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THE INFLUENCE OF THE TYPE OF GREASE ON THE SYNERGY OF ITS COMPOSITION WITH PTFE POWDER AND COPPER POWDER

WPŁYW RODZAJU SMARU PLASTYCZNEGO NA SYNERGIZM JEGO KOMPOZYCJI Z PROSZKIEM PTFE I MIEDZI

Key words:

greases, fillers, synergy

Słowa kluczowe:

smary plastyczne, napełniacze, synergia

Abstract

Studies of the influence of the type of grease on the synergistic effect of its compositions with PTFE powder and of copper during the lubrication of steel sliding pairs working in mixed friction area of were presented. Two greases, car grease 1S with a lithium thickener and grease STP with calcium thickener, were adopted for analysis. As fillers in the two lubricants, powders of two solid lubricants were PTFE and copper were used. Three lubricating compositions were tested for each of the adopted greases. Two compositions contained one filler of 5% by weight, and the third composition contained the two fillers in the same proportion (5% each). The lubricating properties of the adopted

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compositions were evaluated based on an experiment conducted with the use of a four–ball extreme pressure tester according to the standard PN-76/ C04147. The effectiveness of the analysed lubricants was evaluated according to four criterion values (wear of the balls d, fusion point F_z, limit wear load G_{oz}, and wear index I_h). The results were statistically handled at the confidence level of 95% using Student's t-test. The developed test results are shown graphically. Appropriate conclusions were drawn.

INTRODUCTION

The most effective method of minimizing the negative effects of friction is selecting such geometric and material features of sliding nodes so that they operate under conditions of fluid friction, when the rubbing surfaces are completely separated by a thin lubricant layer. However, this the most secure type of friction is often difficult to obtain. Practice shows that the dominant type of friction in moveable sliding nodes is mixed friction. Even in the nodes with hydrodynamic lubrication, it always occurs during starting and stopping. Additionally, a load increase, a reduction in sliding velocity, a reduction in lubricant viscosity, or its insufficient quantity in the lubricating gap can also cause a state of mixed friction in the nodes with hydrodynamic lubrication. Moreover, friction nodes operating in pendulum motion or reciprocating motion operate continually in a mixed friction area. As proposed by the Kragielski **[L. 1, 2]**, a necessary condition for the normal course of friction and wear in sliding nodes operating in that area of friction is to provide a surface layer of the cooperating elements of the positive gradient of the shear strength. Optimization of this gradient value, according to the criterion of minimum friction and wear, is carried out by improving the tribological properties in both of the cooperating materials and the lubricant. Actions to increase the positive gradient of the lubrication are very effective. Garkunov **[L. 3]** showed that, by providing a slight amount of grease into contact zone of mating surfaces, sufficient to form a film having a thickness of 100 nm, produce a 10-fold reduction in the friction force and about a 100-fold reduction of wear. Theory and practice demonstrate that plastic lubricants are effective substances for the lubrication of sliding nodes operating at mixed friction. Their high efficiency is based on the capability to create thick boundary layers. Studies **[L. 4, 5]** showed that the film created by the grease on the mating surfaces has a thickness of 1.2 to 3.5 times as high as the thickness formed by the base oil. However, the components of plastic greases do not ensure their good lubricating properties in the case of heavy loads, the reason for this is a relatively low desorption temperature of the boundary layer formed on the mating surfaces of lubricated parts. These properties can be improved in various ways. The easiest and fairly effective way is to put fillers in the composition of the greases, and the fillers are substances of different concentrations, insoluble in a grease's matrix and not disturbing the colloidal structure of the grease **[L. 6, 7]**. Generally speaking, while friction occurs, the fillers form a thin film physically or chemically strongly linked to the substrate, marked by low shear strength and high ductility and heat resistance on the mating surfaces. Fillers operate in a sliding node in two manners: First, they fill elevations and irregularities on the mating surfaces, thus increasing the factual contact area as well as reducing the unit pressures; second, they form thin films, protecting friction surfaces from direct contact and, with their relative movement, they advance in the area of these layers.

