Mihaela VLAD*, Czesław KAJDAS, Remigiusz MICHALCZEWSKI***

THE EFFECT OF MODEL COMPOUNDS ON LOAD-CARRYING CAPACITY OF A-C:H:W COATED ELEMENTS. PART II. SELECTED ORGANIC SULPHUR AND PHOSPHORUS COMPOUNDS

WPŁYW WYBRANYCH DODATKÓW NA NOŚNOŚĆ WARSTWY SMAROWEJ SKOJARZEŃ CIERNYCH Z ELEMENTAMI POKRYTYMI POWŁOKĄ a-C:H:W. CZĘŚĆ II. WYBRANE ZWIĄZKI ORGANICZNE ZAWIERAJĄCE SIARKĘ I FOSFOR

Key-words:

a-C:H:W coating, organic sulphur compounds, organic phosphorus compounds, scuffing resistance, four-ball tribosystem

Słowa kluczowe:

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* Institute for Sustainable Technologies – National Research Institute, 6/10 Pulaskiego, 26-600 Radom, Poland.

** Institute for Fuels & Renewable Energy, 55 Jagiellońska, 03-301 Warsaw and Warsaw University of Technology, Institute of Chemistry in Płock, 17 Łukasiewicza, 09-400 Płock.

Summary

This paper is the continuation of previous research and reflects the results of sulphur and phosphorus containing tribological compounds considered as potential anti-wear additives for heavy-loaded a-C:H:W coated machine parts. In Part I **[L. 1]** the results focused on CHO and CHNO model compounds were presented. In the present work four kinds of organic sulphur compounds and two kinds of organic phosphorus compounds were investigated. The compounds were added at 0.1% wt. and 1% wt. concentration in PAO-8 base oil. The a-C:H:W coating was deposited on bearing steel (100Cr6) balls using PVD reactive sputtering. The load-carrying capacity was measured as scuffing load using the T-02 four-ball apparatus. Similarly as in **[L. 1]**, both uncoated steel balls and the steel a-C:H:W coated balls were investigated, and the method with continuously increasing load was applied.

For a-C:H:W coated balls using 0.1% wt. and 1% wt. concentration of organic sulphur compounds, in the base oil, only 1-adamantanethiol showed a slight increase in the scuffing load value. The increase in concentration of benzyl disulphide (BDS) up to 1% wt. increased the scuffing load values for the uncoated steel tribosystem, but the increase in concentration of this compound is harmful for coated balls. Also the both organic phosphorus compounds at the treat rate of 0.1% and 1% wt. in the base oil did not show any improvement in scuffing load values for the coated balls. On the other hand, the increasing concentration of these phosphorus containing compounds in the base oil, improved the load-carrying capacity of the steel tribosystem. Thus, this work also aims at accounting for the action mechanism difference of BDS interaction with steel and the coating. The same is due to the tested phosphorus containing model compounds.

This paper contributes to better understanding the interaction of sulphur and phosphorus containing compounds and shows that such kind of compounds are not effective for increasing the load-carrying capacity of a-C:H:W coated machine parts. Presently the research is being continued with focus on commercial additives and new materials.

INTRODUCTION

The present study was intended to investigate the effectiveness of various model organic sulphur and phosphorus compounds as potential anti-wear or extreme-pressure additives for heavy-loaded a-C:H:W coated steel machine parts. It is an extension of previous research based on model compound tribological additives **[L. 1]**.

Many studies indicated that sulphur-containing additives are widely used in anti-wear and extreme-pressure lubricants because of their ability to provide effective surface film of iron sulphide on ferrous-based surfaces which improve the tribological properties for steel/steel friction pairs by reducing friction, wear and scuffing **[L. 2]**. Numerous products of tribochemical reactions were found for steel-steel tribosystem lubricated with oils containing various organic sulphur compounds **[L. 3–6]**.

Lara Javier et al. investigated sulphur-containing additives (dimethyl disulphide, diethyl disulphide, carbon disulphide) tested using a conventional pin and V-block apparatus, the results show that these additives thermally decompose on the surface to yield an FeS film. Dimethyl disulphide thermally decomposes on an iron surface via half-order kinetics to yield a film that consists of FeS. Dimethyl disulphide also acts as an anti-seizure extreme-pressure additive, and in this case, the seizure load increases with the additive concentration increase **[L. 7].**

Castro Waleska et al. investigated three additives: an organo-sulphur phosphorus anti-wear additive, phosphoroditioate and amine phosphate in the vegetable oils were evaluated in the four-ball wear tester to demonstrate the importance of chemical structure of the base fluids and the effectiveness of the additives in controlling friction and wear. The study shows that organo-sulphur phosphorus and phosphoroditioate additives functioned well as anti-wear additives only in the two unsaturated vegetable oils while amine phosphate was effective in all three fluids **[L. 8]**.

Minami et al. described the lubrication properties of amine salts of diaryl phosphates (triphenyl phosphate, diphenyl phosphate and ortho-phenylene phosphate) in polyether type base oils which were evaluated using four-ball wear test. The unique cyclic phosphate, ortho-phenylene phosphate, prevented wear and reduced friction when combined with tertiary amines. Amine salts of diaryl phosphates reduce wear in polyether fluid. Ortho-phenylene phosphate gave better results than diphenyl phosphate. Adsorptivity, solubility, and corrosivity of the additives were taken into account **[L. 9]**. Detailed action mechanism of AW and EP additives, including sulphide and disulphide compounds along with ZDDP and MDTP additive types was recently presented and discussed by Buyanovsky et al. **[L. 10].** Tysoe & Kotvis **[L. 11]** described mechanisms and effectiveness of extreme pressure additives both, sulphur containing and especially chlorine containing ones.

Recently, Minami et al. in other paper presented that hydroxyalkyl phosphates $[P(O)(OCHRCH_2OH)_3]$, and hydroxyalkyl phosphonates $[P(OH)_n(OCHRCH_2OH)_{3-n}$, where $n = 1, 2]$ prevent wear in polar synthetic esters and are evaluated under the boundary conditions using four-ball apparatus. Effects of substituent in additive molecule on anti-wear properties are found: alkyl and aryl derivatives reduce wear remarkably, whereas allyl derivatives exhibit poor results. It is speculated that the anti-wear inefficiency of allylic compounds is due to auto-oxidation of the additives **[L. 12].**

Earlier research on tribological properties of DLC coating using different ZDDP-based AW and sulphur-based EP compounds in poly-alpha-olefin base oil tested using a load-scanning test rig demonstrated that these additives improve the tribological properties of DLC coatings. It was found that in the DLC/steel combination smoother running-in process proceeds and there is a better tribological performance than in the case of DLC/DLC and steel/steel combination. The standard EP and AW additives tested reduced the steady-state friction of DLC-coated surfaces, probably due to formation of a new type of tribofilm on the exposed steel surfaces, composed from coating material and reaction products from the additives **[L. 13]**.

