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THE EFFECT OF ZINC DITHIOPHOSPHATES ON THE FRICTION AND WEAR OF PARTIALLY STABILISED ZIRCONIA
PART III. LUBRICATION OF FRICTIONAL CONTACT

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ceramics, friction modifiers, boundary, mixed and hydrodynamic lubrication, zinc dialkyl-(aryl)dithiophosphates

Słowa kluczowe:
materiały ceramiczne, modyfikatory tarcia, smarowanie graniczne, mieszané i hydrodynamiczne, dialki(aryl)ditiofosforany

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Summary

Lubrication properties of zinc di-n-alkyldithiophosphates (ZDTPs), zinc di(n-nonylphenyl)-dithiophosphate (MAP) and di(di-n-nonylphenyl) dithiophosphate (DAP) depend on the additive molecular structure and its solution concentration. The effectiveness of friction reduction increases with the increasing length of the hydrocarbon chain in the additive molecule and decreases with increasing sliding speed and load. Lubrication tests of ionic-ZrO₂, partially stabilised by Y₂O₃ (PSZ) were performed with the use of a ball-disk tribometer at 25°C. The lubrication mechanism is discussed based on the Stribeck curve. The loads and sliding speed applications were increased so that the friction contacts ranged from hydrodynamic or mixed to boundary lubrication. The hydrodynamic and mixed regimes are extended with the reduction of the boundary lubrication of tested additives. Results of these lubrication experiments are closely related to the results of the adsorption data of additives on PSZ powder from n-decane solutions, particularly with additive surface layer structure as well as on the differential molar enthalpy of adsorption.

INTRODUCTION

In Parts I and II tribological properties of zinc di-n-alkyl dithiophosphates [L. 1] and zinc di(n-mono- and di(n-dialkylphenyl)dithiophosphates [L. 2] in PSZ frictional contact were investigated. All tested additives exhibit significantly reduced friction coefficients and wear rates in comparison to the base hydrocarbon. The most effective anti-frictional and -wear properties of all the tested additives are exhibited by C₁₂ZDTP a little worse in case of both MPA and DAP at all tested sliding speeds. To better understand the AW/EP and frictional ZDTPs properties adsorption studies on PSZ powder surface have earlier been carried out [L. 3]. It can be deduced from isotherms and enthalpy of adsorption results that probably also during friction, ZDTPs with shorter alkyl chain do not form completely cover densely packed surface layers and weakly bonded to the frictional surfaces. Hence, in frictional condition they can operate mainly in boundary regime. C₁₂ZDTP, MAP and DAP form packed, thicker, high viscosity stable layers on the surface. Under such conditions and at higher additive concentration the contact operates with a viscous layer, thereby forming much thicker hydrodynamic (HD) films.
The loads and sliding speeds are varied so that investigated friction contacts ranged from boundary, mixed and hydrodynamic lubrication.

At now, as the third step, the effect of load, sliding speed, the molecular ZDTPs, MPA and DPA structures and additive concentration on lubrication mechanism have been investigated. The results of the current studies are presented and discussed in relation to the results of the above mentioned adsorption studies.

EXPERIMENTAL SECTION

Preparation of zinc dialkyl(alkyl- and dialkylphenyl) dithiophosphates.

ZDTPs, MAP and DAP were prepared in a three-step laboratory process, according to procedures described elsewhere [L. 4]. The additives were blended in n-decane, at concentrations in the range of 0.01–3.0%. N-decane is not used as base oil for zirconia lubrication, but they were blended in this solvent for consistency with adsorption studies, where they were also used.

Ceramic material

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

Friction test

Friction tests outlined in Part I were followed to generate the data reported in this paper. Experiments were carried out at sliding speeds in the range of 0.01–0.09m/s (five speeds), at loads of 2–50N (9 loads), with 5 minute duration, at the temperature of 20°C. The additives concentrations were in the range of 0.01–3.0% (five concentrations). Two tests were performed for each specimen, with the results showing a deviation of less than 10%.

