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**THE EFFECT OF ZINC DITHIOPHOSPHATES ON
THE FRICTION AND WEAR OF PARTIALLY
STABILISED ZIRCONIA
PART II. ZINC DI(N-NONYLPHENYL,
DI-N-NONYLPHENYL) DITHIOPHOSPHATES
TRIBOLOGICAL BEHAVIOUR**

**WPŁYW DITIOFOSFORANÓW CYNKU NA TARCIE
I ZUŻYCIE CZĘŚCIOWO STABILIZOWANEGO CYRконU
CZĘŚĆ II. TRIBOLOGICZNE ZACHOWANIE
DI(N-NONYLFENYL, DI-N-NONYL-FENYL)
DITIOFOSFORANÓW**

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Słowa kluczowe:

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Abstract

Frictional and wear properties of zinc di(*n*-nonylphenyl)dithiophosphate (MA) and di(-di-*n*-nonylphenyl) dithiophosphate (DA) of *n*-hexadecane solution in frictional contact of ionic-ZrO₂, partially stabilised by Y₂O₃ (PSZ) tested using a ball-disk tribometer, at 25°C, have been studied. It was found that zinc dithiophosphates significantly reduce friction and wear. The effectiveness of friction and wear reduction increases with the increasing number of *n*-nonyl chains of aryl in the additive molecule and with the concentration of additive solution. The sliding speed and load have a detrimental effect on their behaviour. Results of these frictional experiments are closely related to the results of adsorption data of MA and DA on PSZ powder from hydrocarbon solutions.

INTRODUCTION

Recently, the author laboratory has been studying the tribological properties of zinc di-*n*-alkyl dithiophosphates (ZDTPs) in PSZ contact [L. 1]. All tested ZDTPs exhibit significantly reduced friction coefficients and wear rate in comparison to the base hydrocarbon. The most effective anti-frictional and -wear properties from the tested *n*-alkyl ZDTPs are exhibited by C₁₂ZDTP, at all tested sliding speeds. Increasing the sliding speed causes the temperatures to rise in the conjunction, due to flash temperature effects. PSZ low thermal conductivity temperatures results in high temperatures in contact. C₁₂ZDTP shows the highest thermal stability among tested ZDTPs. Hence, more thermally resistant zinc dialkyl(aryl)dithiophosphates than C₁₂ZDTP are investigated in zirconia-zirconia friction contacts of PSZ. Currently, we are investigating the effect of load, sliding speed, the number of *n*-nonyl chain and additive concentration of MA and DA on friction and wear, to relate these results with adsorption data [L. 2]. The results of the current studies are presented and discussed in relation to the results of ZDTPs.

EXPERIMENTAL

Preparation of zinc di(n-nonyl- and di-n-nonyl-phenyl) dithiophosphates

The MA and DA additives were prepared from mono-n-nonylphenol and di-n-nonylphenol and phosphorous pentasulphide, in a three-step laboratory process, according to procedures described elsewhere [L. 3]. These dithiophosphates were characterized [L. 1] and blended in n-hexadecane, at concentrations in the range of 0.5–3.0%.

Ceramic material

Details of the balls and discs of ZrO₂ partially stabilized by Y₂O₃ are recorded in Part I.

Friction and wear tests

Friction and wear tests were done like in Part I.

SEM/EDX surface analysis

This analysis procedure was done like in Part I.

RESULTS AND DISCUSSION

The effect of sliding speed and additive concentration on friction coefficient

These effects were examined for the load of 50 N and three sliding speeds (0.01, 0.03 and 0.05 m/s), by testing with different concentration of MA and zinc DA in n-hexadecane solution. The results of friction testing are presented in **Figs. 1–4**. For all tests initial friction values are not stable and become steady after some sliding distance. For both MA and DA, at the lowest sliding speed tested (0.01 m/s) they become stable after 10 and 50 m, respectively (**Fig. 1**). The friction coefficient values are disturbed with short time friction peaks during test, much more for DA, in the friction range of 0.08÷0.12. For both additives the values of friction coefficient slightly decrease, more in the case of DA, with test time and linearly for MA. For these additives increasing test speed up to 0.03 m/s and additive concentration significantly decrease the variation in

friction coefficient values and steady range of friction after 80 m of sliding remains up to end of test (**Fig. 2**). Great fluctuations of friction, which also increase with increasing of sliding distance, was observed for n-hexadecane after about a half of rubbing time. The friction coefficient values of MA and DA are very similar and slightly lower in comparison to ones from tests at lower sliding speed (0.01 m/s). At sliding speed-0.05 m/s for tested additives and C12ZDTP low friction is observed % (**Figs. 3 and 4**), slightly the friction increase in the end of duration time for MA and DA at solution concentrations of 0.5% (**Fig. 3**). A steady-

