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THE EFFECT OF ZINC DITHIOPHOSPHATES ON THE FRICTION AND WEAR OF PARTIALLY STABILIZED ZIRCONIA
PART I. ZINC DI-N-ALKYLDITHIOPHOSPHATES TRIBOLOGICAL PROPERTIES

WPŁYW DITIOFOSFORANU CYNKU NA TARCIE I ZUŻYCIE CZĘŚCIOWO STABILIZOWANEGO TLENKU CYRKONU
CZĘŚĆ I. WŁAŚCIWOŚCI TRIBOLOGICZNE DI-N-ALKILODITIOFOSFORANÓW CYNKU

Key words:

ceramics, PSZ, friction, wear, tribochemistry, zinc dialkyldithiophosphates

Słowa kluczowe:

materiały ceramiczne, PSZ, tarcie, zużycie, tribochemia, dialkiloditiofosforany

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Abstract

Tribological properties of zinc di-n-alkyldithiophosphates (ZDTPs) of ionic-ZrO2, partially stabilised by Y2O3 (PSZ), were performed using a ball-disk tribometer, at 25°C. It was found that ZDTPs significantly reduce the friction and wear under boundary conditions. Increasing the sliding speed and load have a detrimental effect on friction and wear. The effectiveness of friction and wear reduction increases with the increasing hydrocarbon chain of the additive molecule and the concentration of additive solution. The wear surface was analysed using an optical microscope and the SEM/EDX technique. The data results of friction and wear are in good correlation with magnitude and molar differential enthalpy adsorption of ZDTPs on PSZ powder from n-decane solutions and with phosphorus concentration on a rubbing surface.

INTRODUCTION

Ceramics are used in a wide range of applications, particularly those related to tribology, due to their favourable engineering properties and availability. Toughened zirconia ceramics have been used as thermal barrier coatings in engines and gas turbines and regarded as potential candidate materials for other tribological applications because of low density and high fracture toughness, hardness, stiffness, strength, refractoriness and thermal expansion coefficient close to those of steel and cast iron. ZrO_2 has been used as material for guides and dies in manufacturing processes. Zirconia exhibits scuffing resistance for heavy duty diesel injectors **[L. 1]**. Plasma sprayed yttria stabilized zirconia coatings prepared with the use of nanostructured powders were more wear resistant than those made of from conventional powders **[L. 2]**. The PSZ nanoparticles also improve mechanical properties of zirconia-alumina nanocomposite **[L. 3]**. Sol-gel-derived zirconia thin films could potentially be applied under severe conditions as protective coatings for wear resistance, anticorrosion and heat resistance against oxidation. These thin films, under low loads in sliding against Si_3N_4 ball, display excellent tribological properties **[L. 4]**. The wear of zirconia-zirconia combination is too high for many application, for example for clinical use. When zirconia was combined with alumina counterface the wear factor of zirconia decreased drastically as compared with zirconia-zirconia combination, because adhesive wear was controlled **[L. 5]**. It is known that ceramics do not exhibit good tribological performance under dry sliding conditions. Therefore, lubricants with suitable characteristics for ceramics have been developed, mostly for reducing wear and friction, with the former usually accompanied by reduction in wear. In sliding systems with insufficient lubrication ceramics can however lead to relatively high friction and wear, distinct running-in behaviour and disturbed run friction peaks **[L. 6]**. Mineral oil is most frequently used in the researches as a base oil; n-hexadecane, esters, silicones, polyalkylene glycols, water and PAO are sometimes used too. The lubricating oil additives for ceramics include fatty acids, alcohols, organic nitrogen, phosphorus and sulfur compounds, halogenated hydrocarbons and polyols. Sasaki **[L. 7]** has investigated tribochemical reactions of benzene, acetone, methane and methanol in vapour atmosphere in sliding of zirconia–zirconia. ZDTPs are most often used as lubricating oil additives for lubrication of SiC, Si_3N_4, Al_2O_3 **[L. 8–11]** and PSZ **[L. 12]**. The fully formulated polyester, mineral oils and silicon oil without any additive were used as lubricants of friction and wear studies of zirconia–zirconia frictional contacts during boundary lubrication. Liquid lubrication of ZrO_2 with the use of antiwear additive ZDTP can generally reduce both friction and wear, but wear may still be significant under conditions of high sliding velocities at elevated temperatures where lubricant film thickness becomes very thin **[L. 12]**. Some preliminary studies were made of the effect of carbon number of ZDTPs hydrocarbon chain and its solution concentration, sliding velocity, load and temperature on friction coefficient **[L. 13, 14]**. Those studies have confirmed that a longer hydrocarbon chain of the additive molecule, higher concentration and temperature, give a higher reduction of friction coefficient. Increasing load increases the friction at its lowest values of load only. At higher temperatures (from 100°C to 200°C) C12ZDTP reduces the friction coefficient with increasing temperature **[L. 15]**. The composition of films formed in ZDTP boundary lubrication of ceramics is fundamentally different and implies a different chemical pathway for ZDTP with ceramics **[L. 7–10]**. Both friction and wear are influenced by adsorption and by tribochemical reaction of lubricant component with the frictional surface **[L. 8–10]**. The magnitude of adsorption, and the rate of adsorption influence both antiwear (AW) and extreme–pressure (EP) properties. Hence, ZDTPs adsorption studies on the powder of PSZ surface have been carried out **[L. 16]**.