Although investigations of DLC-coated surfaces showed improved tribological properties when lubricated by additivated oil, the mechanism responsible is not fully understood. Vizintin and Podgornik determined the mechanism responsible for the low-friction behaviour of W-containing DLC coatings when lubricated with poly-alpha-olefin (PAO) oil containing sulphur-based EP or phosphorus-based AW additives which were tested using a high frequency test rig. The results of the investigation show that low-friction behaviour of boundary-lubricated W-DLC coatings is governed by formation of WS_2-containing tribofilms on the steel countersurface or exposed steel substrate, which reduce friction by up to 50% **[L. 14, 15]**.

The objective of this research was to test the effect of organic sulphur and phosphorus compounds in a poly-alpha-olefin base oil on load-carrying capacity in heavy-loaded sliding contact for a-C:H:W coated specimens.

EXPERIMENTAL

Coatings

Similarly as in the previous research **[L. 1]** a-C:H:W coating was used. The a-C:H:W coating representing a-C:H:Me group of DLC coatings was selected for investigation.

The a-C:H:W coating was deposited using PVD process by reactive sputtering on 100Cr6 chrome alloy bearing steel balls (diameter of 12.7 mm, surface roughness $R_a = 0.032$ µm and hardness 60–65 HRC).

Lubricants

Four various organic sulphur compounds and two organic phosphorus compounds were tested. The compounds are presented in the **Tables 1** and **2**.

Table 1. Organic sulphur compounds
Tabela 1. Organiczne związki siarki

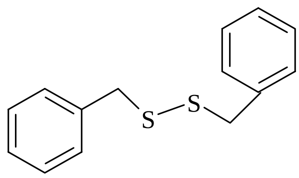
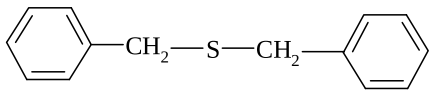
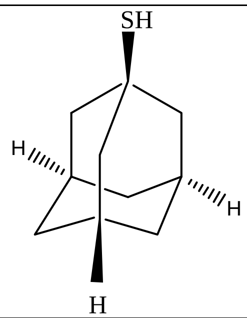
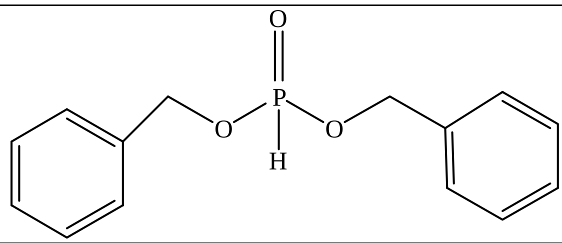
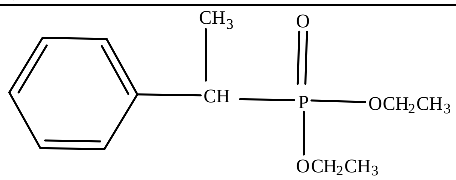
Compound	Code	Chemical structure
benzyl disulphide	S-1	
dibenzyl sulphide	S-2	
octyl sulphide	S-3	$CH_3—(CH_2)_6—CH_2—S—CH_2—(CH_2)_6—CH_3$
1-adamantanethiol	S-4	

Table 2. Organic phosphorus compounds
Tabela 2. Organiczne związki fosforu

Compound	Code	Chemical structure
dibenzyl phosphite	P-1	
diethyl 1-phenylethyl phosphonate	P-2	

The compounds were added at 0.1% wt. and 1% wt. concentration in a poly-alpha-olefin base oil denoted as PAO-8 (viscosity 7.8 mm^2/s at 100°C and viscosity index 136).

Test Method

Similarly as in Part I, both uncoated steel balls and the steel a-C:H:W coated balls were investigated, and the method with continuously increasing load was applied.

Experiments were carried out using a four-ball tester, denoted T-02. According to the test method, the three stationary steel balls are pressed against the upper one in the presence of a lubricant to be tested at the continuously increasing load. The upper ball rotates at the constant speed. During the run friction and load are measured.

The test conditions used are as follows: rotational speed: 500 rpm; speed of continuous load increase: 409 N/s; initial applied load: 0 N; maximum possible load: 7200±100 N; time of a run test 18 seconds. For each oil at least three tests were preformed.

The changes in wear scar surface topography and roughness in dependence of used additives were observed using AFM. To get information on reaction products generated under conditions of T-02 four-ball apparatus, the wear scar surfaces before scuffing initiation were analysed by SEM/EDS and AFM. The surface analyses were performed for wear scars obtained in test runs stopped at 2 sec. (steel-steel tribosystem) or at 10 sec. (a-C:H:W – a-C:H:W tribosystem) before the scuffing initiation.

Surface analyses

To explain the anti-scuffing action of the used compounds, the authors performed surface analyses using Scanning Electron Microscopy / Energy Dispersive Spectrometry (SEM/EDS) and Atomic Force Microscopy (AFM). The aim was to identify possible changes in the wear scar surface layer composition. Prior to analyses, the specimens (balls) were cleaned with 95% *n*-hexane in an ultrasonic washer for 10 min to remove the remnants of the tested oil.

The Q- Scope^{TM} 250 model of AFM manufactured by Quesant was used. 3D images with the nano-meter scale were achieved. All measurements were performed using head with 80 µm range in XY axes in contact and intermittent contact scan modes (scan size 50x50 µm, scan resolution 600 lines). The 3D RMS (Root Mean Square) parameter was measured.

Scanning Electron Microscope model S-2460N manufactured by Hitachi and Energy Dispersive Spectroscopy model Voyager 3050 were used to observe the morphologies of the worn investigated surfaces. All measurements were realized in the following line scan conditions: magnification 100x and 30x, accelerating voltage 15 kV and take-off angle 25°.

RESULTS AND DISCUSSION

Tribological experiments

The tests were performed under conditions of scuffing according to the method described in the Test method subsection, using T-02 four-ball tester.

The results of tribological properties obtained for the tested lubricants, measured by the scuffing load parameter (P_t) are presented in **Fig. 1–Fig. 4**. In all charts the standard deviation is added which reflects the repeatability of the run tests.