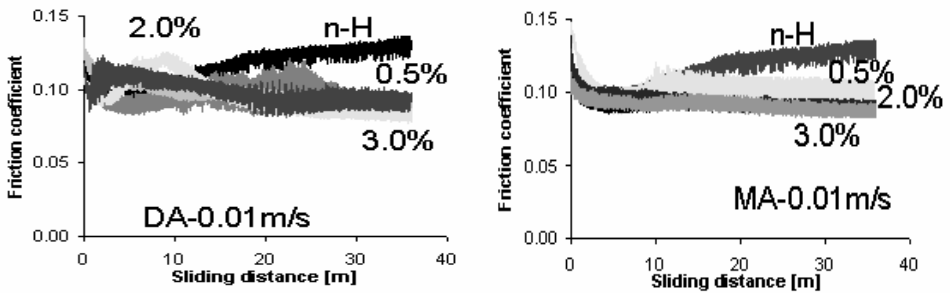


Fig. 1. Effect of sliding distance, solution concentration of DA and MA on friction coefficient, load – 50 N, speed – 0.01 m/s

Rys. 1. Wpływ drogi ślizgania, stężenia roztworu DA i MA na współczynnik tarcia, obciążenie – 50 N, prędkość ślizgania – 0,01 m/s

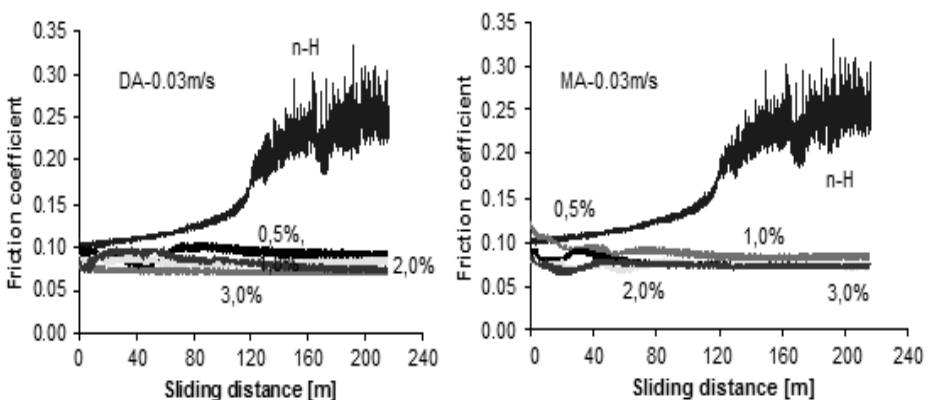


Fig. 2. Effect of sliding distance, solution concentration of DA and MA on friction coefficient, load – 50 N, speed – 0.03 m/s

Rys. 2. Wpływ drogi ślizgania, stężenia roztworu DA i MA na współczynnik tarcia, obciążenie – 50 N, prędkość ślizgania – 0,03 m/s

stable friction coefficient range from the beginning for DA solution and for MA after 120 m of sliding distance at concentration of 3.0% are observed. The friction is slightly lower in the case of DA than MA. For the n-hexadecane alone after very short time of sliding a stable high value of friction is observed (**Fig. 4**). The values of friction coefficient for C12ZDTP 3.0% solution additive concentration is lower than for DA and MA. Lubrication with using C12ZDTP at sliding speed – 0.05 m/s (**Fig. 4**) in the whole sliding distance of 360 m gives very low friction coefficients similar to DA and MA at lower sliding speed (0.01 m/s), which are also strongly differentiated in the range of $0.095 \div 0.11$. The lowest friction coefficients are observed in the case of MA and DA at sliding speed – 0.03 m/s, their values are in the range from 0.07 to 0.09.

