# Andrzej KOTNAROWSKI<sup>\*</sup>

# ANTIWEAR PROPERTIES OF LUBRICANTS MODIFIED WITH METAL PARTICLES

# PRZECIWZUŻYCIOWE WŁAŚCIWOŚCI ŚRODKÓW SMAROWYCH MODYFIKOWANYCH CZĄSTKAMI METALI

#### **Key-words:**

lubricating oils, metal microparticles, metal nanoparticles, antiwear properties

# Słowa kluczowe:

oleje smarowe, mikrocząstki metali, nanocząstki metali, właściwości przeciwzużyciowe

# Summary

The paper presents an influence of lubricant modification with metal particles addition on wear process of tribological couplings elements. Combinations of various materials working in mixed friction condition at rotational or reversible motion were analysed. They were lubricated with, first of all, base oils used for different lubricants compounding which were modified with addition of micro- or nanoparticles of such metals like aluminium, zinc, copper and lead. Presented results attest to positive

<sup>&</sup>lt;sup>\*</sup> Instytut Eksploatacji Pojazdów i Maszyn, Wydział Mechaniczny, Politechnika Radomska, al. Chrobrego 45, 26-600 Radom, tel.: 606 714 696; e-mail: a.kotnarowski@pr.radom.pl

influence of small quantities of metal particles added to oils on frictional couplings tribological characteristics.

# **INTRODUCTION**

Operational efficiency of lubricants depends to a great extent on their tribological properties which can be improved by introducing to lubricants composition powders of metals or their alloys consisting of microor even nanoparticles. Such a conclusion is based on a few existing references as well as on author's investigations [L. 4-15]. Results of the examination testify to effective influence of such lubricants like oils modification with metal powders addition on improvement of their tribological properties, manifested in kinematical joints, like antifrictional and antiwear properties, leading to frictional resistance and wear decrease. Especially interesting seems to be applications of nanopowders or even – in wider scope - nanostructures as they developed in extreme extent in last few years. Tribological processes are these areas where application of metal nanoparticles as additives to oils seems to be possible and profitable because of its specific features. As extremely small (diameter from single nanometers to some tens of nanometers) they possess extraordinary physicochemical properties, quite different from those observed in bulk form of material [L. 1-3]. At least two aspects of nanostructures nature can be utilized in tribotechnology. One of them is quantum aspect, dominating first of all in the nanometric scale, and the other is superficial aspect. The quantum aspect consists in peculiarities connected with electron flow resulting from lack of conduction band characteristic for solid metal. The discrete states occur instead of this band on its borders. For this reason electrons can be trapped in a small enough nanoparticle like in the quantum trap and such nanoparticles will possess properties of so called quantum dot [L. 2]. The superficial aspect results from the fact that the smaller object the bigger relation of atoms quantity existing on the object surface to quantity of all atoms composing this object. For this reason, sets of very small particles are characterized by very big surface in relation to the volume and, because many phenomena occur on the surface, this feature can be used to these phenomena intensification. Thanks to high specific surface nanoparticles possess much more active centres than bigger particles of the same mass and demonstrate very strong catalytic properties. This feature, in the case of nanoparticles addition to lubricants, can facilitate friction process, the more so because that their ability to penetration (on account of small size) is also much bigger what afford possibilities for their closer penetration of friction zone. Tribological process may also be influenced on account of phenomena occurring on quantum level between nanoparticles and materials of rubbing elements.

Considering above some investigations were made to examine possibilities of metal particles application to lubricants improvement. Results of author's investigations made about possibilities of some metals powders use as additives to lubricating oils [L. 7–9] are discussed. Presented results prove generally positive influence of examined powders on tribological properties of lubricants consisting in friction resistance and wear decrease in couples lubricated with these lubricants.

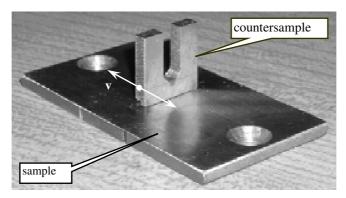
#### EXPERIMENTAL

# Examination methods and used materials

Examinations, in which the influence was investigated of lubricating oils modification with some metals particles addition on wear amount of frictional couple elements, can be divided into three subsequent stages. The first stage examinations referred to influence of metal microparticles addition to oils lubricating frictional couples on wear amount of their rubbing elements. In the second stage the dependence between wear amount and metal particle size was analysed and obtained results became an inspiration to further researches which were continued in the third stage of examinations. These examinations concerned the problems connected with metal nanoparticles application as friction an wear additives to lubricants.