Recent years of research show that the most promising approach to improving anti-friction and anti-wear properties of greases is their modification with not just a single filler but with a package of fillers that will provide plating layers on the mating surfaces and additionally ensure positive tribological characteristics, while increase their efficiency in relation to the plating layers. Such packages are, for example, copper powder and acetyl acetone **[L. 8]** or dual complex of copper and nickel **[L. 9]**. According to **[L. 10, 11]**, the interaction of fillers, which is more effective than the sum of their separate actions, is called *synergy*, *synergism*, or a *synergetic effect*. It is emphasized that, in tribological literature, under the term *synergy* (synergism, a synergetic effect), also, other interactions, not corresponding strictly to the given definition, are also mentioned. For example, in paper **[L. 12]**, a synergistic effect caused by the addition of dialkyl-dithiocarbamate of molybdenum (MoDTC) and dialkyl-dithiophosphate of zinc (ZnDTP) into mineral oil is reported. In this case, as a criterion of the occurrence synergism, the minimum friction coefficient was taken. This coefficient with lubrication with oil with both additives (MoD TC + ZnDTP) amounted to approx. 0.04, which was less than the coefficient obtained under lubrication with only MoDTC (approx. 0.06), and with only ZnDTP (approx. 0.09). Similarly, in paper **[L. 13]**, synergism was equal to the cooperation of fillers that caused the lowest wear. The authors investigated tribological characteristics of grease filled with copper hydroxide (Cu (OH) 2) and caprolactam (C6H11NO). The effect of synergy was evidenced by the relations between the scar diameters of wear of the balls investigated on the extreme pressure tester. This scar diameter at an axial load equal to 1500 N and lubrication with the composition containing copper hydroxide was d = 0.96 mm, and d = 3.9 mm when grease filled with caprolactam was used as a lubricant. The wear of the same balls but lubricated with grease filled with product of the reaction between copper hydroxide and caprolactam was as little as 0.52 mm. Synergism also defined as an interaction of fillers giving the smallest value of criterion quantity (e.g., wear, friction coefficient) can be found in other papers, for instance. in **[L. 14, 15, 16]**., In order to determine the interaction of the analysed fillers, the authors of this study follow the definition given in **[L. 17]**, according to which the action of a package of fillers can be called synergy (synergism or synergetic effect) if one of the following conditions is fulfilled:

1. The combined effect of interaction is greater than the sum of individual actions, and as the criterion of interaction, a positive quantity was adopted, that is the quantity for which the desirable value is always the largest, such as welding load, limit wear load index.
2. The combined effect of interaction is significantly smaller than separate actions, and as a criterion of interaction, a negative quantity was adopted, that is the quantity for which the possible smallest values are always beneficial, for example, wear, and friction coefficient.

In tribological literature on modification of greases, there are papers discussing the use of synergism to increase the effectiveness of these greases in the sliding nodes working in mixed friction areas, for example **[L. 8, 18, 19, 20]**. After analysing these studies, it can be noted that they are mainly focused on demonstrating synergism between the fillers used for lubrication, and sometimes they attempt to explain the reasons for of this specific interaction of package fillers, for example, of powder and PTFE **[L. 21]**. In the Department of Machine Design and Tribology at Wroclaw University of Technology, for many years, studies have been carried out on how to increase the effectiveness of greases by their modification with solid greases. A shortage of research on the effects of the type of grease on the synergistic effect of these compositions with copper powder and PTFE inspired the authors to carry out relevant analysis.

TEST METHOD AND CONDITIONS

A four-ball tester (produced by the Institute for Terotechnology in Radom) was used for testing in accordance with the recommendations of standard PN-76/C-04147 'Tests of Lubricating Properties of Oils and Lubricants'. In order to evaluating the effectiveness of the tested compositions, four criterion values were adopted: fusion point F_z, limit wear load G_{oz}, wear index I_h, and the wear of the balls d. In the graph showing of the relation between the wear of balls and the load applied d = f(F), the value Fz denotes a point that is the origin of the vector represented by dashed line. The compositions of greases 1S or STP, which contained 5% by weight of one of the accepted fillers, and the compositions of the two fillers of 5% by weight were analysed. The concentration value was adopted because both the authors' studies and appropriate literature show that the concentration of 5% is a recommended value. PTFE (polytetrafluoroethylene) powder and copper powder were used as fillers.

