The Influence of Synthesis Method of Zinc Dialkyldithiophosphates on the Process of Additivation

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The antioxidant and antiwear additives based on zinc dialkyldithiophosphate were investigated. The relationship between the method of preparation and their utility as additives in lubricant oils were studied. The performances of zinc dialkyldithiophosphates ZnDTPh, obtained by different methods of synthesis, used as additives in lubricant and industrial greases were pointed out. ZnDTPh obtained by non-classical method has afforded excellent oxidation resistance and exhibit superior antiwear properties.

Keywords: antiwear, antioxidant, dialkyldithiophosphate

There are many instances, particularly under "Bowndary Lubrication" conditions, where two rubbing surfaces must be lubricated or otherwise protected, so as to prevent wear and to insure continued movement [1-3]. As it is well known, both wear and friction can be reduced with various degrees. The addition of a suitable additive or combination thereof, to a natural or synthetic lubricant, reduce both wear and friction of contacting surfaces and the energy required to effect movement.

This class of compounds has been extensively used in lubrication for over forty years. The most commonly used additives of this class are the zinc dialkyldithiophosphates that are conventionally added in lubricant compositions [4].

The advantage of these compounds is expressed by several highly desirable lubrication properties and by load carrying capacity properties. Their features may be offered by molecular structure. Other nonnegligible advantages include acceptable thermal stability, moderate toxicity, and considerable ease of storage and application; the zinc dialkyldithiophosphates are used in lubricants in concentrations not exceeding 1.5 % weight.

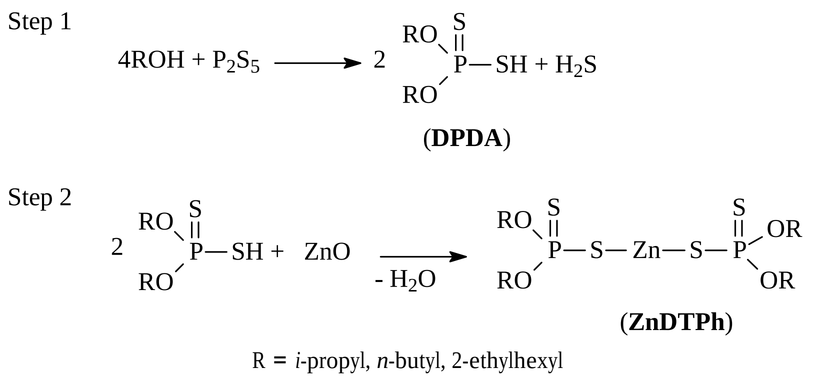
Continuing our studies on synthesis of additives for lubricating oils [5-7], we present in this paper a new technology of synthesis for zinc dialkyldithiophosphates and the influence of this synthesis method on the process of additivation. We note in this paper, **ZnDTPh** obtained by classical method with **ZnDTPh(A)**, and by the new tehnology (non-classical method), **ZnDTPh(B)**.

Experimental part

General procedures for the preparation of zinc dialkyldithiophosphates

ZnDTPh(A): Zinc dialkyldithiophosphates are synthesized in two steps (Scheme 1). In the first step *o,o'*-dialkylphosphorodithionic acid (**DPDA**) is synthesized by reaction of 4 moles of alcohols with phosphorus penta-sulfide (1.1 moles). It is better to use alcohol mixture consisting of 50-80 % a lower alcohol, (isopropanol or isobutanol) and 50-20 % a higher one (preferably 2-ethylhexanol). Due to the exotermic nature of reaction, the temperature of the reaction mixture rose to 80 °C. After addition, the temperature was maintained at 90-100 C for 3 hours under continuous stirring. The completion of reaction took place on the disappearance of O-H stretching vibration at 3300 cm^{-1} (corresponding to OH of alcohols) in the IR spectra of product. The resulting dialkyldithio-phosphoric acid is neutralized with a basically reacting zinc compound, such as zinc oxide (Step 2).