In the first stage of examinations, consisted in wear tests carried with the help of 77MT-1 apparatus at reciprocatory sliding friction, as materials of both cooperating elements of friction couple steel C45 was used. Friction couple, which is presented in **Fig. 1**, was lubricated with base oil Hydrorafinat II of kinematic viscosity  $v_{50} \approx 58 \text{ mm}^2/\text{s}$ .

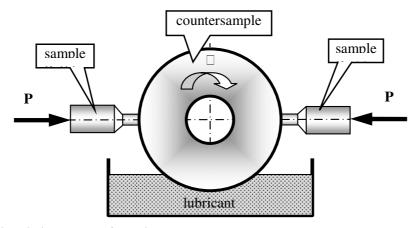
For oil modification microparticles of aluminium, copper, lead and zinc were used of following sizes: Al –  $(12\div14)$  µm, Cu – 2 µm, Pb –  $(18\div20)$  µm and Zn –  $(90\div100)$  µm. Concentration of metal particles was 0.003% (wt) in all cases.



**Fig. 1. Friction couple of 77MT-1 apparatus** Rys. 1. Para tarciowa urządzenia 77MT-1

Results obtained in the first stage (which are cited below) became a incentive to further investigations concerning the influence of metal particles size on effectiveness of their action in friction couple. The relevant investigations were carried out in the second stage described below.

Tribological tests in the second stage were made at the sliding friction in rotational motion with the help of MT-2 friction machine (designed in Technical University of Radom with author's participation). The model friction couple of the apparatus is presented in **Fig. 2**.

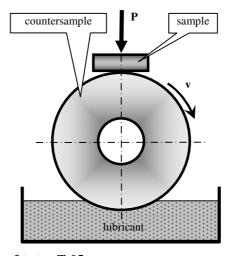


**Fig. 2. Friction couple of MT-2 apparatus** Rys. 2. Skojarzenie tarciowe urządzenia MT-2

It consisted of two samples in the shape of rod of 2 mm diameter pressed against a countersample in the form of ring (of outer diameter equal 40 mm and 10 mm width), immersed in lubricant. This apparatus enabled to control the countersample rotational speed  $\omega$  and the load force P. It enables also to measure and record these values as well as friction force, resistance of the contact between the countersample and the samples, and temperature of the samples and of the oil bath. The possibility of contact resistance between each sample and countersample measurement allows for easy detection of mixed friction which correlates with low resistance value. Moreover, thanks to this feature the minimum value of unit pressure assuring mixed friction in tested couple was determined and taken into consideration in subsequent examinations.

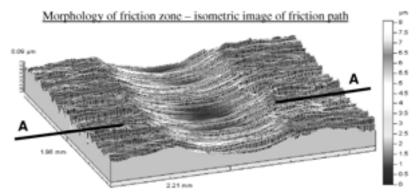
In mentioned tests all rubbing elements (samples and countersample) were made of steel C45. They were immersed in base oil Hydrorafinat II modified with copper particles of mean diameter 0.002 and 0.01  $\mu$ m or molybdenum particles of mean diameter 0.003 and 0.01  $\mu$ m.

Examinations in the third stage were made to evaluate the influence of metal nanoparticles addition to lubricating oils on tribological properties, and among others, on wear of frictional joints working in modified oils. In this connection copper nanoparticles of mean diameter 66 nm and molybdenum nanoparticles of mean diameter 54 nm were used separately as base oil Hydrorafinat II modifiers. The tests were carried out with the help of T-05 tribological tester equipped with the friction couple presented in **Fig 3** and consisting of sample made of steel SW18 or sintered carbide S20S and countersample made of steel C45.

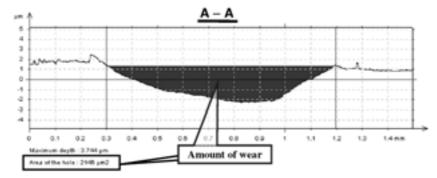


**Fig. 3. Friction couple of tester T-05** Rys. 3. Skojarzenie tarciowe testera T-05

Wear amount were analysed using scanning profilemeter Form Talysurf Series 2. This apparatus enables to obtain isometric pictures of the friction surface and to calculate a wear factor as the surface area of the right section A – A of friction path representing amount of wear (**Fig. 4**).