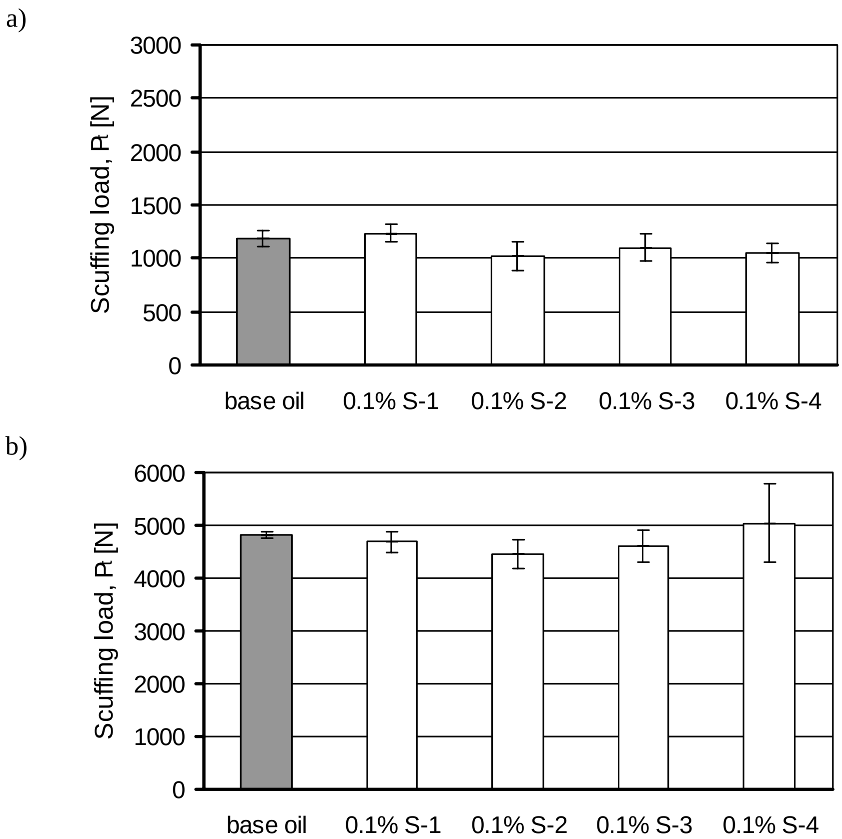


Fig. 1. Scuffing load (P_t) for organic sulphur compounds at 0.1% wt. in PAO-8 base oil: a) uncoated steel–steel tribosystem, b) coated a-C:H:W–a-C:H:W tribosystem

Rys. 1. Obciążenie zacierające (P_t) dla skojarzeń smarowanych olejem PAO-8 z 0,1% w/w dodatkiem organicznych związków siarki: a) skojarzenie stal–stal, b) skojarzenie a-C:H:W–a-C:H:W

As can be seen from **Fig. 1a**, in the uncoated tribosystem only one organic sulphur compound denoted as 0.1% S-1 showed a higher P_t value than the one obtained for the base oil.

It has been generally accepted that the extreme pressure performance of disulphides is better than that of monosulphides. Overall action mechanism of these additives has been discussed by Buyanovsky et al. **[L. 10]** and Vizintin **[L. 16]**, also considering the mechanism based on the anionic-radical lubrication model according to work **[L. 17]**.

If the coating is applied P_t values are approximately fourfold bigger than for uncoated tribosystem (see **Fig. 1b**). Only one organic sulphur compound (1-adamantanthiol) denoted as 0.1% S-4 presents P_t value bigger than the base oil. In **Fig. 2** is presented the effect of concentration; in the case where coating was applied. It is interestingly to note that the 10 times higher concentration of the model additive S-4 provides the same P_t value like in case when it was used at 0.1% wt. concentration. The results are of particular interest due to very special chemical structure of this sulphur containing compound (see **Table 1).**

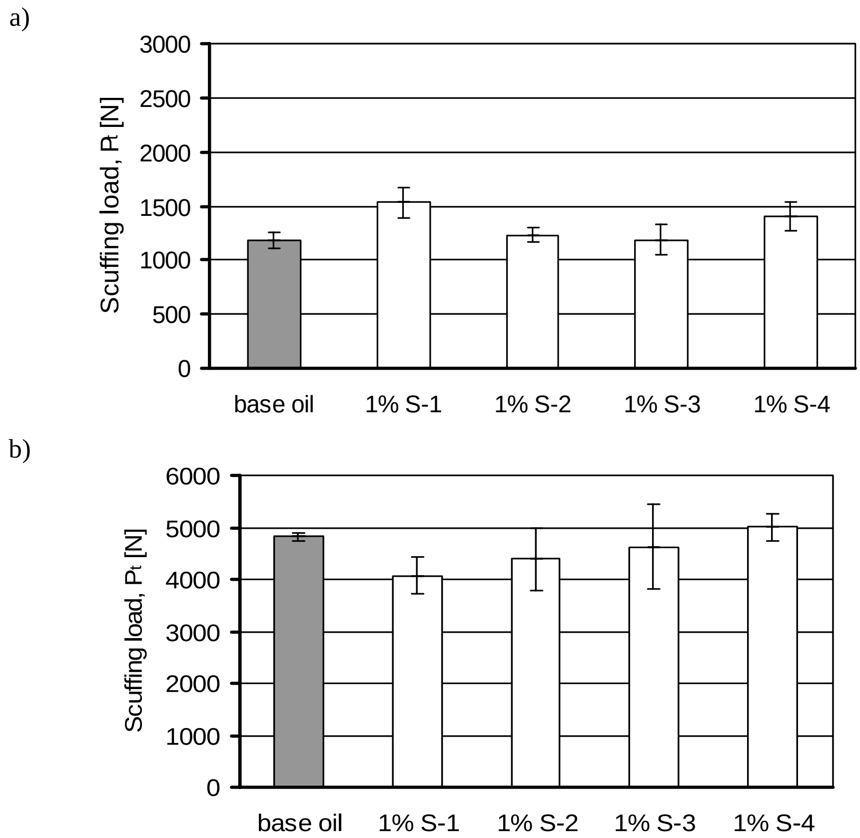


Fig. 2. Scuffing load (P_t) for organic sulphur compounds at 1%wt. in PAO-8 base oil: a) uncoated steel–steel tribosystem, b) coated a-C:H:W–a-C:H:W tribosystem

Rys. 2. Obciążenie zacierające (P_t) dla skojarzeń smarowanych olejem PAO-8 z 1% w/w dodatkiem organicznych związków siarki: a) skojarzenie stal–stal, b) skojarzenie a-C:H:W–a-C:H:W