RESULTS AND DISCUSSION

The effect of rubbing time on the friction coefficient.

This effect was examined for some selected loads, sliding speeds, by testing different ZDTPs, MAP and DAP with their different concentration in n-decane solution. The most representative friction coefficients results in relation to rubbing time presented in Figs. 1–4, are
chosen from a large amount of data. Two patterns of behavior can be clearly distinguished for two different sliding speeds for the same additive and solution concentration of 0.5% (Figs. 1a–f). The values of friction coefficient for ZDTPs with shorter alkyl chains increase linearly with test time, and faster for the lower sliding speed, increasing with load.

Fig. 1. The effect of rubbing time, selected loads and sliding speeds on friction coefficient of C4 ZDTP, additive concentration – 0.5%

Fig. 2. The effect of rubbing time, selected loads and sliding speeds on friction coefficient of C12ZDTP, additive concentration – 0.5%
The fluctuations of friction coefficient values are observed which are similar to stick-slip effect, much stronger at lower sliding speed (Figs. 1a–c) and decreasing with the length of the n-alkyl chain of the additive to become negligible in case of C12ZDTP (Figs. 1d–f and 2a–c). The increasing test speed decreases the variation in friction coefficient values during the test. Zirconia materials are stiff enough so that the stick-slip effect may be less probable. The presence of stick-slip friction spikes may also suggest grain pull out and abrasion, indicating wear. As for C12ZDTP, the experimental curves for both tested sliding speeds (0.01 and 0.07 m/s) were the same, only the results for the higher sliding speed are presented here. No differences in friction coefficient values were observed for tests with C12ZDTP for all loads and additive concentration higher than 0.1%, friction coefficients are lower in comparison with C4ZDTP. For lower; 0.1% concentration of MAP, bigger variation of friction values is observed (Fig. 3a). Increase of MAP concentration from 0.1% to 0.5% decreases evidently this variation and friction coefficient value (Fig. 3b) was observed. Figs. 3b–d show that lubrication with 0.5% MAP solution concentration with increasing load friction coefficients increase slightly and are similar in comparison to C12ZDTP lubrication. A higher friction and fluctuations of friction values, which also increase with increasing of load in the course of friction testing, were observed for DAP (Figs. 3e, f) but they appear much lower in value in comparison with the case of C4ZDTP (Figs. 1a–c). The effects of rubbing time and sliding speed under a constant 20N load and additive concentration, on values of the friction coefficient for

![Fig. 3. The effect of rubbing time, selected loads, additive concentration and sliding speed on friction coefficient of MAP and DAP](image)

Rys. 3. Wpływ czasu tarcia, wybranych obciążzeń, stężenia dodatku i prędkości ślizgania na współczynnik tarcia MAP i DAP
MAP and DAP are shown in Figs. 4. The friction coefficients strongly increase with increasing sliding speed in case of MAP (Fig. 4a–c) and in case of DAP also with time (Fig. 4d–f). The values of friction coefficient are about 1.5 and 3.0 times higher for the highest sliding speed, (0.09 m/s) than for the lowest speed, (0.01 m/s), for MAP and DAP, respectively. For the higher additive concentrations of MAP, 1.0% and 3.0% (results not presented here), the values of friction coefficients are lower and do not change or slightly increase up to 0.18 with increasing sliding speed and load. In case of DAP, friction coefficient increases from about 0.16 up to 0.45 for concentration of 0.5% and is strongly reduced at the highest additive concentration (3.0%) even at higher sliding speeds (results are not shown). It was deduced from isotherms and enthalpy of adsorption results [L. 3] that during friction, contrary to C12ZDTP, C3 and C4ZDTPs do not form densely packed surface layers and are weakly bonded to the frictional surfaces. ZDTPs with longer n-alkyl chains form more stable boundary layers.