Wear factor as area of cross-section A-A through friction path parallel to motion direction



- Fig. 4. Wear factor evaluation (of sample made of steel SW 18 after work in pair with countersample made of steel C45 in base oil Hydrorafinat II without any addition) carried out with scanning profilemeter Form Talysurf Series 2 use
- Rys. 4. Ocena wskaźnika zużycia (próbki ze stali SW 18 po pracy w parze z przeciwpróbką ze stali C45 w oleju bazowym Hydrorafinat II bez dodatku) wykonana z wykorzystaniem profilometru skaningowego Form Talysurf Series 2

#### **Results and discussion**

Results of wear tests made in the first stage of examinations with the help of 77MT1 apparatus at reciprocating motion are presented in **Fig. 5**. They proved that microparticles of all tested metals added to lubricating oil decreased wear amount of friction couple elements.

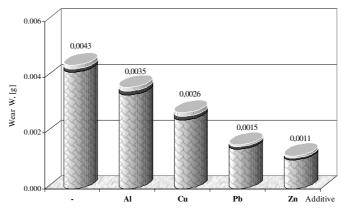
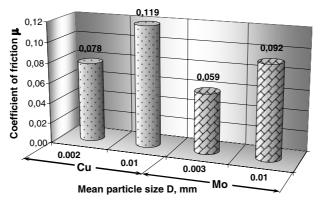


Fig. 5. Influence of some metals (Al, Cu, Pb, Zn) microparticles (added to oil Hydrorafinat II in amount of 0.03% by weight) on wear amount of steel C45/steel C45 friction couple of 77MT1 apparatus

Rys. 3. Wpływ dodatku 0,03% (wag.) mikrocząstek Al, Cu, Pb, Zn do oleju bazowego Hydrorafinat II na wartość zużycia elementów skojarzenia stal C45/stal C45 urządzenia 77MT1

In the wake of so positive results of wear tests, examinations of metal particle size influence on friction resistance were carried in the second stage using MT-2 apparatus and obtained results are presented in **Fig. 6**. They clearly showed that decrease of metal particles size led to the improvement of frictional joints tribological properties which was observed in the case of particles of both examined metals i.e. copper and molybdenum.



- Fig. 6. Influence of sizes of Cu and Mo microparticles (added to oil Hydrorafinat II in amount of 0.25% by weight) on friction resistance of steel C45/steel C45 couple of MT-2 apparatus
- Rys. 6. Wpływ rozmiarów mikrocząstek Cu i Mo (dodanych do oleju bazowego Hydrorafinat II w stosunku wagowym 0,25%) na opory tarcia skojarzenia stal C45/stal C45 urządzenia MT-2

TRIBOLOGIA

Outcomes obtained in two first examination stages, testifying to effectiveness of metal particles in frictional resistance and wear decreasing in the degree higher the particles size lower, gave an impulse to use as lubricating oils modifiers metal nanoparticles that are much smaller than microparticles. Relevant test were carried in the third stage of examinations using tribological tester T-05. Samples after this test were analysed with scanning profilemeter to evaluate amount of wear as the wear factor according to **Fig. 4**. Obtained results are collected in **Table 1** bellow.

- Table 1. Values of wear factor of samples after work in friction couples lubricated with base oil Hydrorafinat II unmodified and modified with Cu or Mo nanoparticles
- Tabela 1. Wartości wskaźnika zużycia próbek po pracy w skojarzeniach tarciowych smarowanych olejem bazowym Hydrorafinat II niemodyfikowanym oraz modyfikowanym nanocząstkami Cu lub Mo

	Oil nanoadditive		
Sample material	-	Cu	Мо
	Wear factor [µm <sup>2</sup> ]		
SW18	2137	1221	1626
S20S	630	585	278

Analysis of above data shows that nanoparticles of both metals (Cu and Mo), when added to lubricant, have in all examined cases a positive effect on wear of friction couple elements. This effect is positive for copper as well as for molybdenum nanoparticles. The effectiveness of each kind of nanoparticles depends on rubbing materials combination in friction pair. For combination of the sample made of steel SW18 and the countersample made of steel C45 more effective are copper nanoparticles while for combination of the sample made of steel S20S and the countersample made of steel C45 more effective are nanoparticles of molybdenum.