In the case of steel-steel combination increasing of concentration play a significant role for improving tribological properties. At 1% wt. concentration in base oil for lubricants denoted as 1% S-1 and 1% S-4 are obtained higher P_t values than for 0.1% wt. concentration in base oil (see **Fig. 2a**).

a) b)

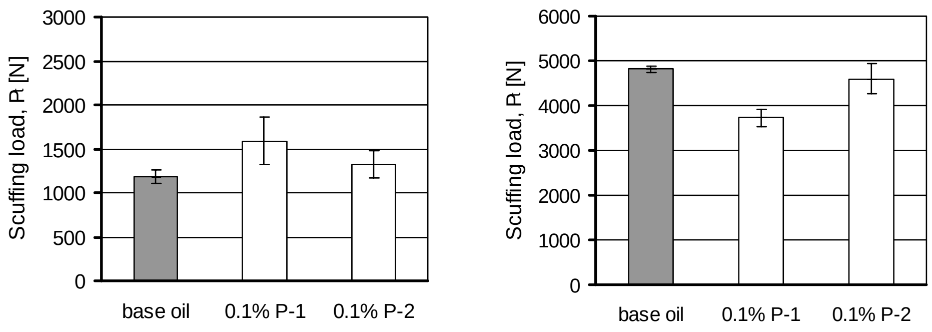


Fig. 3. Scuffing load (P_t) for organic phosphorus at 0.1% wt. in PAO-8 base oil: a) uncoated steel–steel tribosystem, b) coated a-C:H:W–a-C:H:W tribosystem

Rys. 3. Obciążenie zacierające (P_t) dla skojarzeń smarowanych olejem PAO-8 z 0,1% w/w dodatkiem organicznych związków fosforu: a) skojarzenie stal–stal, b) skojarzenie a-C:H:W–a-C:H:W

In **Fig. 3a** are presented the results for scuffing load parameter at 0.1%wt. in base oil of the organic phosphorus compounds using steel-steel combination. It is showed that for the both investigated organic phosphorus compounds the P_t values are higher than base oil, a visible improvement is showed by the one of the organic phosphorus compound denoted as 0.1% P-1. For a-C:H:W-a-C:H:W combination are obtained smaller P_t values for both investigated lubricants than base oil (see **Fig. 3b**).

In **Fig. 4** is presented the effect of concentration for both organic phosphorus compounds investigated. It can be seen in the case of steel-steel combination (**Fig. 4a**) at high concentration (1% wt.) was obtained an increasing for scuffing load for both lubricants. For small concentration (0.1% wt.) and in the case of a-C:H:W-a-C:H:W tribosystem (**Fig. 4b**) no effect of concentration was observed. The P_t values are smaller even than that obtained for pure base oil.

a) b)

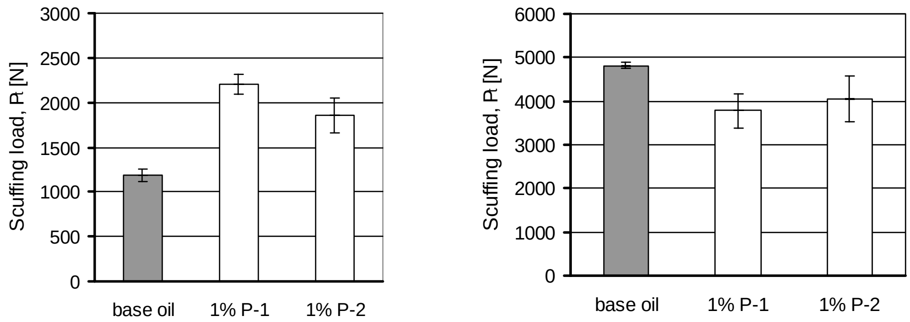


Fig. 4. Scuffing load (P_t) for organic phosphorus at 1% wt. in PAO-8 base oil: a) uncoated steel–steel tribosystem, b) coated a-C:H:W–a-C:H:W tribosystem

Rys. 4. Obciążenie zacierające (P_t) dla skojarzeń smarowanych olejem PAO-8 z 1% w/w dodatkiem organicznych związków fosforu: a) skojarzenie stal–stal, b) skojarzenie a-C:H:W–a-C:H:W

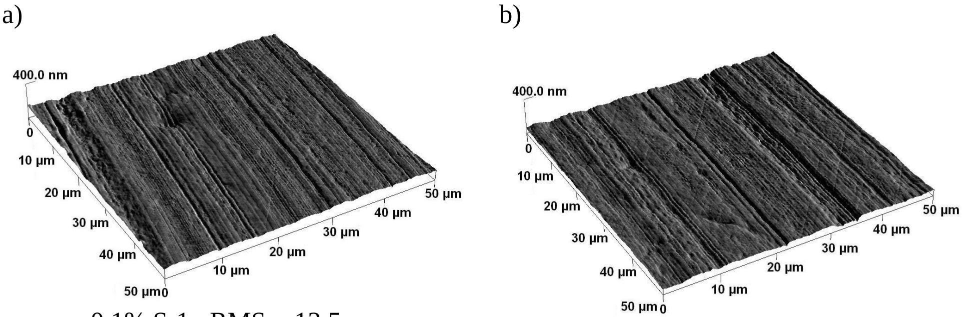
Surface analyses

AFM (Atomic Force Microscope) analyses

For AFM investigations, the worn surfaces were obtained using four-ball apparatus settled at 10 sec. for a-C:H:W (coated) balls and at 2 sec. for steel balls, before scuffing propagation.

The AFM measurements are presented in **Fig. 5–Fig. 8**.

a) b)



0.1% S-1, RMS = 13.5 nm   1% S-1, RMS = 12.2 nm

Fig. 5. AFM images and RMS values for the wear scars of uncoated steel balls obtained for various concentration of S-1 compound in PAO-8 base oil: a) 0.1% S-1, b) 1% S-1

Rys. 5. Obrazy AFM oraz parametr chropowatości RMS dla śladów zużycia na kulkach stalowych (bez powłoki) uzyskane dla różnych stężeń dodatku S-1 w oleju PAO-8: a) 0,1% S-1, b) 1% S-1

In **Fig. 5** are presented the 3D AFM images of the wear scars for uncoated steel balls lubricated by PAO-8 used as base oil with 0.1% wt. and 1% wt. of benzyl disulphide (denoted as S-1).