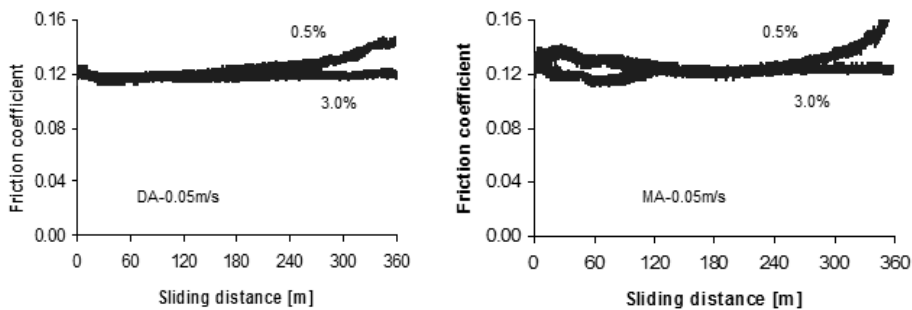


Fig. 3. Effect of sliding distance, solution concentration of DA and MA on friction coefficient, load – 50 N, speed – 0.05 m/s

Rys. 3. Wpływ drogi ślizgania, stężenia roztworu DA i MA na współczynnik tarcia, obciążenie – 50 N, prędkość ślizgania – 0,05 m/s

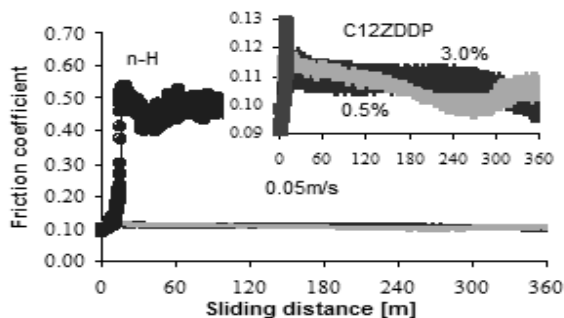


Fig. 4. Effect of sliding distance, n-hexadecane and its solution concentration of C12ZDTP on friction coefficient, load 50 N, sliding speed – 0.05 m/s, sliding distance – 360 m

Rys. 4. Wpływ drogi ślizgania, n-heksadekanu i C12ZDTP stężenia na współczynnik tarcia, obciążenia – 50 N, szybkość ślizgania – 0,05 m/s, droga tarcia – 360 m

Wear behaviour

The ZrO_2/Y_2O_3 ball wear rates (wear coefficients) were calculated from the lost volume of ball [mm^3/mN] vs. sliding distance [m/s]. The average values of ball wear rates are presented in **Table 1**. The MA and DA wear rates are much lower than in the wear test with n-hexadecane alone. For the tests at 0.01 m/s and all solution concentration of both additives these wear rates are from five to ten times lower. The wear rates decrease with increasing solution concentrations, slightly more for DA. The wear decreasing tendency in comparison to n-hexadecane alone, but with lower degree, is also observed in the tests for higher sliding speed of 0.03 m/s. At this sliding speed, the wear coefficients increased comparing to sliding speed – 0.01 m/s by one order magnitude. The wear coefficients of DA and MA are nearly at same values. The higher increasing tendency of wear rates is also observed in the tests for higher sliding speed of 0.05 m/s. For a longer rubbing distance at this sliding speed, the wear coefficients increased by three orders magnitude in comparison to the lowest sliding speed (0.01 m/s) The wear rates reduction in the presence of

Table 1. Wear rates [$mm^3 \times N^{-1}$, m^{-1}] of n-hexadecane and MA and DA n-hexadecane solutions, load – 50 N

Tabela 1. Szybkość zużycia [$mm^3 \times N^{-1}$, m^{-1}] n-heksadekanu i n-heksadekanowych rozтворów MA i DA, obciążenie