The lubrication results of PSZ by ZDTPs are limited **[L. 7, 13–15]**, therefore, in this paper the effect of load, sliding speed, the n-alkyl of ZDTP chain and additive concentration on friction and wear behaviour of PSZ frictional contacts have been studied. The SEM /EDX wear surface analysis has also been performed. The findings of studies are presented and discussed in relation to the results of the above mentioned adsorption studies.

EXPERIMENTAL

Preparation of zinc dialkyl(aryl)dithiophosphates

The ZDTPs, were prepared from n-alcohols with different alkyl chains: C3, C6, C12 (and phosphorus pentasulphide, in a three-step laboratory process, according to procedures described elsewhere **[L. 17].** Zinc dithiophosphates were characterised using 31P NMR spectroscopy. The pure ZDTPs were blended in n-decane at concentrations in the range of 0.5–3.0%. Increasing additive concentration to 3.0% of ZDTP results increase the viscosity of solutions up to 4.8% in comparison with viscosity of n-decane alone. N-decane was used as model substitute for different oils in adsorption studies, so ZDTPs were also blended in this solvent.

Ceramic material

The balls and discs for friction experiments were made from hot pressed ZrO_2, partially stabilized by Y_2O_3 in Advance Ceramic Department, University of Science and Technology (AGH). Physical and mechanical properties, temperature and sintering time of tested ceramics are presented in **Table 1**.

Table 1. The physical and mechanical properties of partially stabilized zirconia
Tabela 1. Fizyczne i mechaniczne właściwości częściowo stabilizowanego tlenku cyrkonu

Density	Temperature (°C)		Elastic Modulus	Hardness	Fracture Toughness	Bending Strength	Grain size	Impurities	Roughness of surface Ra µm	
g/cm^3	sintering	time (hours)	GPa	GPa	$MPa\ m^{1/2}$	MPa	µm	%	disc	ball
6.08	1500	2.0	210	14	6	1000	0.3–0.5	Y_2O_3-3	0.25	0.36

Friction and wear tests

Friction and wear tests were performed using a ball-on-disc machine on unidirectional sliding contact, under lubricated conditions at ambient atmosphere. The friction force was continuously transmitted to a recorder by a transducer, from which the friction coefficient was obtained. Experiments were carried out using PSZ 1/8″ ball and 1.0″ disc diameters, respectively, at sliding speeds of 0.01, 0.05, and 0.07 m/s, at loads of 25, and 50 N. The additive concentrations of lubricant were in the range of 0.5, 1.0, 2.0 and 3.0%. The time of friction test duration was two hours. The test lubricant was dropped onto the rubbing surfaces, so that the lubricant immersed frictional contact during the entire test process. Duplicate test were run under various conditions to check the reliability and/or reproducibility of friction and wear data, producing results showing a deviation of less than 10%. Before and after tests, the specimens were cleaned in chloroform and n-hexane. The wear scar of ball was measured under an optical microscope with a micrometer stage. The wear volume, of the ball only was estimated by the equation $V = \Pi r^4 / 4R$, where r is the radius of the wear scar and R is the radius of the ball. Each wear scar was washed using chloroform and hexane, and next, the worn surfaces were examined with the use of SEM/EDX technique of surface elemental analysis.

SEM/EDX surface analysis

After a four-ball wear test, scar balls were rinsed with acetone prior to surface analysis. The wear scar surfaces were analysed by SEM/EDX to obtain indication elements (S, P, N, C) present in the surface film formed during friction.

An LED-435VPi instrument was used for SEM/EDX analysis.

RESULTS AND DISCUSSION

Friction

The representative friction test results are presented in **Figures 1–6** as friction coefficient versus sliding distance curves, at different sliding speeds and additive concentrations for two loads of 25 and 50 N. The tests were conducted for sliding distances of 72 m, 360 m and 504 m. The friction coefficient values are disturbed with short time friction peaks during some test. Increasing test speed and molecule of the additive decrease them. The zirconia materials are stiff enough that for stick slip to be very unlikely. The presence of these friction peaks may also suggest grain pull out and abrasion, indicating wear. It could be deduced from isotherms and enthalpy of adsorption results **[L. 15]** that probably also during friction with shorter alkyl chain of ZDTPs do not form densely packed surface layers bonded to the frictional surfaces are not formed. In contrast C6 and C12ZDTPs form thicker more stable boundary layers and fluctuation of friction coefficient values are observed. The ZDTPs strongly reduce friction, in comparison to n-decane. The increase of the n-alkyl chain length of the additive evidently decreases friction coefficient, as is observed at lower load at the end of friction test (**Fig. 1a**). For a higher load of 50 N (results are not presented) it is observed at much shorter sliding distance, after about 20 m of sliding the friction sharply increases to the level of friction of n-decane alone. For both loads and additive concentration of 1.0 and 3.0% friction starts out low and after very short (about 10 m), sliding distance becomes steady at low level (**Fig. 1b**). The shapes of friction coefficient curves in case of C6ZDTP are very similar for both loads applied, here, (the curve for the load of 50 N only is presented in **Fig. 1c**). The friction starts out at low and steady values; however, half through the test, there is a sudden transition to higher values after 50–60 m of sliding distance and they are about twofold higher than at the load of 25 N (results are not presented). For both 1.0 and 3.0% of C6 concentrations the steady friction values are nearly twice lower than C3 ones. For the additive with longest n-alkyl chain (C12) tested, friction coefficients are the lowest among the tested ZDDPs and stable in the whole range of sliding distance for both tested loads, (the results for load 50 N is only presented (**Fig. 2**)).