The AFM images demonstrate that the increasing concentration of benzyl disulphide in the base oil generates a little bit smoother surfaces than using smaller concentration of benzyl disulphide compound in PAO-8 base oil (see **Fig. 5a** and **5b**).

In the case of coated a-C:H:W-a-C:H:W tribosystem the effect of benzyl disulphide is different than in the steel – steel tribosystem In the latter one, at 0.1% wt. in base oil of benzyl disulphide was obtained a smoother surface, compared by RMS value (RMS = 54.1 nm) – see **Fig. 6a** than for 1% wt. of benzyl disulphide when was obtained a rough surface (RMS = 66.5 nm) – see **Fig. 6b**.

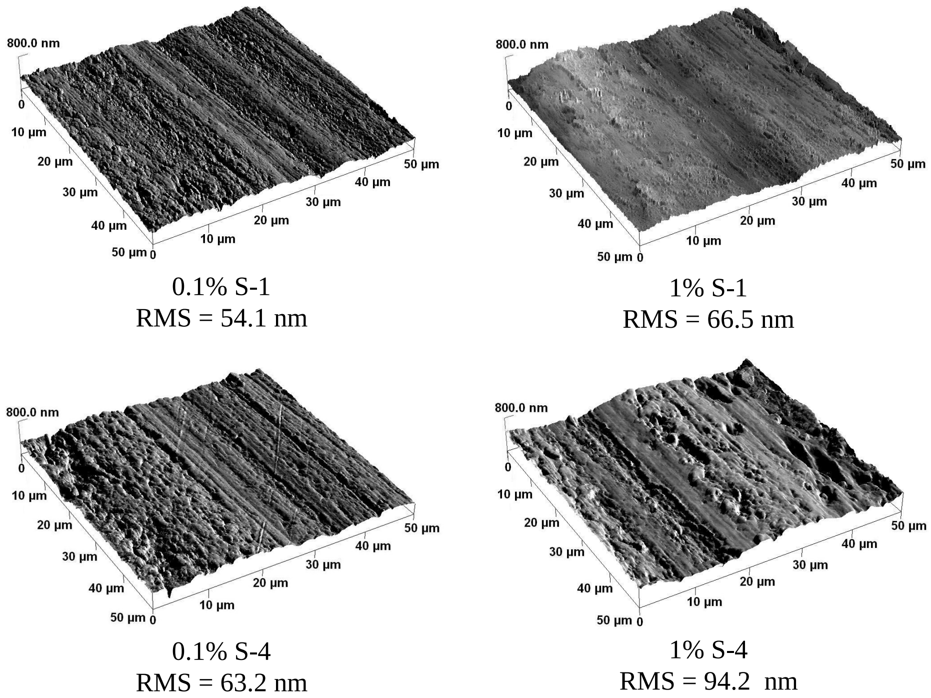


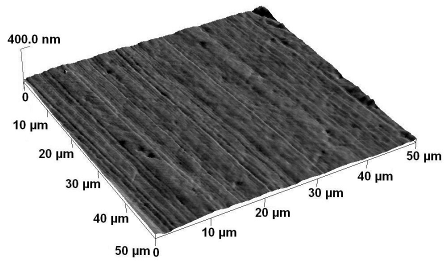
Fig. 6. AFM images and RMS values for the wear scars of a-C:H:W coated balls obtained for various concentration of organic sulphur compounds in PAO-8 base oil: a) 0.1% S-1, b) 1% S-1, c) 0.1% S-4, d) 1% S-4

Rys. 6. Obrazy AFM oraz parametr chropowatości RMS dla śladów zużycia na kulkach stalowych z powłoką a-C:H:W uzyskane dla różnych dodatków organicznych związków siarki w oleju PAO-8: a) 0,1% S-1, b) 1% S-1, c) 0,1% S-4, d) 1% S-4

The AFM results confirmed the tribological behaviours of these organic sulphur compounds.

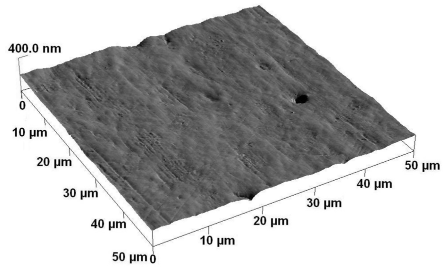
In **Fig. 7** are described the 3D AFM images for the wear scars of dibenzyl phosphite (P-1) and diethyl 1-phenylethyl phosphonate (P-2) at 0.1% wt. and 1% wt. in PAO-8 for uncoated steel – steel tribosystem.

a)



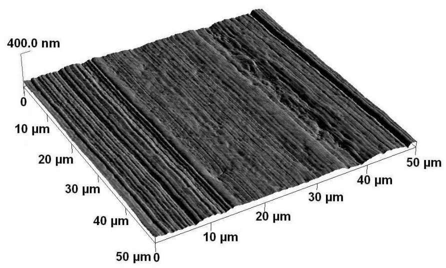
0.1% P-1
RMS= 9.9 nm

b)



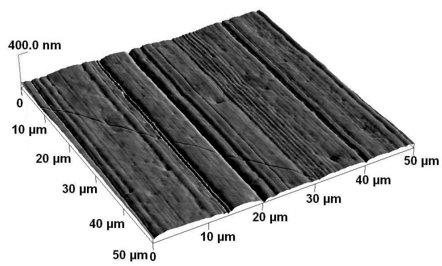
1% P-1
RMS= 11.3 nm

c)



0.1% P-2
RMS= 11.7 nm

d)



1% P-2
RMS= 12.0 nm

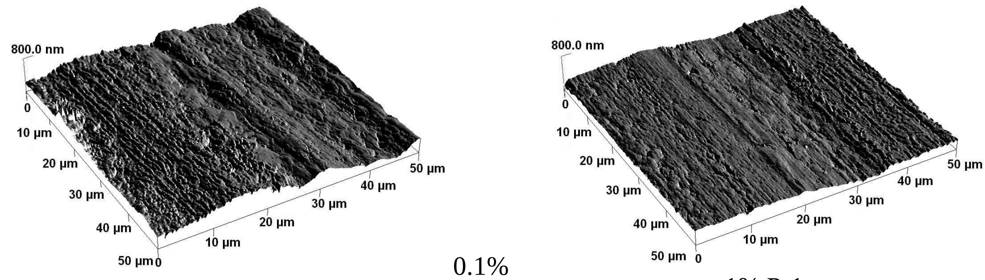
Fig. 7. AFM images and RMS values for the wear scars of uncoated steel balls obtained for various concentration of organic phosphorus compounds in PAO-8 base oil: a) 0.1% P-1, b) 1% P-1, c) 0.1% P-2, d) 1% P-2

Rys. 7. Obrazy AFM oraz parametr chropowatości RMS dla śladów zużycia na kulkach stalowych (bez powłoki) uzyskane dla różnych stężeń dodatków organicznych związków fosforu w oleju PAO-8: a) 0,1% P-1, b) 1% P-1, c) 0,1% P-2, d) 1% P-2

It can been seen in **Fig. 7** that increasing of concentration for both phosphorus compounds does not have an improvement effect on surfaces of steel-steel tribosystem lubricated by organic phosphorus compounds (P-1 and P-2) in base oil; the RMS values for both phosphorus compounds at 1% wt. are slightly higher than RMS values for 0.1% wt.