The rationale for adopting these fillers was that, in previous studies the authors, their effects were seen in lithium plastic grease with evoked synergy in the lubrication of steel sliding pairs working in the area of mixed friction **[L. 17, 20]**. The wear value and the fusion point F_z were determined on the basis of 10-second runs of the set of four steel balls (three stationary balls pressed by a fourth rotating at n = 1450 rpm/min) immersed in the tested lubricant. The value of limit load index of wear G_{oz} was calculated from the size of an average diameter of scars created on the fixed balls working for 60 seconds under a given load of F = 150 daN. The balls' wear d was measured parallel and perpendicular to the wear scar. Scars below 1mm were measured (with an accuracy of 0.01 mm) under a microscope, and the other scars were measured under a magnifying glass (with an accuracy of 0.1 mm). The tests were repeated five times for each measuring point. The results were statistically handled at a confidence level of 95% using Student's t-test.

MATERIALS AND THEIR DESCRIPTION

The following materials were used in the tests:

1. Grease STP: It contains a highly refined mineral oil and calcium soaps of high molecular weight fatty acids. The grease is recommended for periodical lubrication of chassis of motor vehicles, bolts, joints and other friction nodes. This is unsuitable for the lubrication of rolling bearings.
2. Car grease 1S: It is a high quality lithium grease based on lithium hydroxystearate and mineral oil with the viscosity around 60–79 mm^2/s at 40°C. It contains lithium hydroxystearate as a thickener and three additives: antioxidants, corrosion inhibitors, and an adhesive addition. This is suitable for the lubrication of the joints of the main drive shaft and the other sliding nodes in motor vehicles.
3. Bearing balls (12.7 mm in diameter), made of bearing steel 100Cr6, in accuracy class 16 and dimensional group S = 0_m: Other features of the balls were consistent with PN-83/M-86452.

The following solid lubricants were selected to perform as fillers:

- Polytetrafluoroethylene (PTFE) – suspension Tarflen, manufactured by Nitrogen Plant in Tarnow: It has a density of 2.185 g/cm^3 and a granulation of 20 to 40 mm.
- Copper powder, grain size up to 40 mm: It is obtained by cathodic deposition, by electrolysis of aqueous solutions of copper sulphate. The system of the powder particles is dendritic.

ANALYSIS OF CHEMICAL COMPOSITION OF GREASES

Chemical analysis of the adopted greases included the determination of the content of soap therein. This indication was performed according to PN/C-04976. It was based on the decomposition of grease with hydrochloric acid in benzene solution and then the extraction of soaps with suitable solvents. Soap content is calculated stoichiometrically after determining the content of associated fatty acids and their acid value. The results of the assays are given in **Table 1**.

Table 1. Contents of soap in greases
Tabela 1. Zawartość mydła w smarach plastycznych

Name of grease	Soap content in %
STP	13.5
1S	5.2

By comparing the data, we can conclude that calcium grease STP is more than twice as thick as lithium grease 1S.

RESULTS AND CONCLUSIONS

Summary of research results seen as dependence of the wear of the balls upon the load for the analysed compositions is shown in **Figures 1** and **2**. The calculated values of the wear index I_h and the limit wear load index G_{oz} are shown in **Figs. 3, 4, 5** and **6**. In addition, on all the graphs, for the sake of comparison, the characteristics of grease 1S and STP are provided, which were the basis for the preparation of lubricating compositions. The value of load limit wear G_{oz} for both base lubricants is zero, because, during the tests, the balls became welded to each other in three or four of the six tests performed.

