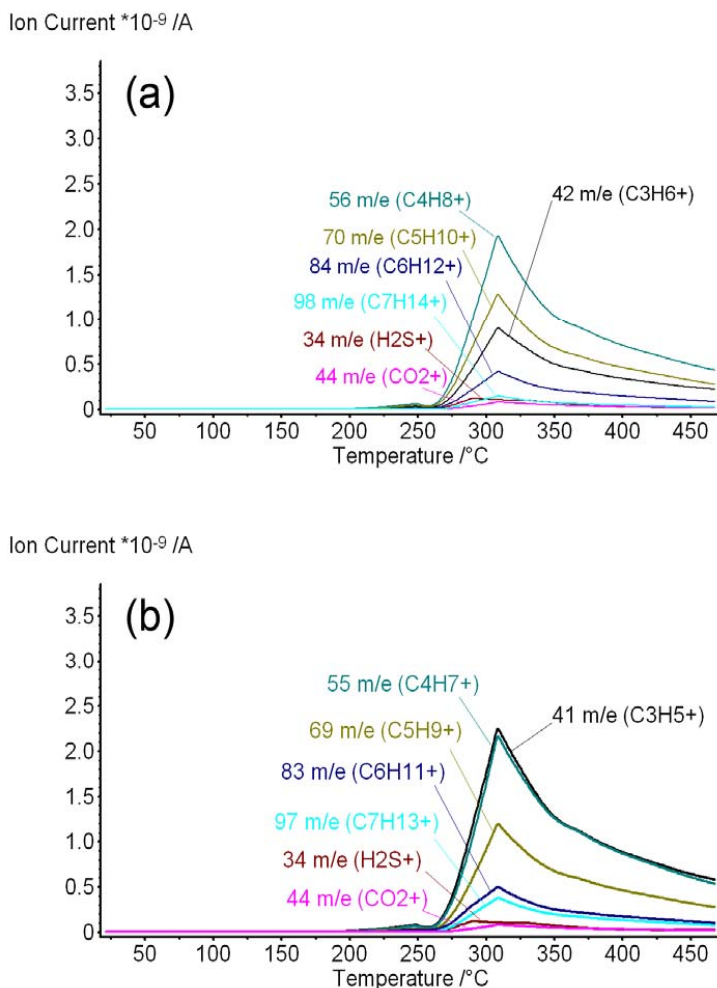


Figure 5. QMS profiles of DDB-EDTP at a heating rate of 20°C/min and argon flow rate of 100 ml/min. (a) Even molecular weight hydrocarbon fragments, (b) Odd molecular weight hydrocarbon fragments.

### 3.3 Tribological Evaluation

The antiwear and friction properties of the organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate were evaluated in comparison with ZnDTP using the same tribological test conditions. Figure 5 shows variations of the WSD measured on the steel balls lubricated with the base oil containing DOB-EDTP, DDB-EDTP or ZnDTP as additives in the mineral

base oil at different concentrations: All three compounds under study are prone to reduce wear when they are admixed with the base oil even at very small concentrations.

Table 2. Variations of the WSD (mm) and the friction coefficient (an average over last 10 min) with additives concentration (wt %).

Additive concentration (%)	ZnDTP		DOB-EDTP		DDB-EDTP	
	WSD $\pm$ (SD) mm	Friction coefficient $\pm$ (Variation)	WSD $\pm$ (SD) mm	Friction coefficient $\pm$ (Variation)	WSD $\pm$ (SD) mm	Friction coefficient $\pm$ (Variation)
0	0.602 (0.012)	0.042 (0.006)	0.602 (0.012)	0.042 (0.006)	0.602 (0.012)	0.042 (0.006)
0.1	0.546 (0.017)	0.082 (0.007)	0.504 (0.014)	0.057 (0.004)	0.472 (0.014)	0.058 (0.005)
0.2	0.533 (0.013)	0.074 (0.006)	0.483 (0.008)	0.056 (0.006)	0.450 (0.011)	0.059 (0.004)
0.4	0.493 (0.008)	0.065 (0.005)	0.456 (0.013)	0.054 (0.006)	0.445 (0.010)	0.063 (0.007)
0.6	0.473 (0.011)	0.072 (0.005)	0.493 (0.010)	0.051 (0.006)	0.455 (0.003)	0.063 (0.006)
0.8	0.492 (0.008)	0.066 (0.005)	0.503 (0.012)	0.052 (0.005)	0.474 (0.014)	0.061 (0.005)
1.0	0.516 (0.016)	0.066 (0.005)	0.494 (0.012)	0.055 (0.005)	0.463 (0.016)	0.069 (0.006)

For organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate (DOB-EDTP and DDB-EDTP), a decrease in the WSD found upto 0.4 wt % of the additives in the base oil. Then, WSD increases slightly with an increase of concentration of these additives. WSD for balls tested in the base oil with ZnDTP also follows a similar way as those for lubricants with the novel boron additives studied here. WSD first decreases and reaches its minimum at 0.6 wt % of ZnDTP and then WSD increases with the following increase of concentration of ZnDTP in the base oil. The latter increase in WSD for ZnDTP (DOB-EDTP and DDB-EDTP) is, probably, due to a corrosive action of sulphur in these additives [46-48]. Optimum concentrations found for the wear reducing ability of an additive in the base oil were 0.4 and 0.6 wt % for the new additives and ZnDTP, respectively, at the conditions of the tribological test (30 min under load 392 N at room temperature *ca* 294 K, see Fig. 5 and Table 2).

A comparison of the antiwear propensity of the novel boron based additives as a function of their concentrations in the mineral base oil reveals that both DOB-EDTP and DDB-EDTP reduce wear even at relatively low concentrations (< 0.4 wt %). On the contrary, the wear scar

diameter is considerably larger for samples with ZnDTP at concentrations lower than 0.6 wt %. Also, WSD increases when concentration of ZnDTP is increased from 0.6-1.0 wt %, while Comparing these three compounds under discussion, DDB-EDTP in the mineral base oil has the best antiwear performance at all concentrations studied (0.1 – 1.0 wt %).

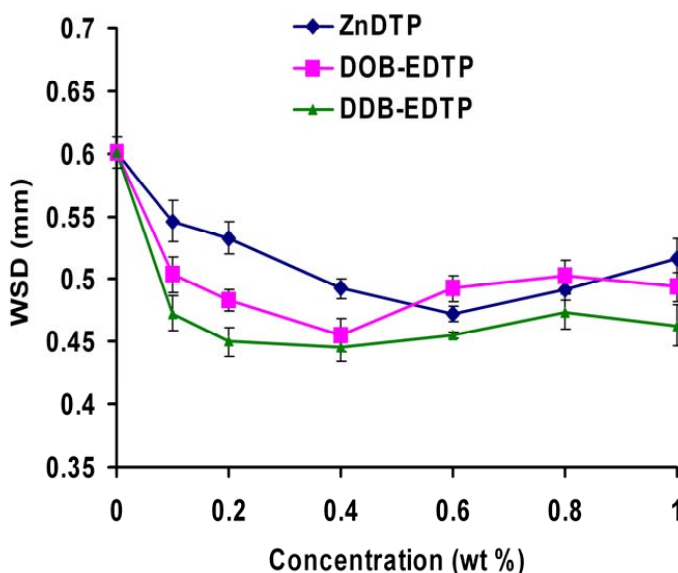


Figure 6. Variations in the mean WSD (mm) on the lower three steel balls with additives concentration (wt %). Top (blue): ZnDTP, middle (pink): DOB-EDTP; bottom (green) DDB-EDTP.

Figure 7 shows variation in the coefficient of friction with concentration (wt %) of the novel additives and ZnDTP in the base oil. Incorporation of either of the aforementioned additives in the base oil increases coefficient of friction of the formulated lubricant. An increase in the friction coefficient is found even at a very low additives concentration (0.1 wt %), however, the former is smaller for both DOB-EDTP and DDB-EDTP as compared with ZnDTP. In addition, the coefficient of friction remains more stable for the oil with DOB-EDTP and DDB-EDTP as compared with ZnDTP in the concentration range tested, 0.1-1.0 wt % (see Fig. 7 and Table 2). An increase in the friction coefficient upon admixture of additives in the base oil is caused by the formation of stable tribofilms as a result of tribochemical reactions of the additives with steel surfaces during the wear processes. It is already known that the

tribofilms formed by ZnDTP increase their friction coefficient, which is probably due to the higher shear strength of the films formed by ZnDTP [49, 50]. Both these DOB-EDTP and DDB-EDTP also increase their friction coefficient. It turned to be that all additives in the base oil at as low concentration as 0.1 wt % do form tribofilms on the steel surfaces.