In **Fig. 8** are presented the AFM images of wear scars of dibenzyl phosphite (P-1) at 0.1% wt. and 1% wt. in PAO-8 for a-C:H:W- a-C:H:W coated tribosystem.

a) b)



0.1% P-1
RMS= 91.0 nm

1% P-1
RMS= 67.1 nm

Fig. 8. AFM images and RMS values for the wear scars of a-C:H:W coated balls obtained for various concentration of organic phosphorus compounds in PAO-8 base oil: a) 0.1% P-1, b) 1% P-1

Rys. 8. Obrazy AFM oraz parametr chropowatości RMS dla śladów zużycia na kulkach stalowych z powłoką a-C:H:W uzyskane dla różnych stężeń dodatków organicznych związków fosforu w oleju PAO-8: a) 0,1% P-1, b) 1% P-1

It can be seen that wear scar surface for coated a-C:H:W- a-C:H:W tribosystem lubricated by dibenzyl phosphite at 0.1% wt. in base oil obtained after tribological tests at 10 sec. the surface is much rougher compared by RMS value, in this case RMS = 91.0 nm (see **Fig. 8a**) than the surface obtained using 1% wt. of dibenzyl phosphite which is smooth and the RMS value is significantly smaller (RMS = 67.1 nm) – see **Fig. 8b**.

SEM/EDS analyses

The SEM pictures of the worn surfaces are given in **Fig. 9** and **Fig. 12.**

It is seen that after tribological test (after 10 sec. of running) when organic sulphur compounds are used, the coating is still present (showed in **Fig. 9**) and confirmed by EDS analysis (see **Fig. 10**) indicating of W appearance on the worn surfaces.

Effect of concentration of benzyl disulphide (S-1) on coated a-C:H:W- a-C:H:W tribosystem reflects that for high concentration was obtained a rough surface, the coating was removed (see **Fig. 9b**); for small concentration a smooth surface was obtained (see **Fig. 9a**). The effect of 1-adamantanethiol (S-4) on coated steel balls after 10 sec. of running was similar for both concentrations (0.1% wt. and 1% wt.) the surfaces are smoother (see **Figs. 9c** and **9d**).

a) b) c) d)

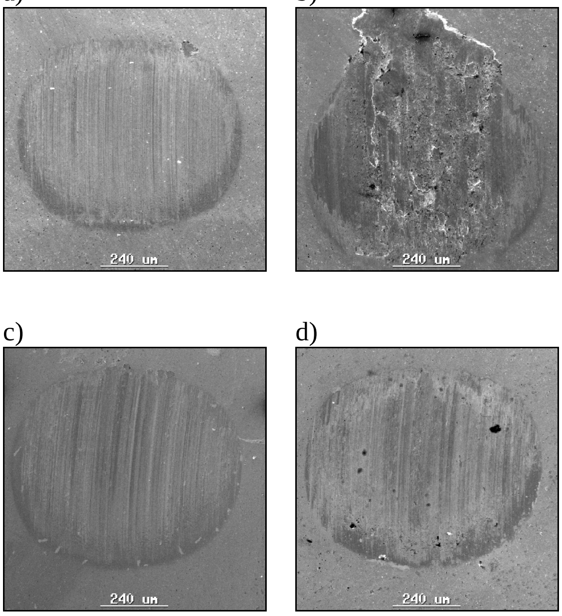


Fig. 9. SEM images of the wear scars of a-C:H:W coated balls for organic sulphurs compounds at 0.1% wt. and 1% wt. in PAO-8 base oil: a) 0.1% S-1, b) 1% S-1, c) 0.1% S-4, d) 1% S-4

Rys. 9. Obrazy SEM ze śladów zużycia na kulkach stalowych pokrytych powłoką a-C:H:W otrzymanych dla różnych stężeń organicznych związków siarki: a) 0,1% S-1, b) 1% S-1, c) 0,1% S-4, d) 1% S-4

In **Fig. 10** are presented the EDS results for benzyl disulphide (S-1) and 1-adamantanethiol (S-4) for coated steel balls at 0.1% wt. and 1% wt. concentration in base oil.

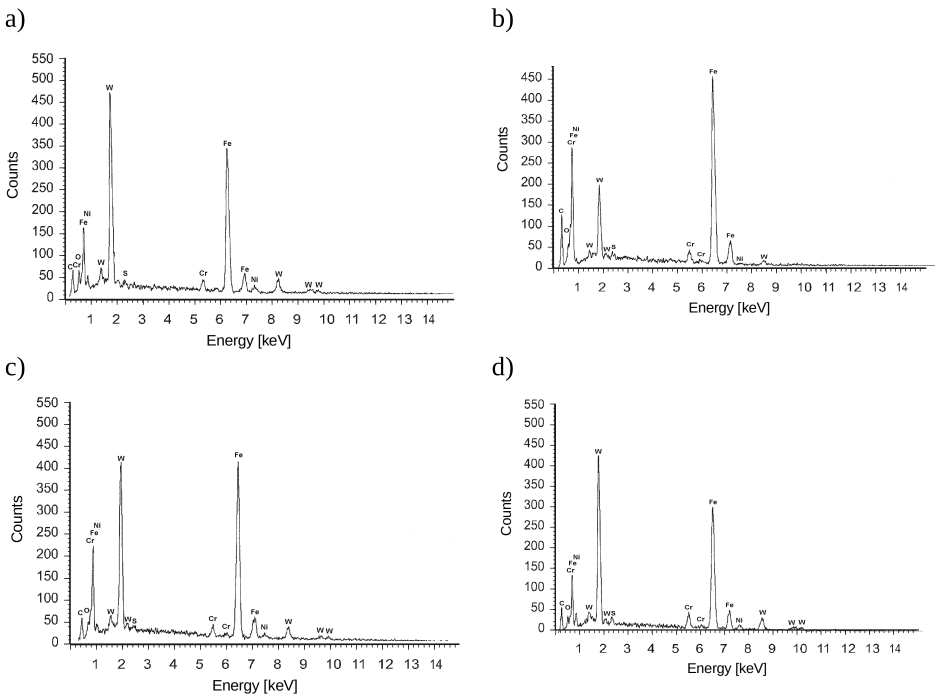


Fig. 10. EDS analysis of the wear scars of a-C:H:W ball sliding against a-C:H:W ball in base oil with organic sulphur compounds: a) S-1 at 0.1% wt., b) S-1 at 1% wt., c) S-4 at 0.1% wt., d) S-4 at 1% wt.