# CONCLUSIONS

The results of examinations described in the paper lead to general conclusion that nanoparticles of some metals may be effectively used as modifiers of lubricants changing their tribological properties that are manifested in frictional joints, that is ability to wear decrease of rubbing elements.

As nanotechnology is very dynamically developing discipline bringing all the time new ideas and products, it is reasonable to carry on researches continuously on introducing to lubricants nanoparticles possessing new properties. For instance, nanoparticles with surfaces protected against agglomeration using thin film of silanes or oleic acid.

#### REFERENCES

- Baraton M.I.: Synthesis, Functionalization and Surface Treatment of Nanoparticles. American Scientific Publishers, Stevenson Ranch, California 2003.
- 2. Bhushan B. (ed.): Nanotribology and nanomechanics. An Introduction. Ed.: Springer Verlag 2008, 1516 p.
- Burda C., Chen X., Narayanan R., El-Sayed M.A.: Chemistry and properties of nanocrystals of different shapes. Chemical Reviews, 2005, Vol. 105, Issue 4, p. 1025÷1102.
- 4. Hernándes Battez A. et al.: CuO, ZrO<sub>2</sub> and ZnO nanoparticles as antiwear additive in oil lubricants. Wear 2008, Vol. 265, Issues 3-4, p. 422÷428.
- 5. Kajdas Cz.: Additives for metalworking lubricants-Review. 6<sup>th</sup> Intern. Kolloquium, Technische Akademie Esslingen, 1988.
- Kołodziejczyk L. et al.: Surface modified Pd nanoparticles as a superior additive for lubrication. Journal of Nanoparticle Research 2007, Vol. 9, No. 4, p. 639÷645.
- Kotnarowski A.: Tribological Properties of Oils Modified with the Addition of Metals Nanoparticles. Solid State Phenomena 2006, vol. 113, 393÷398.
- Kotnarowski A.: Modyfikacja środków smarowych za pomocą nanocząstek metali. Tribologia 2/2008, s. 309÷319.
- Kotnarowski A.: Selective Transfer Phenomenon in Copper-Steel Tribological Systems. Solid State Phenomena 2009, Volume 147–149, p. 558–563.
- 10. Lee K. et al.: Understanding the role of nanoparticles in nano-oil lubrication. Tribology Letters 2009, Vol. 35, No. 2, p.127+131.
- 11. Lesnikovich A.I., Shpenkov G.P.: Ultra Dispersed Metals and Oxides as Perspective Additives for Metal-plating lubricants. Conference Proceedings, Taganrog, 1991.
- 12. Shpenkov G.P.: Tribological properties of greases and lubricating water emulsions with additives containing ultradispersed particles of copper oxide. Problemy Eksploatacji 6/1995, 208–213 (in Polish).
- Li B. et al.: Tribochemistry and antiwear mechanism of organic-inorganic nanoparticles as lubricant additives. Tribology Letters 2006, Vol. 22, Issue 1, p. 79+84.

- Ma J., Mo Y., Bai M.: Effect of Ag nanoparticles additive on the tribological behavior of multialkylated cyclopentanes (MACs). Wear 2009, Vol. 266, Issues 7–8, p. 627÷631.
- 15. Tarasov S., Belyaev S.: Alloying contact zones by metallic nanopowders in sliding wear. Wear 2004, Vol. 257, Issues 5–6, p. 523÷530.

Recenzent: Janusz JANECKI

#### Streszczenie

W artykule przedstawiono wpływ, jaki na proces zużywania elementów skojarzeń tribologicznych wywiera modyfikacja stosowanych w nich środków smarowych, za pomocą dodatku cząstek metali. Przeanalizowano skojarzenia różnych materiałów konstrukcyjnych pracujące w warunkach tarcia mieszanego, przemieszczające się względem siebie ruchem obrotowym i posuwisto-zwrotnym. Do ich smarowania wykorzystano, przede wszystkim, oleje bazowe, stosowane do komponowania różnego rodzaju środków smarowych, natomiast do ich modyfikacji użyto zarówno mikro-, jak i nanocząstek takich metali, jak aluminium, cynk, miedź, molibden, ołów. Zaprezentowane w referacie wyniki badań własnych świadczą o korzystnym wpływie niewielkich ilości cząstek metali, dodawanych do olejów, na charakterystyki tribologiczne smarowanych nimi węzłów tarcia.