ZnDTPh(B): To the mixture of alcohols, same like in the preparation of **ZnDTPh(A)**, phosphorus pentasulfide is added as a dispersion in a 75N mineral oil, ISO-VG-46, in ratio of 1/3-1/6, P_2S_5/oil. After addition, the temperature was maintained at 90-100 °C for 3 hours under continuous stirring. The reaction was monitorized by the IR spectra of product. The resulting dialkyldithiophosphoric acid is



Scheme 1

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Table 1
CHARACTERISTICS OF THE BASE OIL

Charateristics	
Density, 20 °C	0.195
Flash Point, °C	160
Viscozity at 50 °C, cSt	5,5-5,6
Viscozity index., min.	60
Pour Point °C, max.	+6

Table 2
ELEMENTAL ANALYSES AND DECOMPOSITION TEMPERATURES

Additive	S (%)	P (%)	Zn (%)	Decomposition temperature
ZnDTPh(A)	14,5-18	8-9.5	8-9.5	130-140
ZnDTPh(B)	6-6.5	3.5-4.5	4-4.5	> 200

neutralized with a basically reacting zinc compound such as zinc oxide (Step 2).

The antiwear, antioxidant, antirust and the anticorrosion performance was tested in base oil at the 0.052, 0.07, and 0.105 % P levels for **ZnDTPh(B)**, (corresponding to 1.5; 2; and 3 % additive), and at 0.09; 0.135 and 0.180 %P levels for **ZnDTPh(A)**, (corresponding to 1; 1.5 and 2 % mass additive).

Antiwear Performance

A four-ball machine was used for studying antiwear performance of synthesized dialkyldithiophosphates according to ASTM D 2266. The antiwear performance was measured by recording the wear scar diameter under following conditions:

Load 20 daN, 40 daN
Temperature 25°C
Rotation 1500 rot/min.
Test duration 100 min ; 60 min.

Antioxidant Performance

Antioxidant performance of **ZnDTPh** (**A**) and (**B**) was determined by Rotary Bomb method (ASTM D 942).

Copper Corrosion Behaviour

The Copper corrosion behaviour was determined by the ASTM D 130:

Temperature: 100 °C
Test duration: 3 h

Rust Test

Rust test was determined by ASTM D 665. The base oil used in investigation was a parafinic oil, having characteristics presented in table 1.

Oxidation stability of lubricating greases

Antioxidant performance of **ZnDTPh** (**A**) and (**B**) in industrial greases was determined by the Oxigen Bomb Method (ASTM D 942; IP 142). This method describes the test for determining the resistance of lubricating greases to oxidation for long periods of time.

The samples of modified greases were oxidised in a bomb heated to 99 °C and filled with oxygen at 785 KPa (7.85 barr). The level of pressure was observed and recorded on stated intervals. The degree of oxidation after a given period of time was determined by the measured decrease in oxygen pressure. For the majority of commercial greases, condition for decrease in oxygen pressure at 100 hours is less than 0.33 barr (33 KPa).

Results and discussion

In the classical procedure, the reaction between alcohol ROH and phosphorus pentasulfide takes place directly, and the geometric features of P_2S_5 (the size of pellets, the surface of contact) influence the progress of reaction. On the other hand, due to the exotermic reaction, the warmth is giving off secondary products such as ketones, alkenes, aldehydes and so one. These compounds generate others undesirable reactions. In this new method, phosphorus pentasulfide is introduced in reaction, at the mixture of alcohols, like a dispersion in a 75N mineral oil, ISO-VG-46, in ratio of 1/3-1/6, P_2S_5/oil. In this way, it can be achieved a homogenous dispersion of P_2S_5, the surface of contact is increasing and, consequently, pentasulfide reacts in a higher yield. The reaction warmth is mitigated in reaction medium (oil environment used for dispersion). Thus, the formation of secondary products is decreasing. The neutralization of reaction product (dithiophosphoric acid) with zinc oxide is identically applied as in classical method. The elemental analysis of these additives are shown in table 2.

It is observed that the content of active particles in **ZnDTPh(B)** is much smaller than in the case of **ZnDTPh(A).** However, **ZnDTPh(B)** is much stable due to the higher decomposition temperature.

According to literature, phosphorus plays a key role in imparting antiwear properties of lubricants [8]. We decided to evaluate the synthesized zinc dialkyldithio-phosphates for their antiwear and antioxidant performance with respect to the phosphorus concentration in lubricating compositions. The results are presented in table 3. It may be observed that both dithiophosphates have good performances as antiwear, antioxidant, antirust and anticorrosion for international levels of performances for hydraulic oils.