Rys. 10. Widma EDS ze śladów zużycia na kulkach stalowych pokrytych powłoką a-C:H:W otrzymanych dla różnych organicznych związków siarki: a) 0,1% S-1, b) 1% S-1, c) 0,1% S-4, d) 1% S-4

After tribological tests (10 sec.) in the surface layer of the wear scars oxygen and sulphur were detected by EDS analysis in the cases of benzyl disulphide (S-1) at 0.1% wt. and 1% wt. and 1-adamantanethiol (S-4) at 0.1% wt. and 1% wt. when it used coated a-C:H:W – a-C:H:W tribosystem (see **Fig. 10**). In the case when was used benzyl disulphide (S-1) at 0.1% wt. was detected a higher content of W on wear scar than for 1% wt. benzyl disulphide (S-1), the tungsten (W) was detected only in the zones which are not scuffed. The presence of oxygen and sulphur might come from chemical reactions of active compounds with the steel substrate existing in some zones where coating was partially removed.

In the case of uncoated steel – steel tribosystem, the EDS results showed that at high concentration of benzyl disulphide (S-1) was detected an amount of sulphur on wear scar (see **Fig. 11b**) while, for small concentration of benzyl disulphide (S-1) was found only the elements contained on the steel substrate (see **Fig. 11a**).

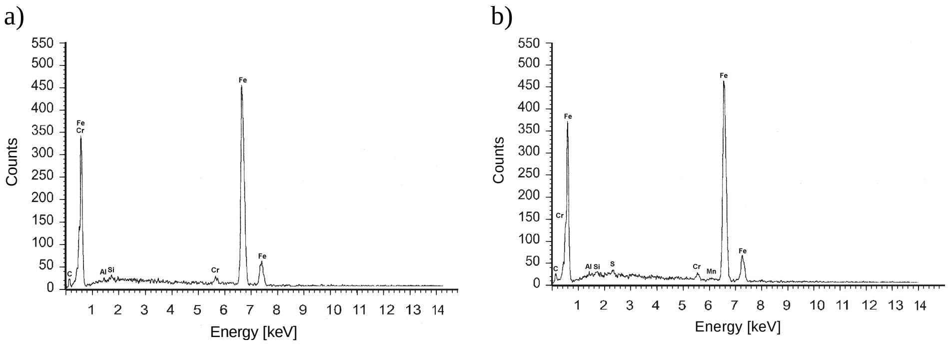


Fig. 11. EDS analysis of the wear scars of uncoated steel ball sliding against uncoated steel balls in base oil with organic sulphur compounds: a) S-1 at 0.1% wt., b) S-2 at 0.1% wt.

Rys. 11. Widma EDS ze śladów zużycia na kulkach stalowych (bez powłoki) otrzymanych dla różnych organicznych związków siarki: a) 0,1% S-1, b) 0,1% S-2

In **Fig. 12** are presented SEM images for coated balls using the both organic phosphorus compounds at 0.1% and 1% wt. in PAO-8 after 10 sec. of running. It is seen that after tribological test when dibenzyl phosphite (P-1) is used at 0.1% and 1% wt. in PAO-8, the coating is still present (showed in **Figs. 12a** and **12b**) and confirmed by EDS analysis (see **Fig. 13**) indicating the presence of tungsten (W) on the worn surfaces while, for diethyl 1-phenylethyl phosphonate (P-2) at both concentrations after 10 sec. the coating was removed (see **Figs. 12c** and **12d**).

As can be seen in **Fig. 13a** at 0.1% wt. in PAO-8 of dibenzyl phosphite (P-1) was detected an amount of oxygen on wear scar of coated ball while, with increasing concentration of dibenzyl phosphite (P-1) were found on wear scar the presence of oxygen and phosphorus (see **Fig. 13b**). Their presence might come from reaction of chemical active components from oil with steel substrate existing in some zones where coating was partially removed. Additional and more detailed surface analysis, e.g. XPS and FTIRM, is needed for explanation of tribochemical mechanism which is taking place.

a) b)

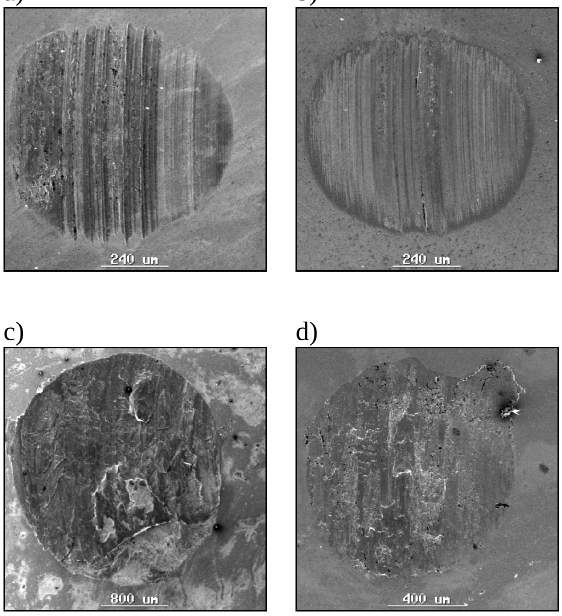


Fig. 12. SEM images of the wear scars of a-C:H:W coated balls for organic phosphorus compounds at 0.1% wt. and 1% wt. in PAO-8 base oil: a) 0.1% P-1, b) 1% P-1, c) 0.1% P-2, d) 1% P-2

Rys. 12. Obrazy SEM ze śladów zużycia na kulkach stalowych pokrytych powłoką a-C:H:W otrzymanych dla różnych stężeń organicznych związków fosforu w oleju PAO-8: a) a) 0,1% P-1, b) 1% P-1, c) 0,1% P-2, d) 1% P-2

a) b)