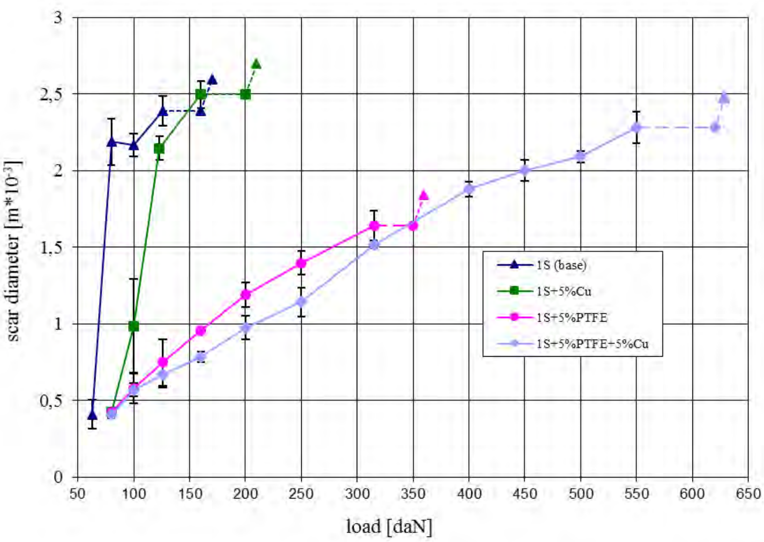

Fig. 1. Wear (scar diameter) vs. load for grease 1S composition
Rys. 1. Zależność zużycia od obciążenia dla kompozycji ze smarem 1S

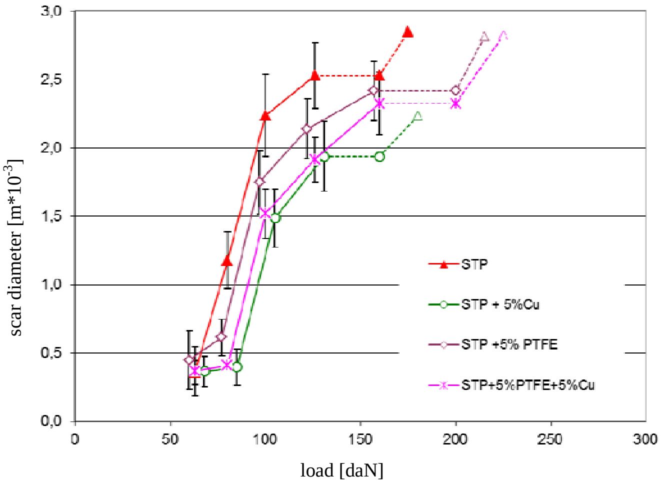

Fig. 2. Wear (scar diameter) vs. load for grease STP composition
Fig. 2. Wear (scar diameter) vs. load for STP grease composition

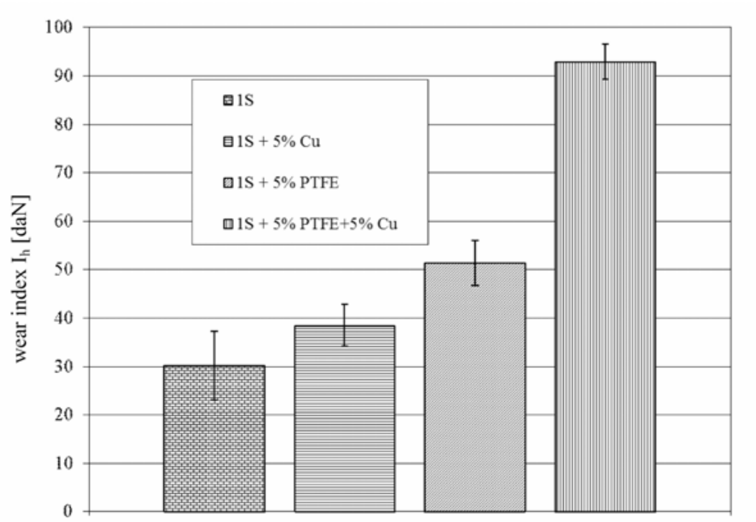

Fig. 3. Wear index I_h for composition with grease 1S
Fig. 3. Wear index I_h for composition with 1S grease

When comparing the obtained values of the adopted criterion quantities, we can clearly see that the synergism of PTFE powder and copper powder is present only in the compositions created from lithium grease 1S. Here, all the of the criterion quantities demonstrate the occurrence of synergy of PTFE powder and copper powder in grease 1S during friction between mating steel surfaces working in the area of mixed friction.