Fig. 4. The effect of rubbing time and selected sliding speed on friction coefficient of MAP and DAP, additive concentration – 0.5%, load – 20 N
Rys. 4. Wpływ czasu tarcia i wybranych prędkości ślizgania na współczynnik tarcia MAP i DAP, stężenie dodatku – 0.5%, obciążenie – 20 N

EFFECT OF LOAD, SLIDING SPEED AND ADDITIVE CONCENTRATIONS ON FRICTION COEFFICIENT ZINC N-ALKYLDITHIOPHOSPHATES
The effect of load and sliding speed on friction coefficient is illustrated in Figs. 5a-f, for pure n-decane and tested ZDTPs at different solution concentrations. For pure n-decane with increasing of sliding speed and
load the friction coefficient (Fig. 5a) strongly increases. The increase of the sliding speed leads to a rise of friction at lower loads. The use of a relatively low additive solution concentration (0.1%), at the lowest speed of 0.01m/s, results in a significant reduction of friction for all tested additives (Fig. 5b). At lower loads (below 20N) for all tested ZDTPs, a steady-state friction coefficient is visible. At higher loads, the values of friction coefficient increase gradually with increasing load, the increase being the highest for C3ZDTP and a little lower for C4ZDTP. The highest reduction of friction is achieved by C12ZDTP and friction coefficient value is nearly constant in the whole range of tested loads. Such a behavior of tested additives may be explained in relation to the results of adsorption studies. In case of C3 and C4ZDTPs, the additive molecules do not completely cover the surface and adsorption enthalpies are relatively low. C6ZDTP forms more densely packed monolayer; hence the friction coefficient is lower. The biggest additive molecule

![Graphs showing the effect of load, solution concentration, and selected sliding speeds on friction coefficient of n-alkyl ZDTPs.](image)

**Fig. 5.** Effect of load, solution concentration, and selected sliding speeds on friction coefficient of n-alkyl ZDTPs

**Rys. 5.** Wpływ obciążenia, stężenie dodatku i wybranych prędkości ślizgania na współczynnik tarcia n-alkilowych ZDTPs
of C12ZDTP forms bilayers on the surface, and the reduction of friction coefficient in the whole range of tested loads is the largest, here. Additionally, the latter additive starts to form the adsorption film at the lowest equilibrium concentration. The increase in the sliding speed up to 0.07 m/s (Fig. 5c) at the same additive concentration (0.1%) reduces the range of the steady-stage of friction to the load of about 15N, with a sudden strong increase up to about two fold of the friction coefficient for all ZDTPs in comparison to lowest sliding speed presented in Fig. 5b. In this range of high friction coefficient, the frictional system operates in the boundary regime, as it is illustrated in the Stribeck diagram (Fig. 6a). At higher additive concentration (0.5%), the shapes of load versus friction coefficient curves show strong reduction of friction for all ZDTPs and all loads at sliding speed of 0.01 m/s (Fig. 5d) and even at 0.07 m/s ones with exception of ZDTPs with shorter n-alkyl chains and for higher loads friction coefficient are also low (Fig. 5e) in comparison to those at lower additive concentrations (Fig. 5c). In the lower load range (up to about 20N), the values of friction coefficient decrease significantly for lower sliding speed (Fig. 5d), in contrast to the results for lower additive concentration (0.1%). They slightly increase only for C3 and C4ZDTPs at higher loads (more than 30N) and sliding speed (Fig. 5e). Higher additive concentration (1.0 and 3.0%), at all sliding speeds, also results in a strong reduction of friction which strongly decreases at lower loads (up to about 20N), at higher loads they decrease slightly further (Fig. 5f). Generally, the increase of n-alkyl chain length and concentration of ZDTPs reduce friction coefficient very strongly, even for the lowest additive concentration tested (0.1%), however, in case of C6 and C12ZDTPs, only for lower sliding speeds. For all ZDTPs at 0.5% and higher additive concentration in the whole ranges of load and sliding speeds, the measured friction decreases significantly (Figs. 5b-f). It is seen From the Stribeck curves that at the lowest C3ZDTP concentration, the system operates in the high friction boundary regime (Fig. 6a), but with the concentration raised to 0.5% the values of friction coefficient diminish strongly and the boundary lubrication range decreases about twofold (Fig. 6b). For the lowest sliding speed (0.01 m/s) No boundary lubrication is observed for the lowest sliding speed (0.01 m/s) with further raised additive concentrations (up to 3.0%), boundary lubrication ranges disappear and elastohydrodynamic lubrication ranges are not seen, hydrodynamic film develops (Fig. 6c). The transition from mixed to
hydrodynamic lubrication takes place at the slowest speed and higher loads. The variations of friction in relation to Stribeck curves for C12ZDTP are shown in Figs. 7a–c. At additive concentration 0.1% the system operates in boundary lubrication (Fig. 7a), but its ranges are lower than in case of 3ZDTP. For additive concentrations from 1.0% to 3% the friction behaviour is similar (Figs. 7b,c), with increasing concentrations extending the hydrodynamic friction region. Two minima of friction coefficient on Stribeck curves are seen. From the surface area coverage