The friction with rubbing time for C3 (**Fig. 3**) and C6ZDTPs (**Fig. 4**), increases strongly at higher sliding speed – 0.05 m/s at additive solution concentrations of 0.5% and 1.0%, to stable high values which are about as high as the n-decane. For these additive concentrations, one can see the higher the concentration the longer the initial sliding distance with relatively low friction. The increase of concentration up to 3.0% of C6 ZDTP prolongs the lower steady – stable friction coefficient range at the start of sliding for a while but not to the level of friction of n-decane alone. Increases with the of up to 0.07 m/s speed for C3ZDTP, the beginning ranges of the lowest friction values are shortened, after that a high level of friction (more than 0.6) is achieved (**Fig. 5**).

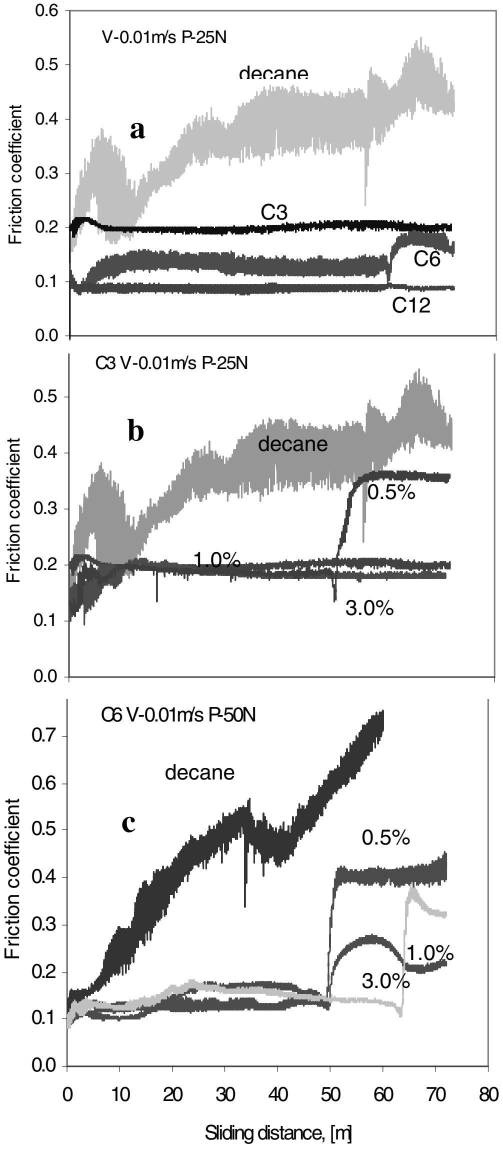

Fig. 1. Additive hydrocarbon chain length and sliding distance at additive concentration –1.0%, load – 25 N (a), effect of C3 ZDTP oncentration and sliding distance at load 25 N (b), effect of C6ZDTP concentration and sliding distance at 25 N (c) on friction coefficients, sliding speed 0.01 m/s

Rys. 1. Wpływ długości łancucha węglowodorowego i drogi ślizgania przy stężeniu dodatku –1,0%, obciążenie –25 N (a), wpływ stężenia C3ZDTP i drogi ślizgania przy obciążeniu 25 N (b), wpływ stężenia C6ZDTP i drogi ślizgania przy 50 N na współczynniki tarcia, szybkość ślizgania – 0,01 m/s

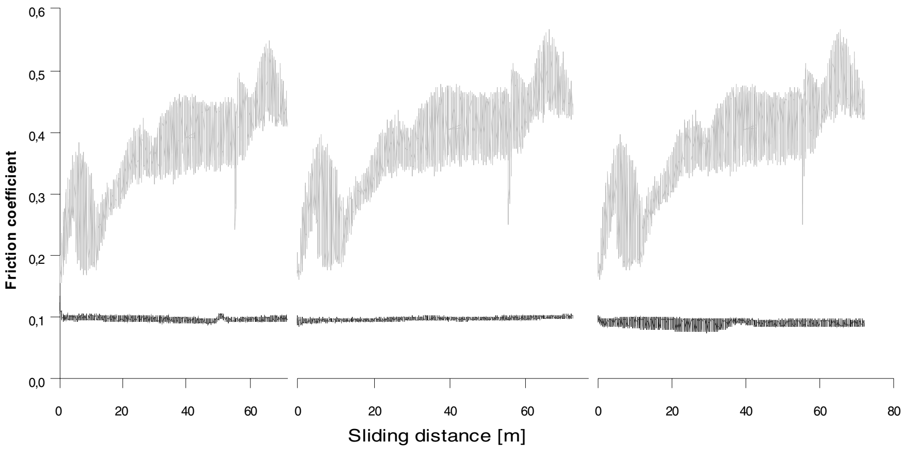

Fig. 2. Effect of C12ZDTP concentration (0.5, 1.0 and 3.0% from left to right) and sliding distance on friction coefficient, load – 50 N, sliding speed – 0.01 m/s