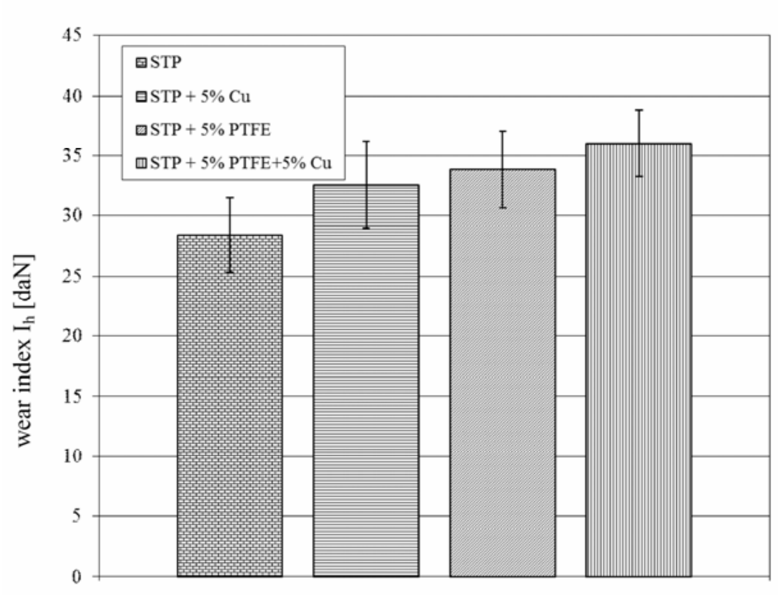

Fig. 4. Wear index I_h for composition with grease STP
Rys. 4. Wskaźnik zużycia I_h dla kompozycji ze smarem STP

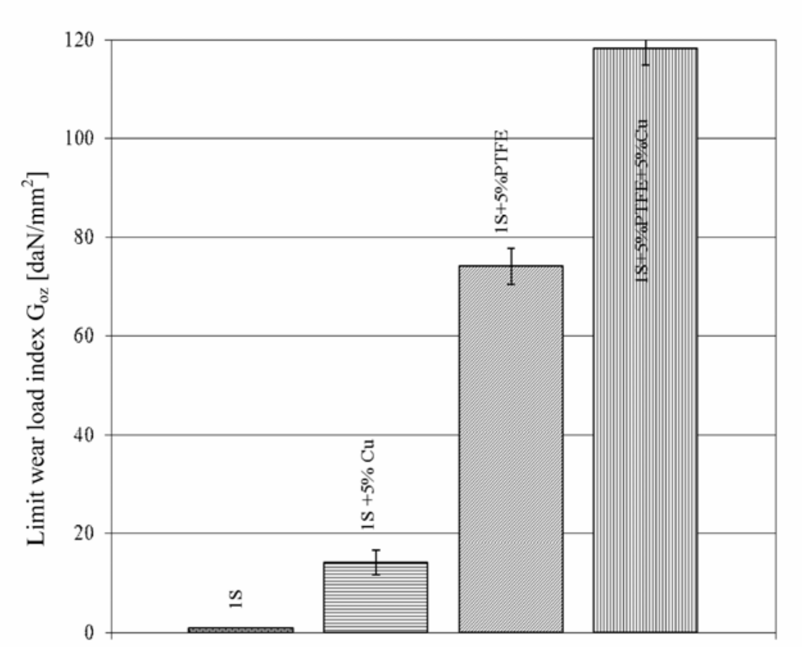

Fig. 5. Limit wear load index G_{oz} for composition with grease 1S
Rys. 5. Graniczne obciążenie zużycia G_{oz} dla kompozycji ze smarem 1S