Sliding speed and distance- 0.01 m/s, 72 m			Sliding speed and distance- 0.03 m/s, 216 m			Sliding speed and distance- 0.05 m/s, 360 m		
n- Hexadecane alone		7.88×10^{-7}	n-Hexadecane alone		3.12×10^{-6}	n- Hexadecane alone		2.85×10^{-4}
	Conc. %	Wear rates		Conc. %	Wear rates		Conc. %	Wear rates
MA	0.5	1.72×10^{-7}	MA	0.5	1.37×10^{-6}	MA	0.5	1.67×10^{-4}
	1.0	0.94×10^{-7}		1.0	1.17×10^{-6}		3.0	1.38×10^{-4}
	3.0	1.04×10^{-7}		3.0	0.78×10^{-6}			
DA	0.5	1.57×10^{-7}	DA	0.5	1.45×10^{-6}	DA	0.5	1.75×10^{-4}
	1.0	0.94×10^{-7}		1.0	1.03×10^{-6}		3.0	0.99×10^{-4}
	3.0	0.75×10^{-7}		3.0	0.89×10^{-6}			
						C12	0.5	1.08×10^{-4}
							3.0	$0,84 \times 10^{-4}$

additives are also lower in comparison to a rubbing test with n-hexadecane alone. The wear rates decrease with increasing solution concentrations, the wear rates are the lowest in the case of C12ZDTP. The wear coefficients of DA are also a little lower than for MA.

The representative SEM micrographs of balls worn surfaces at the end of tests are presented in **Figs. 5, 6**. The worn surfaces after lubrication with n-hexadecane at sliding speed 0.01 m/s exhibit rough topography with many microfractures, local microcracks, deep grooves, pores

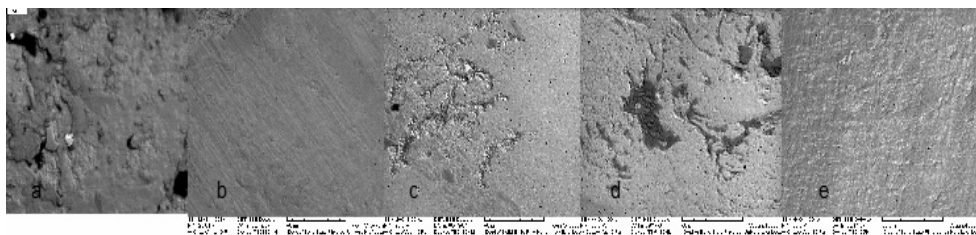


Fig. 5. SEM image of worn surface lubricated; n-hexadecane(a), MA solution concentration of 0.5% (b), 1.0% (c) and DA solution concentration of 1.0% (d), 3.0% (e), load – 50 N, sliding speed – 0.01 m/s, sliding distance – 72 m

Rys. 5. Obraz SEM powierzchni zużycia smarowanych; n-heksadekanem(a), roztworami MA o stężeniach – 0,5% (b), 1,0% (c) i roztworami DA o stężeniach – 1,0% (d), 3,0% (e), obciążenie – 50 N, szybkość ślizgania – 0,01 m/s, droga ślizgania – 72 m

and some grains. The wear scars is covered by black carbon residue formed from n-hexadecane in high temperature decomposition process (**Fig. 5a**). The surface is smooth and show a dense structure with much less grooves very small ploughing after friction tests with MA with 0.5% of additive solution concentration (**Fig. 5b**). At higher concentration (1.0%) on smooth surface are showing damage by plastic deformation from the direction of sliding with microfractures, deep grooves (**Fig. 5c**). At this same DA solution concentration (1.0%) wear surface is more destroyed (**Fig. 5d**) and rubbing surface contain more black particles than in the case of MA. A less smooth surface than 0.5% AM with small grooves, pores and some grains is observed after rubbing by 3.0% additive solution concentration of DA (**Fig. 5e**). At a higher sliding speed (0.05 m/s) the wear mechanism is microploughing, the topographies of the wear scar surfaces show much higher destruction than those observed after rubbing at 0.01 m/s. Deep grooves, intergranular fracture, plastic de-

formation, delamination, some debris and carbon black residues are seen on all worn surfaces lubricated by n-hexadecane (**Fig. 6a**). The increase of MA solution concentration up to 1.0% results in smoother scar surfaces, less microcracks and no grains (**Fig. 6c**), in comparison to worn surfaces lubricated with lower additive concentration (**Fig. 6b**). The worn surfaces lubricated by 1.0% solution concentration are less destroyed by MA (**Fig. 6c**) than of DA (**Fig. 6e**). They are more smooth than the rubbing surfaces lubricated by higher (3.0%) of C12ZDTP solution concentration (**Fig. 6d**). At this concentration, this additive shows much more surface film destruction than DA (**Fig. 6f**). SEM morphologies of this wear scar shows deeper grooves, some cracks propagation resulted in spalling of material.