Rys. 2. Wpływ stężenia C12ZDTP (0,5, 1,0 and 3,0% z lewa na prawo) i drogi ślizgania na współczynnik tarcia, obciążenie – 50 N, szybkość ślizgania – 0,01 m/s

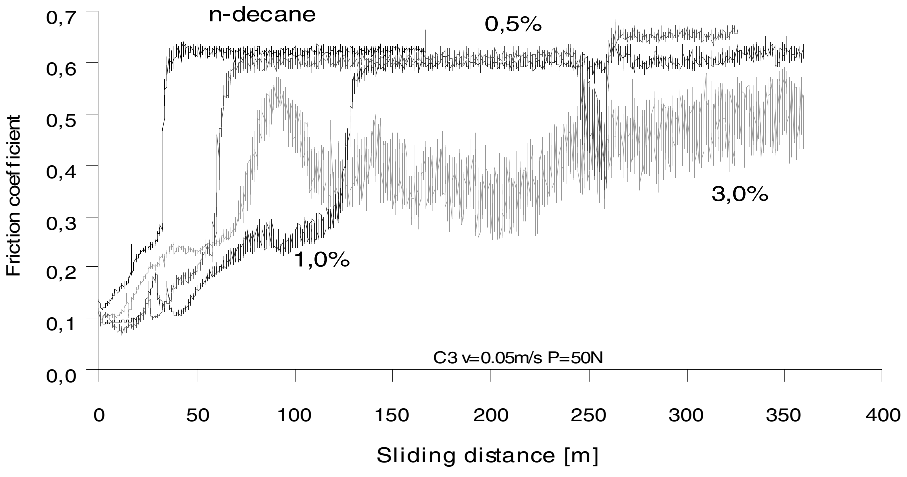

Fig. 3. Effect of C3ZDTP concentration and sliding distance on friction coefficient, load – 50 N, sliding speed – 0.05 m/s

Rys. 3. Wpływ stężenia C3ZDTP i drogi ślizgania na współczynnik tarcia, obciążenie – 50 N, szybkość ślizgania – 0,05 m/s

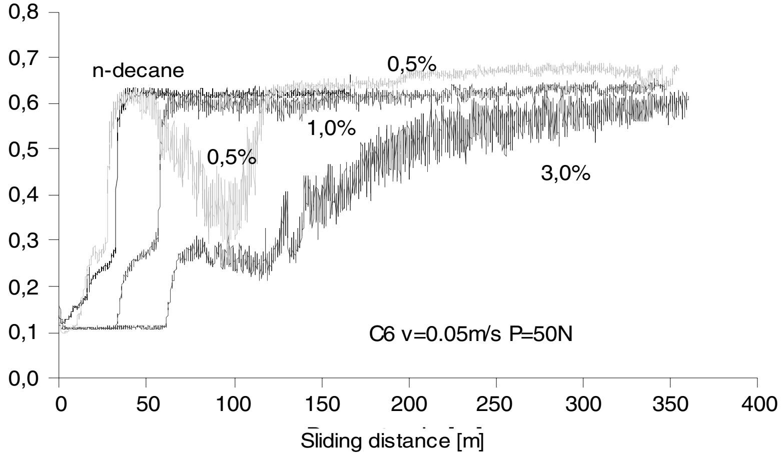

Fig. 4. Effect of C6ZDTP concentration and sliding distance on friction coefficient, load – 50 N, sliding speed – 0.05 m/s

Rys. 4. Wpływ stężenia C6ZDTP i drogi ślizgania na współczynnik tarcia, obciążenie – 50 N, szybkość ślizgania – 0,05 m/s

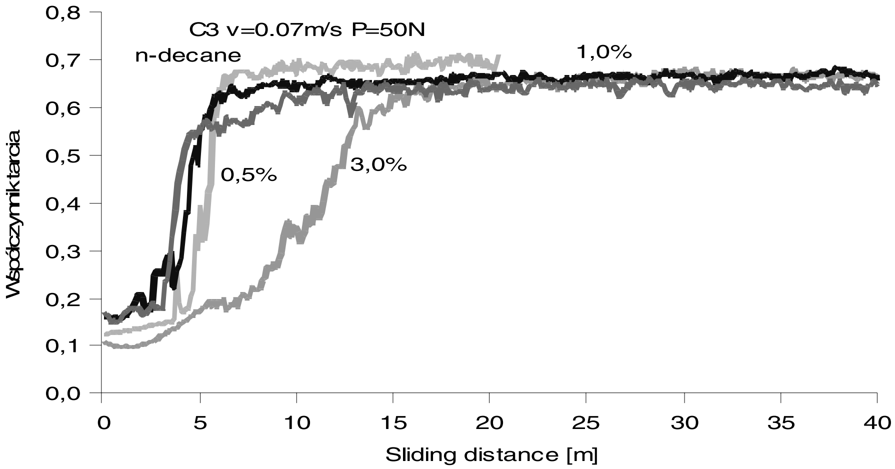

Fig. 5. Effect of C3ZDTP concentration and sliding distance on friction coefficient, load – 50 N, sliding speed – 0.07 m/s