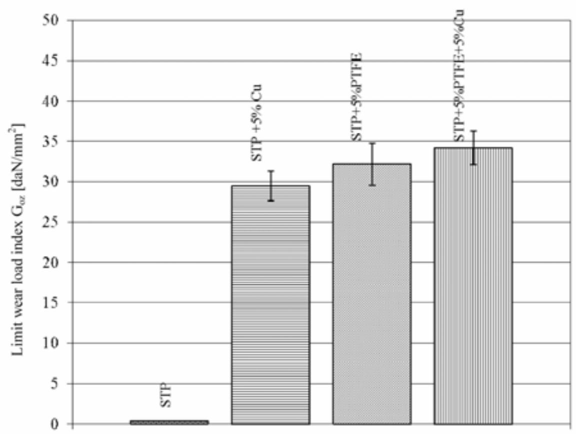

Fig. 6. Limit wear load index G_{oz} for composition with grease STP
Rys. 6. Graniczne obciążenie zużycia G_{oz} dla kompozycji ze smarem STP

For example, the fusion point Fz is 200 daN for the 1 S + 5% Cu composition, 350 daN for the 1S + 5% PTFE composition, and 620 daN when lubricating composition is 1 S + 5% + PTFE 5% Cu. We are dealing with similar wear, which occurring with a load of 160 daN, is equal to 0.96 mm for lubrication with 1 S + 5% PTFE composition, 2.49 mm with 1 S + 5% Cu composition and 0.78 mm for 1 S + 5% + PTFE 5% Cu. The same relationships exist when values of other criterial quantities are compared, namely, the wear index I_h and limit wear load index G_{oz}. Analysis of criterion quantities obtained with the lubrication based on calcium STP compositions shows that PTFE powder and copper powder added to calcium STP grease of 5% by weight do not cause any synergetic effect in the process of friction in sliding steel nodes working in the area of mixed friction. The authors studies **[L. 22]** showed that the three additives, which contains grease 1S (antioxidants, corrosion inhibitors and adhesion additive), had no influence upon the synergy of the PTFE powder and copper powder in this lubricant. Therefore, it is justified to conclude that the type of thickener contained in the basic grease has a significant impact upon the synergism of plastic grease composition with PTFE powder and copper powder. In order to conclusively confirm the above observation, additional studies of chemical composition of the surface layers of cooperating sliding surfaces are required.

REFERENCES

1. Kragelskij I.V., Frikcionnoje vzaimodejstvie tverdych teł, Trenie i iznos, 1980, T. 1, No 1, s. 12–29.
2. Kragelskij I.V., Dobryčin M.N., Kombalov V.S.: Osnowy rasčetov na trenjie i iznos, Mašin. Mašinostroenie, Moskva 1977.