Fig. 6. Stribeck curves of C3ZDTP lubrication at different sliding speeds and additive solution concentration
Rys. 6. Krzywa Stribecka smarowania C3ZDTP w różnych prędkościach ślizgania i stężeniach roztworu

Fig. 7. Stribeck curves of C12ZDTP lubrication at different sliding speeds and additive solution concentration
Rys. 7. Krzywa Stribecka smarowania C12ZDTP w różnych prędkościach ślizgania i stężeniach roztworu
by the additive molecules, calculated on the basis of adsorption data, it appears that the most packed and thick bilayer among tested ZDTPs is the C12ZDTP. In these conditions, the contact operates with a viscous layer, thereby forming much thicker HD films, giving higher friction than the lower hydrodynamic one, due to the low viscosity lubricant. Additionally, the latter additive starts to form the adsorption film at the lowest equilibrium concentration.

Striebeck curves with similar shapes were observed by Smeeth et al. [L. 5] in their studies of boundary film formation by viscosity index improvers. Polymers and friction modifiers form a highly viscous surface deposit. At lower Hersey numbers, the contact with this deposit operates in the hydrodynamic range. Furthermore, additive concentration and sliding speed significantly affect the friction. For the lowest additive concentrations, the boundary regime can be seen at any sliding speed, while at the lowest speeds, and higher additive concentration, ZDTPs even with shorter alkyl chains show no boundary lubrication, only a transition to mixed/hydrodynamic region. For lubrication using the highest additive solution concentration at any sliding speed, no boundary but hydrodynamic lubrication regime is observed.

Zinc di-n-alkylarylpidithiophosphates

The influence of load and MAP and DAP solution concentration at two, the lowest and the highest tested sliding speeds, on friction are shown in Figs. 8a–d. In case of the loads for these both additives below 20N and 10N at 0.01m/s and 0.09m/s sliding speeds, respectively, the friction of all additive solution is the same as that of base oil. Above these loads, at the lower sliding speed, friction of both MAP and DAP (Figs. 8a and c) is seemingly independent of load and, in relation to additive solution concentration, except the lowest solution concentration (0.01%), is virtually indistinguishable, but differentiation of the friction values in the case of DAP is twofold bigger than MAP. As is evident from Figs. 8a and b, the friction coefficients at higher sliding speed and for two lower additive concentrations above 10N are over three times higher than at lower sliding speed, but for 3.0% additive concentration, the friction coefficients are the same at 0.09m/s and at 0.01m/s. No effect of load, sliding speed, for 1.0% and 3.0% additive solution concentrations of DAP on friction are observed. As shown in Fig. 8d, the value of friction
coefficient at the lowest tested solution concentration (0.5%) is Fig. 8d, the value of friction coefficient at the lowest tested solution concentration (0.5%) is twofold bigger than at the lowest sliding speed. The friction coefficient of MAP and DAP at the lowest and highest sliding speeds are a little higher than observed with C12ZDTP.