Rys. 5. Wpływ stężenia C3ZDTP i drogi ślizgania na współczynnik tarcia, obciążenie-50 N, szybkość ślizgania – 0,07 m/s

When using C12ZDTP (**Fig. 6**), in the whole sliding distance of 360 m very low friction coefficients, similar to the ones at lower sliding speed (0.01), are observed. They are strongly differentiated in the range of 0.07÷0.11.

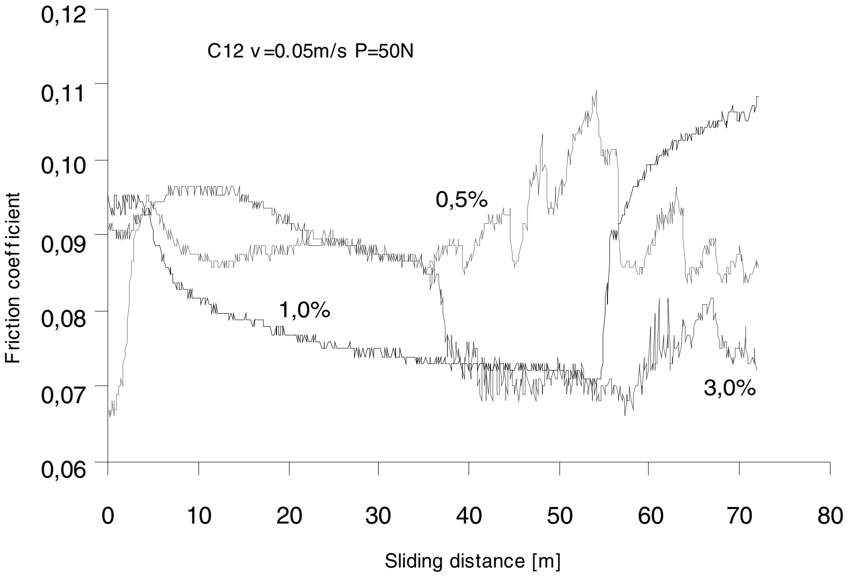

Fig. 6. Effect of C12ZDTP concentration and sliding distance on friction coefficient, load – 50 N, sliding speed – 0.05 m/s

Rys. 6. Wpływ stężenia C12ZDTP i drogi ślizgania na współczynnik tarcia, obciążenie – 50 N, szybkość ślizgania – 0,05 m/s

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] and load [N]. The values of ball wear rates for the loads of 25 N and 50 N are presented in **Table 2**. For 0.5% solution concentration of C3ZDTP and both loads the wear rates are similar to the results of the wear test with n-decane alone. For other ZDTPs wear rates are much lower than in the wear test with n-decane. The magnitude and rate of adsorption **[L. 15]** at lower solution concentration of C3ZDTP additive molecule do not completely cover the surface and adsorption enthalpies are relatively low. The boundary and dry friction dominate, hence, the reduction of friction (**Fig. 1a**) and wear rates (**Table 2**) are high. At the lowest sliding speed (0.01 m/s), the wear rates decrease with increasing ZDTPs solution concentrations their values much decreasing with the increase concentration from 0.5 to 1.0%. The same decreasing tendency, but with lower degree, is also observed in the tests for higher sliding speed of 0.05 m/s. The wear rates reduction in the presence of additives are also lower in comparison to the rubbing test with n-decane alone, but the reduction is not so high as at lower sliding speed. For these tests the wear coefficients increased by three orders of magnitude in comparison to lower sliding speed. For some results, at sliding speed of 0.01m/s (**Figs. 1**), wear correlates well with friction. Increasing the concentration to 1.0 and 3.0% decreases the friction and wear rate significantly. At lubrication with 0.5 and 1.0% of C3 and C6ZDTPs at higher sliding speed, friction after some sliding distance goes to higer values, the same as for n-decane (**Figs. 3a** and **b**) and higher wear close to n-decane alone is seen. The increase of additive concentration up to 3% causes higher friction reduction and wear. For all tested C12ZDTP solution concentrations at both speeds and loads, the friction and in most cases wear rates are lower than ZDTPs with shorter alkyl chain.