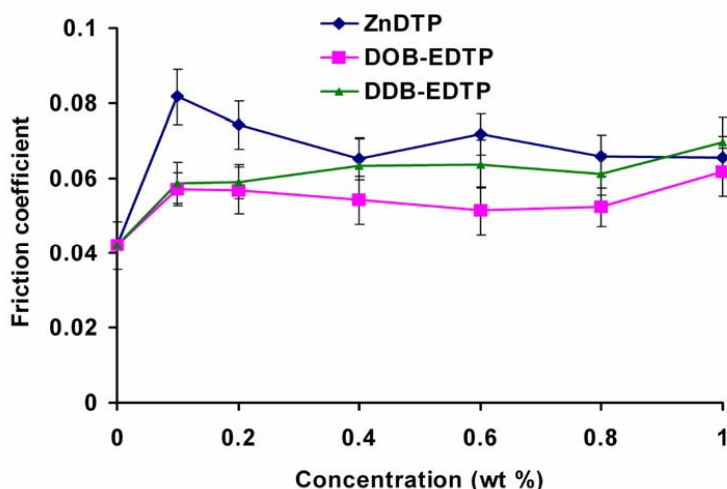


Figure 7. Variation in the friction coefficient (an average over last 10 min) with additives concentration (wt %) in the base oil. Top (blue): ZnDTP, middle (green) DDB-EDTP; bottom (pink): DOB-EDTP.

A variation in the friction coefficient with time is shown in Figure 8 for the base oil only and the oil containing the aforementioned additives (mean values of the friction coefficient over ten last minutes of the tribological test are also given in Figure 7). The friction coefficient with the base oil is lower as compared to the oil with additives but it is not stable and varies considerably during the test. Similarly, the friction coefficient for the base oil containing ZnDTP at concentration 0.2 wt % is not stable and it increases slowly with time (Fig. 8a). At higher concentrations ( $>0.8$  wt %) it is more stable. The friction coefficient for the oil containing either DOB-EDTP or DDB-EDTP does not vary much with time at both low (0.2 wt %) and high (1.0 wt %) additive concentrations (Figs. 8a and 8b). To conclude, stability of the friction coefficient with time can be ranked as DDB-EDTP > DOB-EDTP > ZnDTP > BO.

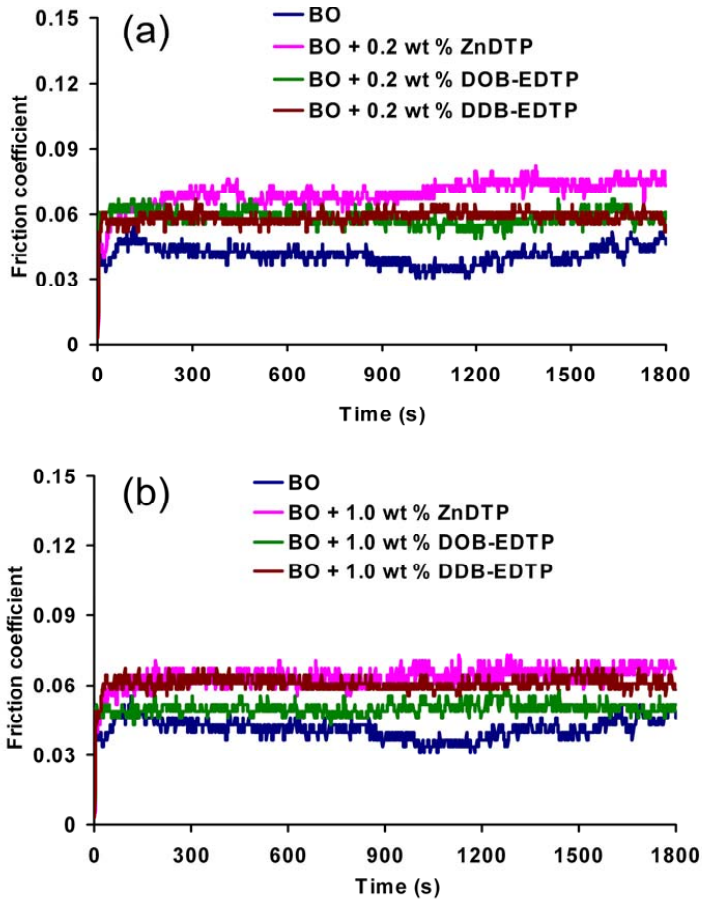


Figure 8. Variations of the friction coefficient with time (s) for the base oil (BO), base oil with ZnDTP, base oil with DOB-EDTP and base oil with DDB-EDTP. (a) 0.2 wt % and (B) 1.0 wt % of the additives. Top (pink): ZnDTP, upper middle (maroon): DDB-EDTP, lower middle (green): DOB-EDTP, bottom (blue): BO