3. Garkunov D.N., Tribotechnika, Moskva „Mašinostrojenie" 1985.
4. Švarcman V.Š., Šojchet V.H., Imerlišvili T.V., Čchaidze G.R., Tołščina plenki plastičnych smazok pri različnych režimach raboty tjažełonagružennych uprugo-gidrodinamičeskich kontaktov, Trenie i iznos, 1988, T9, No 1, s. 129–136.
5. Bakašcili D.L., Imerlišvili T.V., Prognozirovanie tołščiny plenki płastičnych smazok v uprugogidrodinamičeskich kontaktach, Trenie i iznos 1987, T. 8, No 2, s. 236–243.
6. Fuks I.G., Dobavki k płastičnym smazkam, Moskva, Chimja 1982.
7. Wachal A., Kulczycki A., Trybologiczne własności smarów plastycznych zawierających polimery niskotarciowe, Trybologia, 1986, nr 4–5, s. 21–23.
8. Kužarov A.S., Oniščuk N.JU., Sučkov V.V.,Vlijanie medsoderžaščich dobavok na tribotechničeskie svojstva plastičnoj smazki lita, Trenie i iznos, 1989, T. 10, No 5, s. 901–908.
9. Kužarov A.S., Fisenko O.V., Issledovanie tribotechničeskich svojstv metalloplakirujuščich smazok na osnove ciatim-201 legirovanych medno-nikelevymi kompozicijami, Trenie i iznos, 1992, T. 13, No 6, s. 1057–1064.
10. Kopaliński W., Słownik wyrazów obcych i zwrotów obcojęzycznych, Wiedza Powszechna, Warszawa 1988.
11. Słownik Wyrazów Obcych, PWN, Warszawa 1995.
12. Muraki M., Yanagi Y., Sakaguchi K., Synergistic effect on frictional characteristics under rolling - sliding con ditions due to a combination of molybdenum dialkyldithiocarbomate and zinc dialkyldithiophosphate, Tribology International, 1997, vol. 30, No. 1, pp. 69–75.
13. Morar V.E., Kračun A.T., Čobany A.C., Issledovanie smazočnych svojstv nekotorych soedi nenij medi, Trenie i iznos, 1987, T. 8, No 2, s. 274–280.
14. Cho M.H., Bahadur S., Study of the tribological synergistic effects in nano CuO-filled and fiber-reinforced polyphenylene sulfide composites, Wear 258 (2005), pp. 835–845.
15. Płaza S., Reakcje tribochemiczne powierzchni tarcia, Tribologia, 1995, 4, s. 335–348.
16. Suzuki M., Prat P., Synergism of an MoS2 sputtered film and a transfer film of a PTFE composite, Wear 225–229 (1999), pp. 995–1003.
17. Krawiec S. The synergistic effect of copper powder with PTFE in a grease lubricant under mixed friction conditions, Archives of Civil and MeMechanical Engineering. 2011, vol. 11, nr 2, s. 379–390.
18. Muraki M., Yanagi Y., Sakaguchi K., Synergistic effect on frictional characteristics under rolling - sliding con ditions due to a combination of molybdenum dialkyldithiocarbomate and zinc dialkyldithiophosphate, Tribology International, 1997, vol. 30, No. 1, pp. 69–75.
19. Morar V.E., Kračun A., Čobanya A.C., Issledovanie smazočnych svojstv nekotorych soedinenij medi, Trenie i iznos, 1987, T. 8, No 2, s. 274–280.
20. Krawiec S., Wpływ synergizmu wybranych napełniaczy w smarze na zwiększenie trwałości ślizgowych węzłów maszyn, Oficyna Wydawnicza PWR, Wrocław 1998.
21. Krawiec S., On the mechanizm of the synergistic effect of PTFE and copper in lithium grease lubricant, Industrial Lubrication and Tribology, Vol. 63, No 3, 2011, pp. 171–177.

22. Krawiec S., Krawiec M., Leśniewski T., Wpływ dodatków uszlachetniających w smarze plastycznym na efektywność smarowania jego kompozycjami z PTFE i Cu, Tribologia, 2014, Nr 3 (255), s. 109–117.

Streszczenie

Przedstawiono badania wpływu rodzaju smaru plastycznego na efekt synergetyczny jego kompozycji z proszkiem PTFE i miedzi podczas smarowania stalowych węzłów ślizgowych pracujących w obszarze tarcia mieszanego. Do analizy przyjęto dwa smary plastyczne, tj. smar samochodowy 1S z zagęszczaczem litowym oraz smar STP z zagęszczaczem wapniowym. Napełniaczami tych smarów były proszki dwóch smarów stałych – PTFE i miedzi. Dla każdego z przyjętych smarów plastycznych przebadano trzy kompozycje smarowe. Dwie kompozycje zawierały po jednym napełniaczu w ilości 5% wagowo, a trzecia – oba napełniacze w tej samej ilości (po 5%). Własności smarne przyjętych kompozycji oceniano na podstawie eksperymentu tribologicznego przeprowadzonego na aparacie czterokulowym zgodnie z wytycznymi normy PN-76/C04147. Efektywność analizowanych smarów oceniano według czterech wielkości kryterialnych, tj. zużycia kulek d, obciążenia zespawania F_{z}„ wskaźnika zużycia I_h oraz granicznego obciążenia zużycia G_{oz}. Wyniki eksperymentu zostały opracowane statystycznie przy poziomie ufności 95%, stosując test t-Studenta. Opracowane wyniki badań przedstawiono graficznie. Podano stosowne wnioski.