Table 2. Wear rates [mm^3 x N^{-1} x m^{-1}], of n-decane and ZDTP n-decane solutions
Tabela 2. Szybkości zużycia [mm^3 x N^{-1} x m^{-1}] n-dekanu i roztworów ZDTP w n-dekanie

Sliding speed, sliding distance – 0,01 m/s, 72 m				Sliding speed, sliding distance – 0,05 m/s, 360m			
Loads		25 N	50N	Loads		25 N	50N
n-decane		6.05 x 10^{-7}	10.05 x 10^{-7}	n-decane		2.76 x 10^{-4}	3.1 x 10^{-4}
ZDTP	Concentrations %			ZDTP	concentrations %		
C3	0.5	5.4 x 10^{-7}	9.33 x 10^{-7}	C3	0.5	3.7 x 10^{-4}	2.0 x 10^{-4}
	1.0	0.81 x 10^{-7}	0.48 x 10^{-7}		1.0	2.2 x 10^{-4}	1.02 x 10^{-4}
	3.0	0.64 x 10^{-7}	0.85 x 10^{-7}		3.0	0.76 x 10^{-4}	0.38 x 10^{-4}
C6	0.5	3.1 x 10^{-7}	2.41 x 10^{-7}	C6	0.5	2.2 x 10^{-4}	1.9 x 10^{-4}
	1.0	0.84 x 10^{-7}	2.27 x 10^{-7}		1.0	2.8 x 10^{-4}	1.4 x 10^{-4}
	3.0	0.22 x 10^{-7}	1.43 x 10^{-7}		3.0	1.8 x 10^{-4}	0.92 x 10^{-4}
C12	0.5	2.8 x 10^{-7}	2.1 x 10^{-7}	C12	0.5	2.22 x 10^{-4}	2.4 x 10^{-4}
	1.0	2.0 x 10^{-7}	1.97 x 10^{-7}		1.0	2.15 x 10^{-4}	1.9 x 10^{-4}
	3.0	0.62 x 10^{-7}	0.84 x 10^{-7}		3.0	0.15 x 10^{-4}	1.08 x 10^{-4}

The representative SEM micrographs of balls worn surfaces at the end of tests are presented in **Figs. 6–7**. White wear debris are observed on and outside and on the wear scar surfaces after completion of rubbing tests, but before washing. The worn surfaces after lubrication with n-decane at sliding speed – 0.01 m/s exhibit rough topography with microfractures, local microcracks, deep grooves, pores and some grains (**Fig. 6a**). The surfaces are more smooth and show a dense structure with considerably fewer microfractures, grains and pores, after friction tests with 3.0% of C3 solution concentration (**Fig. 6b**) and C6ZDTPs (**Fig. 6c**) at load of 50 N. The smoothness of surface increases with the increase of the length of hydrocarbon chain and additive solution concentration. Wear scars lubricated with additive with the longest length of carbon chain C12 and all solution concentrations for both loads of 25 and 50 N are the smoothest (**Figs. 6d, e**). The concentration increase of this additive strongly reduces the pits on the rubbing surface (**Fig. 6e**); at lower this

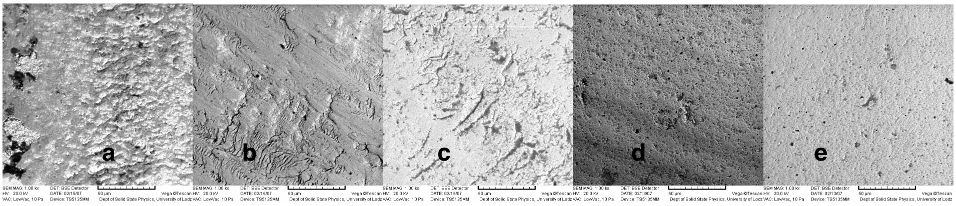

Fig. 6. SEM image of worn surface lubricated; hydrocarbon (a), C3ZDTP solution concentration of 3.0% (b), C6ZDTP solution concentration of 3.0% (c), C12ZDTP solution concentration of 0.5% (d) and of 1.0% (e), load – 50 N, sliding speed – 0.01 m/s

Rys. 6. Obraz SEM powierzchni zużycia smarowanych; węglowodorem (a), 3% roztworem C3ZDTP (b), 3% roztworem C6ZDTP (c), 0,5% (d) i 1,0% (e) roztworami C12ZDDP, obciążenie – 50 N, szybkość ślizgania – 0,01 m/s

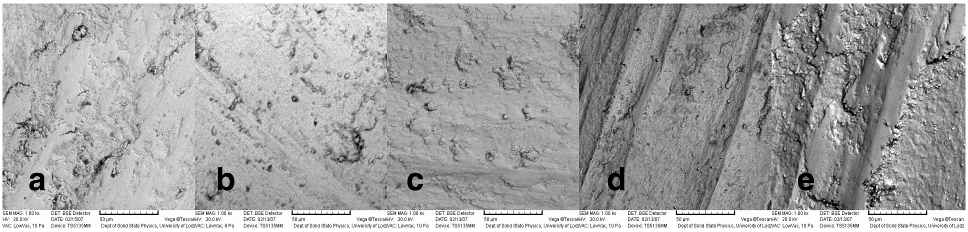

Fig. 7. SEM image of worn surface lubricated; hydrocarbon (a), C3ZDTP solution concentration of 0.5% (b) and 3.0% (c) and C12ZDTP solution concentrations of 1.0% (d) and of 3.0 % (e), load – 50 N, sliding speed – 0.05 m/s