### 3.4 Surface Analysis

The surface topography of the wear scars on the steel balls after tribological tests were studied by an optical profiler. Figure 9 shows 3D images of the worn surfaces lubricated with the base oil only and those containing 1 wt % of the three additives under study. These images clearly indicate steel antiwear properties of these additives in the base oil. Balls lubricated with the base oil only have acquired significantly larger wear scars (Fig. 9a) as compared to these lubricated with the base oil containing additives (Fig. 9b - 9d).

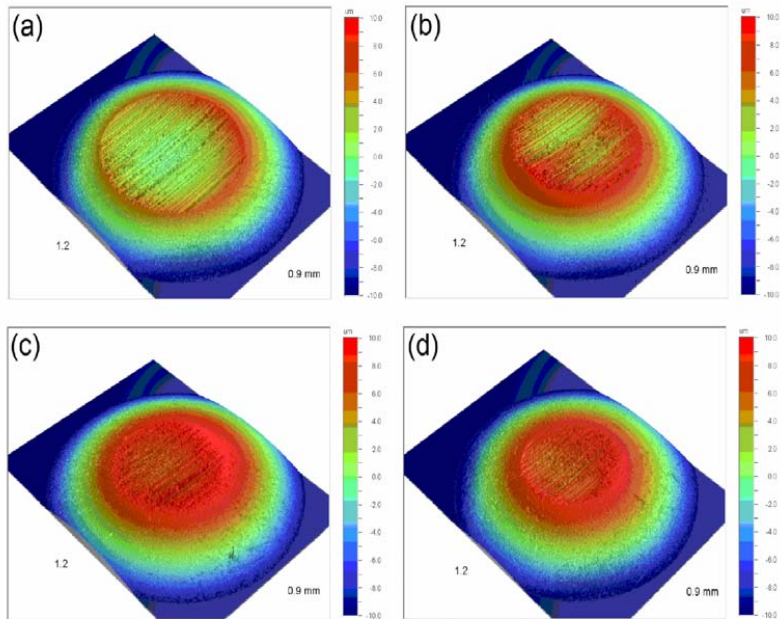


Figure 9. 3D images of worn ball surfaces lubricated with base oil (a); base oil with 1.0 wt % ZnDTP (b); base oil with 1.0 wt % DOB-EDTP (c) and base oil with 1.0 wt % DDB-EDTP (d).

Figures 10-12 show results of the surface analysis obtained using Scanning Electron Microscopic/Energy Dispersive X-ray Spectroscopy (SEM/EDS) techniques: Both morphologies and compositions of tribofilms formed in wear scars on steel ball surfaces in the tribological tests using the base oil with the aforementioned additives were studied. SEM/EDS data obtained suggest on the formation of tribofilms containing both sulphur and phosphorus at various relative compositions depending on the type of additive and its concentration.

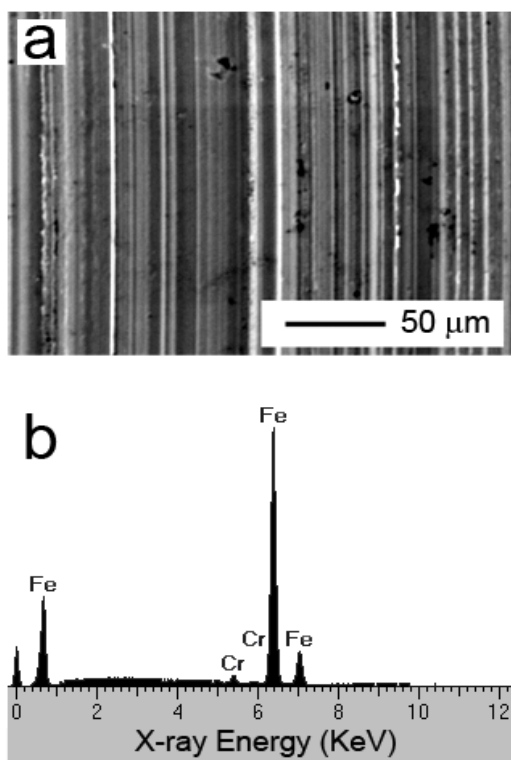


Figure 10. SEM micrograph and the corresponding EDS analysis of worn ball surface lubricated with the mineral base oil without additives.