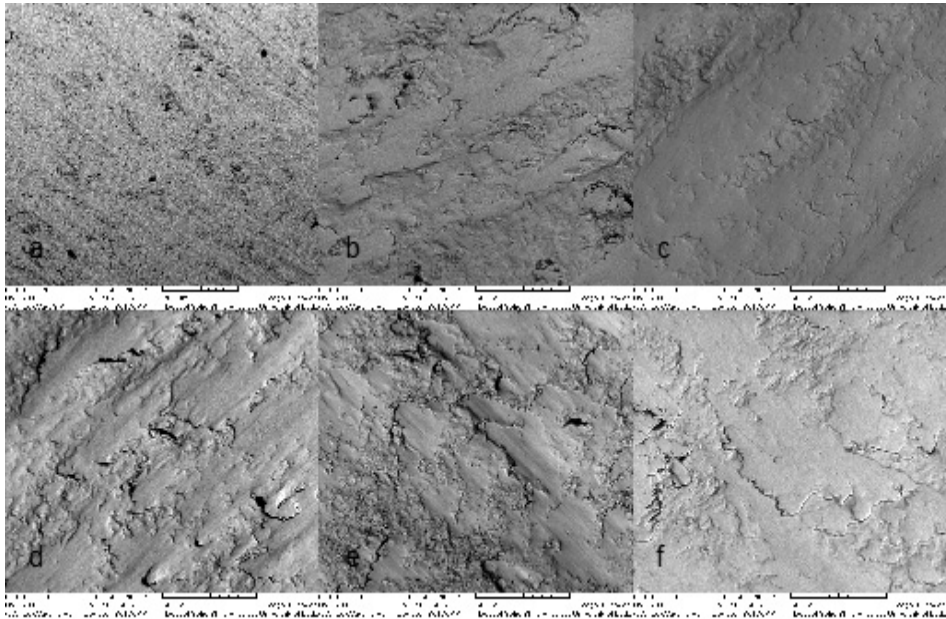


Fig. 6. SEM image of worn surface lubricated; n-hexadecane(a), MA solution concentration of 0.5% (b), 1.0%(c), C12ZDTP solution concentration of 3.0% (d), and DA solution concentration of 1.0% (e), 3.0% (f), load – 50 N, sliding speed – 0.05 m/s, sliding distance – 360 m

Rys. 6. Obraz SEM powierzchni zużycia smarowanych; n-hexadekaniem(a), roztworami MA o stężeniach – 0,5% (b), 1,0% (c), roztworem C12ZDTP o stężeniu – 3,0% (d) i roztworami DA o stężeniach – 1,0% (e), 3,0% (f), obciążenie – 50 N, szybkość ślizgania – 0,05 m/s, droga ślizgania – 360 m

The differences of wear coefficients for DA and MA additives are relatively low. The lower the additive solution concentration and the higher the load, the more the surface is destroyed and the higher friction and wear coefficients. The wear coefficients of DA at 0.01 and 0.03 m/s are much lower than at 0.05 m/s (three times). The wear does not correlate with the observed lower friction coefficient of tested additives. Increasing the sliding speed causes the temperatures to rise in the conjunction, due to flash temperature effects, and the severity of contact conditions leads to mixed boundary and dry lubrication, a limited tribochemical reactions may occur, hence, high wear. The results of EDS analysis atomic element concentration, normalized to $[Zn] = 1.0$ of reaction films, presented in **Table 2**, show a change of the surface concentration of zinc, phosphorus and sulfur. The atomic P concentrations of films formed on worn surface lubricated with DA at both sliding speed are higher, at higher speed more twice, while S concentrations are a little lower than for MA. At highest sliding speed (0.05 m/s) for MA on a worn surface lubricated with 3% solution concentration a 0% of Zn was recorded. Originally, the ZDTP contains a Zn:P:S ratio of 1: 2: 4. The wear surface contain mostly phosphorus, sulfur with lesser amounts of zinc. Comparing