Rys. 7. Obraz SEM powierzchni zużycia smarowanych; węglowodorem (a), 0,5% (b) i 3%, (c) roztworem C3ZDTP 1,0% (d) i 3,0% (e) roztworami C12ZDDP, obciążenie – 50 N, szybkość ślizgania – 0,05 m/s additive solution concentration (0.5%) worn surfaces also show ploughing, which is observed at the bottom of image (**Fig. 6d**). For both these concentrations of C12ZDTP the friction and wear are very low. At a higher sliding speed (0.05 m/s) a transition to more severe wear with a change of the mechanism in the contact area to microfracture and microploughing, appear therefore the wear increases dramatically; the topographies of the wear scar surfaces show a larger destruction (**Figs. 7a–e**) than observed after rubbing at 0.01 m/s. Deep groves, intergranular fracture, plastic deformation, delamination and some debris are seen on all worn surfaces lubricated with n-decane (**Fig. 7a**). The increase of C3 solution concentration results in smoother scar surfaces, fewer microcracks and grains (**Figs. 7b, c**).The rubbing surfaces lubricated by C6ZDTP (not illustrated), exhibit shallow microgrooves. C12ZDTP shows much more anti-wear film destruction than C3ZDTP, especially for the highest additive concentration (**Figs. 7 d, e**). SEM morphologies of wear scars for lubricated C12ZDTP solution show deeper grooves at the solution concentration of 3.0%, some cracks propagation resulted in spalling of material and more grains are formed. The differences of wear coefficients for all tested additives are relatively smaller. Generally, the lower the additive solution concentration and the higher the load, the more the surface is destroyed and the friction and wear coefficient are higher. A larger rubbing destruction at 3.0% solution concentration does not correlate with the observed lower friction and wear coefficients for C12ZDTP. The wear does not correlate with the observed lower friction coefficient for C12ZDTP at higher sliding speed (**Fig. 5**). 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 even dry lubrication may occur.

The tribochemical film was not visible on the ball wear surface, but the results of EDS analysis of atomic element concentration, normalized to [Zn] = 1.0 of reaction films, presented in **Table 3**, show a change of the concentration of zinc, phosphorus and sulfur. The higher sliding speed the lower concentration of those elements. The concentrations of Zn, S, P in films formed on worn surface lubricated with C12ZDTP at sliding speed – 0.01 m/s are much lower than for ZDTPs with shorter alkyl chain. At higher sliding speed (0.05 m/s) for all ZDTPs a further decrease of Zn, S, P contents were observed. These atomic elements contents are probably much lower, because in severe frictional sliding speed (0.05 m/s) for all ZDTPs a further decrease of Zn, S, P contents were observed. On a worn surface lubricated with 3% solution concentration of C6ZDTP no Zn was recorded. These atomic elements contents are much lower, probably, because in severe frictional boundary and dry lubrication condition thinner protective tribochemical ZDDP films are easily and quickly removed from the rubbing surface, therefore they are less effective than those formed at lower sliding speed.

Table 3. Composition of frictional surface films, load – 50 N

Tabela 3. Skład pierwiastkowy powierzchni tarcia, obciążenie –50 N

ZDTP	Concentration %	Zn	S	P	Zn	S	P
Sliding speed and distance: 0.01 m/s, 72 m		Normalized to Zn			Atomic element %		
ZDTP original		1.0	4.0	2.0			
C3	0.5	1.0	0.9	3.1	0.14	0.13	0.44
	1.0	1.0	0.4	2.8	0.43	0.19	1.19
	3.0	1.0	0.8	3.8	0.35	0.29	1.34
C6	0.5	1.0	0.5	2.0	0,69	0.33	1.31
	1.0	1.0	0.7	2.9	0.59	0.32	1.56
	3.0	1.0	0.8	1.9	0.71	0.60	1.38
C12	0.5	1.0	2.8	3.2	0.22	0.34	0.75
	1.0	1.0	1.4	3.9	0.17	0.24	0.66
	3.0	1.0	1.1	6.8	0.10	0.11	0.68
0.05 m/s, 360 m							
C3	0.5	1.0	1.2	7.8	0.08	0.10	0.63
	3.0	1.0	1.3	7.4	0.09	0.12	0.67
C6	1.0	1.0	1.2	6.9	0.10	0.12	0.69
	3.0	–	–	–	–	0.34	0.75
C12	1.0	1.0	1.4	7.6	0.06	0.24	0.44
	3.0	1.0	2.7	7.2	0.06	0.16	0.43