Figure 10 shows a SEM micrograph and a corresponding EDS spectrum of the worn ball surface lubricated with the base oil without additives. This micrograph shows clearly wide grooves, which indicates a significant wear. Figure 11 shows worn surfaces lubricated by the base oil with 0.4 wt % of ZnDTP (Fig. 11a), DOB-EDTP (Fig. 11b) or DDB-EDTP (Fig. 11c). It is obvious that the wear process has decreased considerably due to the additives into the base oil. The surfaces are smoother (see Figs. 11a – 11c) as compared to the surfaces lubricated with the base oil without additives (see Fig. 10).



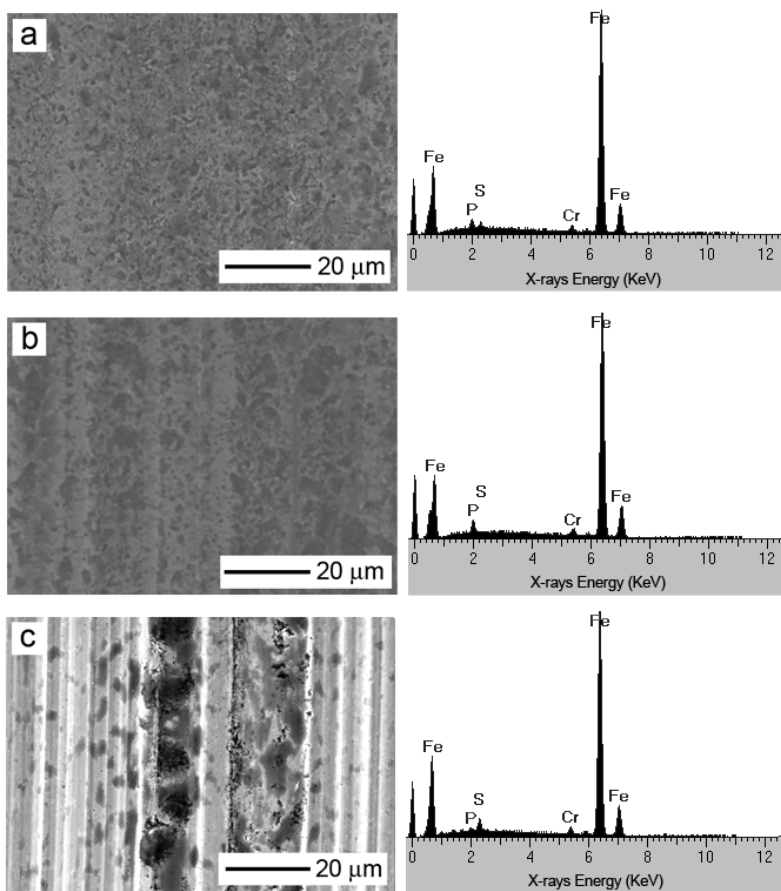


Figure 11. SEM micrographs of worn ball surfaces lubricated with the mineral base oil containing 0.4 wt % of DOB-EDTP (a) 0.4 wt % of DDB-EDTP (b); or 0.4 wt % of ZnDTP (c). Corresponding EDS spectra of the whole shown area in the micrographs are given in the right column.

When the additives concentration was increased to 1.0 wt %, the ball surfaces remain smoother (see Figs. 12a - 12c). The worn ball surfaces lubricated with the mineral base oil containing either DOB-EDTP or DDB-EDTP are smoother as compared to the worn surfaces lubricated by the base oil with ZnDTP.

The corresponding EDS analysis suggests a transfer/adsorption of active elements from the additives to the steel surfaces. Figures 11 and 12 clearly show depositions of sulphur and phosphorus on the worn surfaces at both concentrations (0.4 and 1.0 wt %). Boron was not detected on the worn surfaces lubricated with the base oil containing DOB-EDTP or DDB-EDTP, because of a low sensitivity of the EDS method to light elements including boron.