Table 2. Composition of frictional surface films, atomic element concentration %, normalized to Zn, load – 50 N

Tabela 2. Skład tarciowej warstwy powierzchniowej; atomowe stężenie % pierwiastka i znormalizowane do Zn, obciążenie – 50 N

		Zn	P	S	Zn	P	S
Sliding speed and distance – 0,01 m/s, 72 m		Normalized to Zn			Atomic element %		
MA,DA Concentration %							
Original ZDTP		1.0	2.0	4.0			
MA	0.5	1.0	9.37	3.07	0,14	1,03	0.43
	1.0	1.0	7.45	6.63	0,11	0.82	0.73
	3.0	1.0	13.0	6.30	0.10	1.30	0.63
DA	0.5	1.0	13.7	2.25	0.20	2.74	0.45
	1.0	1.0	12.9	1.60	0.22	2.84	0.35
	3.0	1.0	9.00	1.00	0.28	2.53	0.29
– 0.05 m/s, 360 m							
MA	0.5	1.0	10.0	4.36	0.11	1.10	0.48
	3.0	-	-	-	0.01	3.25	0.39
DA	0.5	1.0	24.6	2.93	0.14	3.44	0.41
	3.0	1.0	29.5	3.54	0.11	3.25	0.39

this ratio to most of the tests the phosphorus contents are from about five to seven and for DA, at sliding speed 0.05 m/s, even fifteen times higher than the theoretical phosphorus concentration. The rubbing surface P concentration lubricating by C12ZDTP is from three to five lower in relation to tested additives concentration of sulfur/zinc of lubricated rubbing surface by DA and C12ZDTP at both sliding speed are lower compared to MA. The analysis results suggest that MA and DA have decomposed in the contact junction to form films relatively high in phosphorus/zinc, and sulfur/zinc ratio and very low atomic Zn concentration. Such results are not observed in films from ZDTP-lubricated wear tests in the case of zirconia [L. 1] and silicon nitride [L. 4]. The composition of these films implies a different tribochemical reactions for MA and DA than ZDTPs with PSZ and with silicon nitride.

Lubrication—the role of adsorption

The different friction and wear behavior of MA and DA can be explained also by isotherm and enthalpy of adsorption results data [L. 2]. The adsorbed quantities on zirconia of MA is similar to C12ZDTP, they are two times higher than of DA. The adsorption at temperature of 35°C of MA is the greatest among tested additives (adsorbed quantity is 1.03 $\mu\text{mol}/\text{m}^2$) higher than that at 25°C and much higher than for DA and C12ZDTP. Such a surprising behavior may be caused by a weak chemisorption. DA and C12ZDTP amounts adsorbed at 35°C are a little higher and lower than at 25°C, respectively. The values of differential molar enthalpies of adsorption at 25°C for the n-alkyl derivatives are exothermic (to 30 kJ/mol) and relatively stable for coverage degree from 0 to 1. The MA molar enthalpy at 25°C is exothermic and is the highest, decreases with increasing surface coverage and is higher from seven to four times than C12ZDTP ones. The exothermic enthalpy is observed when the nature of the additive interactions with the active surface sites are rather physical.

The most endothermic among the tested additives DA enthalpy effect at 25°C is seen at the lower degree of surface coverage, and it decreases with increasing surface coverage, until at degree of 0.6 surface coverage and further becomes exothermic effect. The endothermic enthalpy suggests the chemisorption of this additive on active sites of PSZ. During adsorption at 35°C exothermic differential molar enthalpies are observed only for both MA and DA, for MA this enthalpy is twofold higher than for DA, while all n-alkyl ZDTPs show small endothermic effect. This

effect is particularly evident in the case of MA for both temperatures, the same values of the differential molar enthalpy of adsorption are observed.