Phosphorus was the predominant element on the surface, whereas zinc and sulfur were conspicuously low considering that the atomic ratio for the original molecule was 1Zn:2P:4S. Comparing this ratio to most of the tests the phosphorus contents are slightly higher than in the additive molecule at sliding speed of 0.01 m/s and much higher, nearly four times higher at higher sliding speed of 0.05 m/s. At higher sliding speed for both C3 and C6ZDTPs, the ratio of phosphorus/zinc concentrations is about two times higher than that at a lower sliding speed (0.01 m/s). The concentration of sulfur has decreased by from one and half to ten fold comparing to original ZDTP. The low presence of sulfur suggests that the additive has undergone some kind of decomposition sequence involving scission of both the S-P and S-Zn bonds, resulting in the elimination of sulfur from the reaction product film. Firstly because of the low thermal conductivity of the PSZ material in the contact at higher sliding speed high temperature is generated, and more complete thermal decomposition of the ZDTP occurs to products that are lower in S, Zn and P contents. A second possibility is that, ZDTP decomposed, in the contact junction forms films relatively high in phosphorus concentration and phosphorus/zinc ratio. Such results are not observed in films from ZDTPs wear tests on steels, but are seen in the case other ceramics **[L. 10]**. A very low atomic Zn concentration at higher sliding speed and the lowest contents of sulfur suggests that the products are different than those obtained in the steel lubricated ZDTPs case. All those results imply different tribochemical reactions for ZDTPs with PSZ.

The effect of additives adsorption on wear and friction

The friction coefficients are closely related to rate and magnitude of adsorption and differential molar enthalpies of adsorption. They are also influenced by the organization of boundary layer. It could be deduced from isotherms and enthalpy of adsorption results **[L. 15]**, that probably also during friction with shorter alkyl chain of C3ZDTP there do not appear densely packed surface layers bonded to the frictional surfaces. In contrast C6 and C12ZDTPs form thicker more stable boundary layers and no fluctuation of friction coefficient values is observed. In the case of C3 the additive molecules do not completely cover the surface and adsorption enthalpies are relatively low, hence, the reduction of friction and wear rates are the lowest. Bigger additive molecules (C6 and C12) form bilayers like films or some kind of interfacial aggregates. The C6ZDTP forms more densely packed monolayer and the friction coefficient is lower than with C3ZDTP. It appears from the surface area coverage of the additive molecules, calculated based on adsorption data, that C12ZDTP is the most packed and the thickest bilayer among tested ZDTPs. Additionally, C12ZDTP is most thermally stable among ZDTPs. Under such conditions, the contact operates with a viscous layer, thereby forming much thicker boundary layer associated also with a hydrodynamic lubrication regime, giving the largest reduction of friction and wear in both tested loads. Furthermore, additive concentration and sliding speed significantly affect the friction. Depending on the additive concentrations, the lower the boundary, and the higher concentration boundary, mixed and hydrodynamic lubrication regimes at any sliding speed are observed.

CONCLUSIONS

From the experimental data presented here, the following conclusions can be drawn:

- all tested ZDTPs exhibit significantly reduced friction coefficients and wear rate in comparison to the base hydrocarbon in limiting ranges of loads, sliding speeds and additive concentration.
- the longer the hydrocarbon chain in the additive molecule and the higher its solution concentration, the bigger is the tribological effectiveness. Increasing load and sliding speed have detrimental effect on friction and wear behaviour, except for C12ZDTP and, in case of this additive, tribochemical reaction plays a less significant role. The most effective anti-frictional and anti-wear properties of all the tested additives are exhibited by C12ZDTP, at all tested sliding speeds.
- the main wear mechanism observed was ploughing, adhesive and tribochemical. The increase of sliding speed from 0.01 to 0.05 m/s increases the wear rate by three orders of magnitude. The high wear correlates well with high friction coefficient.
- tribofilm formation occurs on worn surfaces. The contents of phosphorus, zinc and sulphur in tribochemical film decreases with the increase of the sliding speed and length of the additives hydrocarbon chains. The surface film in PSZ is mostly phosphorus with fewer amounts of zinc and sulfur. The composition of these films are different from those formed on lubricated steel, but similar to other ceramics systems **[L. 10]**. It implies the specific tribochemical reaction of ZDTPs with PSZ surfaces.
- the friction coefficients and wear are closely related to rate, magnitude and differential molar enthalpies of adsorption of ZDTPs. They are also influenced by the additive molecules organization by adsorption and/or tribochemical reaction of boundary layer.

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Streszczenie

Tribologiczne właściwości di-n-alkiloditiofosforanów (ZDTPs) w styku pary tarciowej jonowego – ZrO_2 częściowo stabilizowanego Y_2O_3 [PSZ] były badane z użyciem tribometru kula-dysk w 25°C. Stwierdzono, że ZDTPs znacząco zmniejsza tarcie i zużycie. Wzrost prędkości ślizgania i obciążenia ma niekorzystny wpływ na zmniejszenie tarcia i zużycia. Efektywność redukcji tarcia i zużycia wzrasta ze wzrostem długości łańcucha węglowodorowego i stężenia roztworu cząsteczki dodatku. Powierzchnia tarcia była analizowana z użyciem mikroskopu i techniki SEM/EDX. Wyniki tarcia i zużycia dobrze korelują z wielkościami i molową entalpią adsorpcji ZDTP na proszku PSZ z roztworu n-dekanowego i stężeniem fosforu na powierzchni tarcia.