Interestingly, phosphorus was the predominant element in depositions from either DOB-EDTP or DDB-EDTP (may be in the form of glassy boron phosphate glasses), while it was sulphur, which dominates in the surface layers formed by products of decomposition of ZnDTP on steel surfaces. A work on identification of the elemental composition and structure of tribofilms formed in the worn regions of steel surfaces, using surface sensitive methods such as XPS and SIMS (and solid state NMR on solid residuals of DOB-EDTP and DDB-EDTP after pyrolysis) is currently in progress in our group and will be published elsewhere.

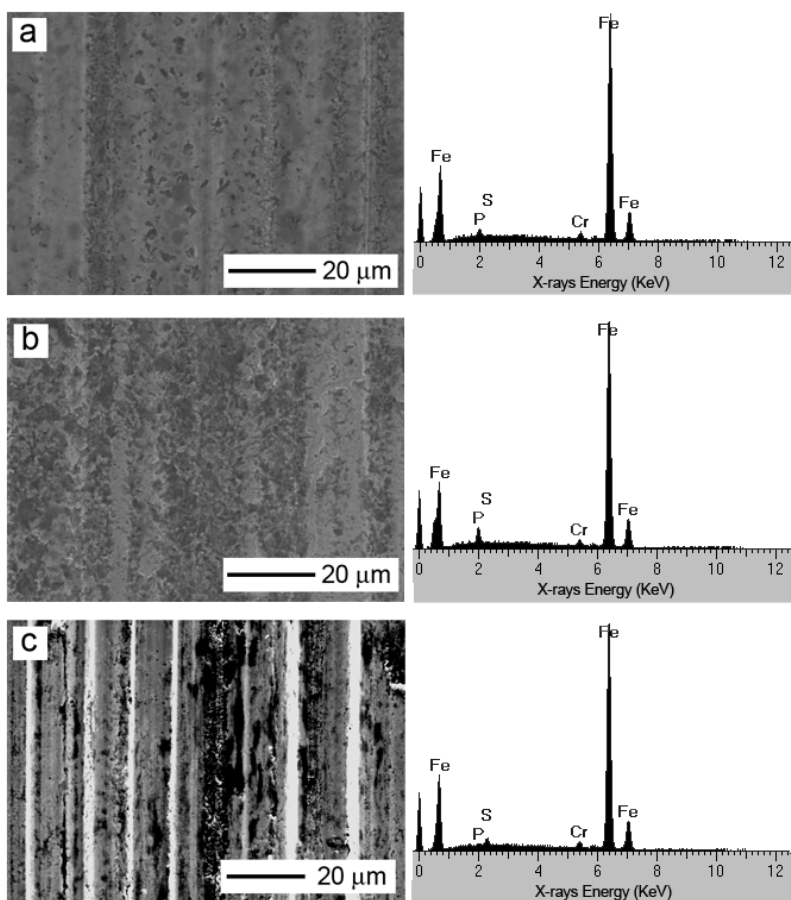


Figure 12. SEM micrographs of worn ball surfaces lubricated with the mineral base oil containing 1.0 wt % of DOB-EDTP (b); 1.0 wt % of DDB-EDTP (c); or 1.0 wt % of ZnDTP (c). Corresponding EDS spectra of the whole shown area in the micrographs are given in the right column.

## 4 Conclusions

The organoboron derivatives of S-hydroxyethyl-*O,O'*-dialkyldithiophosphate (DOB-EDTP and DDB-EDTP) were synthesized and characterized by the elemental analysis, FT-IR and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR spectroscopy. The thermal characterization (TG/DTG, DTA, and QMS analyses) was also carried out. The tribological properties of these novel additives were evaluated in comparison with *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) in mineral base oil. Both these novel compounds (DOB-EDTP and DDB-EDTP) are thermally stable up to *ca* 285 and 295°C, respectively. The parent alkyl chains decompose into several smaller molecular weights hydrocarbons, which were detected by QMS. The dominant hydrocarbon fragments were propenyl and butenyl species. The wear was significantly reduced when the novel additives were mixed in to the base oil but the friction coefficient has increased. Both DOB-EDTP and DDB-EDTP have shown better antiwear and friction properties compared with ZnDTP in the concentration range (0.1-1.0 wt %) studied. The friction coefficient was stable with time for all these concentrations of these novel additives in the base oil, while it was unstable at low concentrations of ZnDTP in the base oil. Phosphorus and sulphur were detected by SEM/EDS analysis on the worn steel surfaces at concentrations studied (0.4, and 1.0 wt %).

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