LUBRICATION – THE ROLE OF ADSORPTION

The adsorption of ZDTPs, MAP and DAP from n-decane solution on ionic ceramic – zirconia stabilized by yttria powder was investigated in static conditions[1, 3]. The magnitude and rate of adsorption of ZDTPs and MAP on ZPS at 25°C are significant and they decrease with the increasing length of the n-alkyl chain of ZDTP. The adsorption isotherms are Langmuir type with a lower equilibrium concentration in the case of all tested additives. For a shorter alkyl chains (3 and 4 of carbons), it seems that molecules do not cover the zirconia surface completely, and for bigger molecules, C12ZDTP and MAP, bilayer films or some kind of interfacial aggregates are formed. The ball-disk test was employed for friction investigation in the same ZDTPs concentrations as used in adsorption. The shape of friction curves (Fig. 9) obtained at 25N of load for C3 and C4ZDTPs concentrations above about 10 μmol/g shows region of a low, steady-state friction. A sudden jump of values of friction coefficient at the constant amount adsorbed of C3ZDTP is seen...
below these additives concentrations. If we look at the amount of C12ZDTP adsorbed on ZPS powder at the concentration used in this friction test, there is an evident correlation between adsorption data and friction coefficient. In case of C6 and C12ZDTPs, the abrupt change from constant values to a strong increase of friction coefficient appeared at low solution additive concentration, e.g. about 2.5 μmol/g. Above that value, friction coefficients are nearly independent of concentration. Such a change of friction curves is connected with some discontinuity of the adsorption curve. Additive surface concentration (0.8 μmol/m²) and/or rate of adsorption, subsequent to the adsorbate layer organization, are probably enough to replace the continuously removed boundary additive film in rubbing process. The dramatic jump of friction suggests a change in lubrication mechanism. It may correspond to the inability of these ZDTPs to become sufficiently adsorbed to protect fully the nascent surface coming into contact with the opposing rubbing surface. Relationships of friction versus additive concentration, presented on Fig. 9, confirm the above shown results, indicating that the length of n-alkyl chain is very important in reduction of friction. It is evident that ZDTPs containing 6 and more carbon atoms in the chains have good anti-frictional properties in lubrication of PSZ surfaces. The relationship between values of friction coefficient and adsorption data for both MAP

![Graph showing friction coefficient and amount of additive adsorption on PSZ versus concentration of ZDTPs, load – 25 N, sliding speed – 0.01 m/s](image)

**Fig. 9.** Plot of friction coefficient and amount of additive adsorption on PSZ versus concentration of ZDTPs, load – 25 N, sliding speed – 0.01 m/s

**Rys. 9.** Zależność współczynnika tarcia i wielkości adsorpcji dodatku na PSZ od stężenia ZDTPs, obciążenie – 25 N, prędkość ślizgania – 0.01 m/s
and DAP additives are drawn from friction investigations at a sliding speed of 0.09 m/s and for different loads of the range 10–25 N. The results for MAP are shown in Fig. 10. The trend in friction curve which is similar to C12ZDTP is also observed for MAP (Fig. 9). The stable friction with a slight increase, measured for MAP is about 1.5 fold bigger than that of C12ZDTP. Evident friction increases start about 0.5% and a sudden jump in friction at about 0.2% additive solution concentration is observed at a low amount of additive adsorbed. The change of friction curve is connected with the beginning of a small discontinuity in the adsorption curve. A more evident transition from steady-state, exhibited by a higher DAP solution concentration than in case MAP, e.g. 0.5%, is observed (Fig. 11). Such a sharp increase of friction coefficient is connected with a little higher than for MAP amounts of the additive adsorbed, when steady-state friction begins with increasing additive solution concentration. The different friction behavior of MAP and DAP can be explained also by adsorption data. The zirconia surface coverage by MAP is similar to C12ZDTP and is two times higher than by DAP. In case of DAP at 25°C the degree of surface coverage is lowest but differential molar enthalpy is endothermic and decreases up to surface coverage of about 0.6. It suggests that there occurs chemisorption of this 