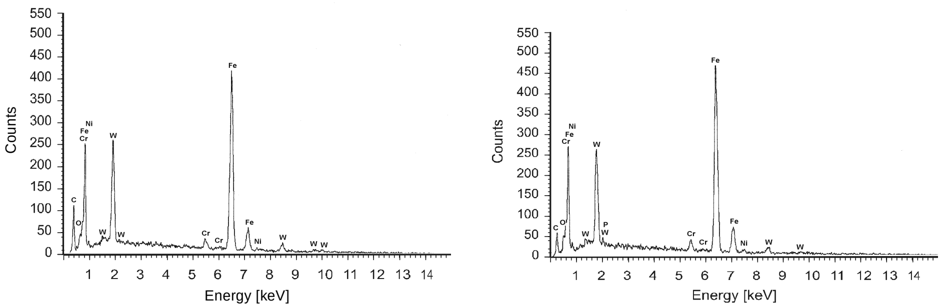


Fig. 13. EDS analysis of the wear scars of a-C:H:W ball sliding against a-C:H:W ball in base oil with organic phosphorus compounds: a) P-1 at 0.1% wt., b) P-1 at 1% wt.

Rys. 13. Widma EDS ze śladów zużycia na kulkach stalowych pokrytych powłoką a-C:H:W otrzymanych dla różnych organicznych związków fosforu: a) 0,1% P-1, b) 0,1% P-2

CONCLUSIONS

The tribological results reflect that for a-C:H:W coated balls using 0.1% wt. and 1% wt. concentration of organic sulphur compounds, in the base oil, only 1-adamantanethiol showed increase in scuffing load value. The increase in concentration of benzyl disulphide (BDS) up to 1% wt. increased the scuffing load values for the uncoated steel tribosystem, but the increase in concentration of this compound is harmful for coated balls.

In the case when are used organic sulphur compounds EDS spectrum indicated presence of an amount of oxygen and sulphur in the surface layer of the wear scars in the cases of benzyl disulphide (S-1) at 0.1% wt. and 1% wt. and 1-adamantanethiol (S-4) at 0.1% wt. and 1% wt. were used for coated a-C:H:W – a-C:H:W tribosystem. The presence of oxygen and sulphur might come from chemical reactions of active compounds with the steel substrate existing in some zones where coating was partially removed. In the case of uncoated steel – steel tribosystem, the EDS results showed that at high concentration of benzyl disulphide (S-1) was detected an amount of sulphur on wear scar while, for small concentration of benzyl disulphide (S-1) was found only the elements contained on the steel substrate.

The both organic phosphorus compounds at the treat rate of 0.1% and 1% wt. in the base oil did not show any improvement in scuffing load values for the coated balls. Nevertheless the increasing concentration of these phosphorus containing compounds in the base oil, improved the load-carrying capacity for the steel-steel tribosystem.

In the case of coated a-C:H:W – a-C:H:W tribosystem, the EDS results showed that when dibenzyl phosphite (P-1) was used an oxygen on wear scar of coated ball was detected. For higher concentration of dibenzyl phosphite (P-1) oxygen and phosphorus were found on the wear scar. Their presence might come from reaction of chemical active components from oil with steel substrate existing in some zones where coating was partially removed. Additional and more detailed surface analysis, e.g. XPS and FTIRM, is needed for explanation of tribochemical reaction mechanism.

Interaction of organic sulphur and phosphorus compounds with coated steel tribological elements showed that such kind of compounds are not effective for increasing the load-carrying capacity of a-C:H:W coated machine parts. Knowing the effect of selected CHO, CHNO, sulphur- and nitrogen containing model compounds on the steel-steel and a-C:H:W – a-C:H:W tribosystems further work will be focused on the steel/a-C:H:W tribosystem using both the most effective model compounds and commercial AW/EP additives.

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Recenzent:
Jarosław SĘP

Streszczenie

Artykuł jest kontynuacją wcześniejszych prac i zawiera wyniki badań organicznych związków siarki i fosforu jako potencjalnych dodatków przeciwzużyciowych dla wysokoobciążonych węzłów tarcia z elementami pokrytymi powłoką a-C:H:W. W części pierwszej [L. 1] przedstawione zostały wyniki badań dla związków typu CHO i CHNO. W bieżącym artykule zaprezentowano wyniki uzyskane dla czterech rodzajów organicznych związków siarki i dwóch rodzajów organicznych związków fosforu. Związki te dodawano w stężeniu

0,1% w/w i 1% w/w do polialfaolefinowego oleju bazowego (PAO-8). Powłokę a-C:H:W osadzono na kulkach wykonanych ze stali łożyskowej (100Cr6) wykorzystując metodę reaktywnego rozpylania PVD. Nośność warstwy smarowej mierzono jako obciążenie zacierające z wykorzystaniem aparatu czterokulowego T-02. Stosowano metodę z ciągłym narastaniem obciążenia. Podobnie jak w części I pracy [L. 1] badania wykonano dla elementów bez powłoki oraz dla wszystkich elementów z powłoką a-C:H:W.

Dla skojarzeń z elementami pokrytymi powłoką a-C:H:W smarowanych olejem z dodatkiem organicznych związków siarki w stężeniu 0,1% w/w i 1% w/w w oleju bazowym, tylko dla 1-adamantanetiolu odnotowano nieznaczny wzrost obciążenia zacierającego. Wzrost stężenia disiarczku benzylu (BDS) do 1% w/w spowodował wzrost odporności na zacieranie skojarzenia stalowego (bez powłoki), jednocześnie okazało to się szkodliwe dla skojarzeń z elementami pokrytymi powłoką. Również dla obu badanych organicznych związków fosforu w stężeniu 0,1% w/w i 1% w/w w oleju bazowym nie odnotowano wzrostu odporności na zacieranie skojarzeń z elementami pokrytymi powłoką. Przy czym zwiększenie stężenia organicznych związków fosforu skutkowało wzrostem wartości obciążenia zacierającego skojarzeń elementów bez powłoki. W pracy wzięto również pod uwagę różnicę w mechanizmie działania dodatku BDS w skojarzeniu elementów stalowych bez powłoki i z powłoką. Dokonano również analizy mechanizmu działania tychże dodatków dla przypadku stosowania organicznych związków fosforu.

Praca jest przyczynkiem do lepszego zrozumienia współdziałania związków zawierających siarkę i fosfor. Dowiedziono, że ten rodzaj związków nie jest efektywnym dodatkiem dla zwiększania nośności warstwy smarowej skojarzeń z elementami pokrytymi powłoką a-C:H:W. Prace będą kontynuowane z uwzględnieniem dodatków handlowych i nowych materiałów.