Organofunctional derivatives, as for example the organophosphonate anion, react strongly with the oxide surface, forming strong bonds with it. Sasaki [L. 5] and Mori [L. 6] have shown that during adsorption on nascent ceramic surfaces, including ZrO_2 , even saturated hydrocarbons chemisorb. ZDTPs are strongly adsorbed onto the aluminum oxide surface [L. 3]. These surfaces do not retain the P = S group and high phosphorus surface concentration is present, in contrast to the alkyl derivatives, which adsorb with the P = S group as an identifiable functional group in the adsorbed species. For both additives at 35°C, and only for MA at 25°C of adsorption a chemisorption reaction occurs on the zirconia surface. Aryl ZDTPs hydrolyze on the PSZ surface, phenolate anion is chemisorbed and phenoxide ion remains on the surface following the initial dissociative adsorption. It is probable that ceramic hydroxyl groups have been replaced by phenoxyl groups while during adsorption of alkyl ZDTPs surface OH are removed by dithiophosphate anion. The highest MA adsorption value at 35°C and endo-thermic enthalpy of DA confirm chemisorbed nature of the adsorption processes. The elemental composition of frictional surface results (Tab. 2) are closely related to the aryl ZDTPs adsorption processes data. The atomic P concentrations of films formed on worn surface lubricated with DA at both sliding speed are higher, at higher speed more twice, while S concentrations are a little lower than for MA. If we consider the phosphorus and sulphur contents normalized to Zn, phosphorus concentrations for all of the tests are from about five to fifteen and from three and half to seven times higher than the theoretical phosphorus concentration in the case DA and MA, respectively. According sulphur surface concentrations for DA they are from two to more than six times lower than for MA. The rubbing surface normalized P concentration lubricating by C12ZDTP is from two to four lower in relation to MA and DA. The analysis results suggest that MA and DA have decomposed in the contact junction to form films with high phosphorus content. It is in good agreement with chemisorption results of aryl ZDTP on aluminium oxide surface. Such results confirm that the differences of mechanism of film formation by n-alkyl ZDTPs [L. 1] and aryl ZDTPs in lubricated zirconia wear tests are caused by tribochemical reactions of aryl derivatives with higher extend for DA.

CONCLUSIOS

From the experimental data presented here, the following conclusions can be drawn. The studies of the effect of the rubbing time on friction coefficient reveals the presence of strong variation in friction coefficient values, higher loads and sliding speed in the case of DA. Both tested aryl derivatives exhibit significantly reduced friction coefficient values, in comparison to base n-hexadecane. The large improvement in anti-frictional performance is caused by additive solution concentration. A sliding speed have the biggest detrimental and the load large effect on the wear behavior of tested frictional system. Despite of relatively low friction a significant wear rates at higher sliding speed are seen. The more the n-hydrocarbon chains in additive molecule and the higher their solution concentration, the greater lubrication effectiveness. The more effective anti-frictional and -wear properties are exhibited by DA.

Tested additives reduce the boundary and mixed/boundary regimes of lubrication. The friction coefficient is closely related to the amount adsorbed, the higher additive solution concentration increases of the amount adsorbed and in consequence the stronger reduction of friction is observed. Friction is also influenced by the organization of boundary layer and also by differential enthalpy of adsorption of additives. The thicker the layer the better its tribological properties. The friction and wear data, worn scar micrographs and surface element analysis, in relation with adsorption friction properties will provide a better understanding of the lubrication mechanism of ZDTP in zirconia-zirconia frictional contact.

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Recenzent:
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Streszczenie

Tarciowe i zużyciowe właściwości n-heksadekanowych roztworów di-n-nonylfenylditio-fosforanu cynku (MA) i di-(di-n-nonyl)fenylditiofosforanu cynku (DA) w styku pary tarciovej jonowego – ZrO_2 częściowo stabilizowanego Y_2O_3 (PSZ) były badane z użyciem tribometru kula-dysk w $25^\circ C$. Stwierdzono, że dodatki te znacząco zmniejszają w porównaniu z n-heksadekanem tarcie i zużycie. Zmniejszanie tarcia i zużycia jest zależne od liczby n-nonylowego łańcucha w fenylu cząsteczki dodatku i wzrasta ze stężeniem roztworu dodatku. Szybkość ślizgania i obciążenie mają wpływ odwrotny na te wartości. Wyniki tych badań są ściśle zależne od wyników adsorpcji tych dodatków na proszku PSZ z roztworów węglowodorowych, szczególnie od struktury warstwy i molowej entalpii adsorpcji dodatku.