![Fig. 10. Plot of friction coefficient results and amount of MPA adsorption on PSZ versus additive concentration, sliding speed – 0.09 m/s](image)

Rys. 10. Zależność wyników współczynnika tarcia i ilości zaadsorbowanego MAP na PSZ od stężenia dodatku, prędkość ślizgania – 0.09 m/s
additive on active sites of PSZ. Additionally, since the DAP adsorbed layer is not densely packed because of molecule steric effect, its frictional properties are worse than MAP. The MAP and DAP differential molar enthalpy data at 35°C are exothermic. From the surface area coverage by the additive molecules, calculated on the basis of adsorption data, it appears that the least and most packed among tested additives are C3, C4 ZDTPs, DAP and MAP, C12ZDTP, respectively. In the ranges of tested loads and sliding speeds at a lower concentration of first additive group, the rubbing system operates in the boundary regime. Bigger densely packed molecules of C12ZDTP, MAP and less DAP oriented perpendicular to the surface form a thick bilayer or superpose onto one another. They can operate with a viscous layer, thereby forming much thicker surface films. In this frictional contact boundary lubrication range disappears, in presented lubrication studies elastohydrodynamic (EHD) lubrication range is not seen and a hydrodynamic(HD) film develops.

CONCLUSIONS

From the experimental data presented here, the following conclusions can be drawn:
– most of the tested additives exhibit significantly reduced friction coefficient values, in comparison to base hydrocarbon. The additive
solution concentration gives large improvement while increasing load and sliding speed have detrimental effect on anti-frictional performance of the tested additives;

– most effective anti-frictional properties of all the tested additives are exhibited by C12ZDTP and MAP. They most significantly extended the range of the hydrodynamic region, with reduction of the boundary and mixed/boundary regimes of lubrication. This extension is the bigger the longer hydrocarbon chain in additive molecule and the higher the solution concentration;

– the studies of the effect of the rubbing time on friction coefficient reveals the presence of significant variation in friction coefficient values and the presence of stick-slip like phenomenon at lower additive solution concentration, higher loads and sliding speed in case of shorter n-alkyl chain C3 and C4ZDTP and less DAP;

– the shape of friction coefficient curves is closely related to adsorption isotherms; the increase of the amount adsorbed at the low additive solution concentration strongly reduces friction, which is influenced by the organization of boundary layer and also by differential enthalpy of additives adsorption;

– at higher sliding speeds and lower additive concentration, except for C12ZDTP and MAP, in bigger friction and wear, there occurs a tribochemical reaction.

REFERENCES


Streszczenie

Właściwości smarowe di-n-alkiloditiofosforanów cynku (ZDTP), di(mono-n-nonylo-fenylo)ditio-fosforanu cynku (MAP) i di(di-n-nonylofenylo)ditiofosforanu cyku (DAP) zależą od struktury cząsteczki dodatku i jego stężenia w roztworze. Efektywność obniżania tarcia wzrasta ze wzrostem długości łańcucha węglowodorowego cząsteczki dodatku i maleje ze wzrostem prędkością ślizgania i obciążenia. Testy smarowania jonowego ZrO₂ częściowo stabilizowanego Y₂O₃ (PSZ) wykonany był na tribometrze kula–dysk w temperaturze 25°C. Mechanizm smarowania jest omawiany z wykorzystaniem krzywej Stribecka. Zastosowane obciążenia prędkości ślizgania wzrastały tak, że styki tarczowe były smarowane w zakresie od hydrodynamicznego, mieszankiego do granicznego. Zakresy mieszankiego i hydrodynamicznego smarowania zwiększają się ze zmniejszeniem zakresu smarowania granicznego w wyniku działania przeciwtarczowego badanych dodatków. Uzyskane wyniki badań smarowania wykazują bliską zależność z wynikami adsorpcji dodatków na proszku PSZ z roztworów n-dekanowych, szczególnie od struktury powierzchniowej warstwy dodatków jak również od różnicowej cząsteczkowej entalpii adsorpcji.