For HL level of performance is necessary:

-0.09 %P level in **ZnDTPh(A)**, it means 1-1.2 % additive.
-0.052 %P level in **ZnDTPh(B)**, it means 1.5 % additive.

For HLM level of performance, is necessary a level of:

-0.135 %P in **ZnDTPh(A)**, it means 1.5 % additive.
-0.07 %P in **ZnDTPh(B)**, it means 2 % additive.

Also, it may be observed that for antiwear and anticorrosion test, there is a maximum value, for both ZnDTPh, after which at a higher concentration, the performance was the same. This value is 0.135 %P (1.5 % mass additive) for **ZnDTPh(A)**, and 0.07 %P (2 % mass additive) for **ZnDTPh(B)**. As concerning the resistance at oxidation, it may be observed that optimum level is 0.18 %P for **ZnDTPh(A)** and 0.105 %P for **ZnDTPh(B)**, it

Table 3
PERFORMANCE TEST FOR **ZNDTPH(A)** AND **ZNDTPH(B)**

Typical characteristics	ZnDTPh(A)			ZnDTPh(B)			Test
	* 1	1.5	2	1.5	2	3	Method
	**0.09	0.135	0.180	0.052	0.07	0.105	ASTM
Demulsibility ml oil-water-cuff (40/37/3), min., max.	30	30	30	30	30	30	D 1401
Rust test	pass	pass	pass	pass	pass	pass	D 665
Copper corrosion (3h/100°C), max.	1b	1b	1b	1b	1b	1b	D 130
Resistance oxidation (Rotary Bomb), minute	75	100	130	75	100	120	D 943
Wear scar Diameter (20 daN/100 minute), mm.	0.37	0.28	0.27	0.36	0.28	0.28	D 2266
Wear scar Diameter (40 daN/100 minute), mm.	0.48	0.41	0.40	0.48	0.41	0.40	D 2266

* mass % additive; ** % Phosphorus

Table 4
ANTIWEAR AND ANTIOXIDANT PERFORMANCE OF **ZNDTPH(A)** AND **ZNDTPH(B)** IN GREASES

Additive	ZnDTPh(A)			ZnDTPh(B	
% Additive	1	2	3	1	1.5
% Phosphorus	0.09	0.18	0.27	0.06	0.08
Typical characteristics in Li Greases	-			-	
Wear Scar Diameter (30daN, 60 min), mm	0.45	0.40	0.35	0.5	0.45
Wear Scar Diameter (40daN, 60 min), mm	0.6	0.5	0.5	0.65	0.62
Wear Scar Diameter (60daN, 60 min), mm	1.2	1.0	0.8	1.25	1.25
Wear Scar Diameter (150daN, 60 min), mm	2.5	2.3	2.2	2.6	2.55
Pressure Drop, Kpa	20	15	8	13	20

means 2 % mass additive for (**A**) and 3 % mass additive for (**B**) respectively.

Table 4 presents the antioxidant performance of synthesized ditiophosphated in Li greases.

It may be observed that both synthesized ZnDTPh are good antiwear and antioxidant additives for Lithium greases. The results for both additives are comparable, although the level of phosphorus in **ZnDTPh(B)** is much smaller than in **ZnDTPh(A)**.

Conclusions

The paper describes the performances of zinc dialkyldithiophosphates **ZnDTPh**, obtained by different methods of synthesis, used as additives in lubricant and industrial greases. It was sown that **ZnDTPh(B),** obtained by a non-classical method, affords excellent oxidation resistance at a concentration of 3 % mass additive (0.105 % P) in lubricant oil and good antiwear and anticorrosion properties when it is used at a concentration of 2 % (0.07 % P). These levels of phosphorus are smaller than in **ZnDTPh(A),** obtained by classical method, for same performances.

Both synthesized ZnDTPh are good antiwear and antioxidant additives for Lithium greases. The results for both additives are comparable, although the level of phosphorus in **ZnDTPh(B)** is much smaller than in **ZnDTPh(A)**.

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