The influence of nanoadditives on the tribological properties of process fluids

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Abstract. Tribology deals with interaction of surfaces in relative motion depending on their design, friction, wear and lubrication. The proper use of process fluids or lubricants can bring a significant reduction in friction and the amount of wear, thereby leading to a reduction in power consumption. During different technological operations contamination of used process fluids or lubricants occurs. Such contamination leads not only to a reduction of the lifetime of the lubricants but it can also change the functional properties and increase the health risks for operators. The quality of the process fluid is among other things influenced by bacterial attacks. The use of nanoadditives is one method for inhibiting the bacteria and improving the bioavailability and stability of the technological fluids. Nanolubricant is a new system composed of nanometer-sized particles dispersed in a base lubricant. The doping of lubricants with nanoparticles is one of the ways to solve problems with the removal of bacteria, whereby improving the biological, chemical and technological stability of process fluids. In the article, we monitor the effects of doping process fluids with nanoparticles of silica (SiO$_2$), titanium dioxide (TiO$_2$), silver nitrate (AgNO$_3$) and ascorbic acid (C$_6$H$_8$O$_6$) on the friction coefficient and on the wear of friction pairs of Si$_3$N$_4$ balls against steel 16MnCr5, EN 10084-94.

1. Introduction

Machining technology is still a rapidly developing sector in the engineering industry. Both machine tools and in particular cutting tools are experiencing rapid development and not the least in the area of process media [1-3]. An important component of the metal cutting process is fluid; its quality often decides the outcome of the machining process and the lifespan of a machine. The correct choice of process fluids leads to cost savings, enhanced machining performance and better product quality [4-7]. The various substances that are received in the process fluid are to be considered as contamination, as they adversely affect the composition of the process fluid, its performance and health characteristics. They can be divided into solid, fluid and biological contamination. In the case of newly produced process fluids strong emphasis is placed on ecology and health and safety in their use and removal. The order of Regulation (EC) No 1907/2006 of the European Parliament and of the Council (REACH - Registration, Evaluation and Authorisation of Chemicals) is applied and authorization of chemicals with ECHA (European Chemicals Agency) also takes place.

The lifetime (degradation) of process fluids in the first instance is affected by bacterial attack. The resistance of process fluids to bacterial attack determines the resulting lifetime of the fluid. The bacteria that attack process fluids are called Anaerobic, i.e. bacteria that multiply the most if no oxygen is present. Emulsifiers, sulfonates, fatty alcohols, corrosion inhibitors and other organic
components serve primarily as food for these bacteria. An important component incorporated into process fluids are biocide additives. Their purpose is to protect the fluid against the biological attack by bacteria or fungi. Another problem that is solved is the protection of users against spores and endotoxins, which would otherwise be formed by these organisms. An increased proportion of these ingredients can lead to the improved lifetime of process media but on the other hand leads to allergic reactions in people who are exposed to the fluid [8, 9]. We are constantly looking for ways to solve these urgent problems. The main objective is to provide a safe environment for a person who in execution of his/her work is in constant contact with process fluids. Given the growing concerns about the environment and regulations on contamination and pollution there is an observable increase in the interest in renewable and biodegradable cutting fluids. In this respect, the significance of the term “green” machining, which includes both the type of process fluid and the methods to be applied during the machining process, is also increasing. [10-12]

The use of nanoadditives in the form of nanoparticles is highly efficient due to their high chemical and biological activity. Application of nanoparticles is one of the possible ways to solve problems with reduce the presence of bacteria and fungi, thus ensuring improved biological, chemical and technological stability of the process fluids. A suitable alternative for the development of antimicrobial solutions is to synthesize the biocide attributes (especially nanoparticles based on silver) of metal nanoparticles. Nanoparticles with dimensions smaller than 100 nm have a large surface area so they can interact easily and in a high rate with biological material. [10-14]

The intensity of the machining process is significantly increased and thus leads to an increase in the cutting speed. The most analyzed parameters are the surface roughness and hardness. In addition to the most analyzed parameters the tribological properties of the newly created functional surfaces are also increasingly analyzed. The tribology evaluates values that affect the mutual interaction of the surface environment and the body during their relative motion. The mechanism of friction can be defined as a resistance to the relative motion of two bodies during their contact. The friction force $F$ depends on the friction coefficient $\mu$ and the loading force $F_N$. The description of friction and the introduction of this concept were first discussed by Coulomb (1799) and the basic relationship is known as Coulomb’s law [15]. Sliding friction arises when two bodies come into contact with one another and leads to their movement relative to each other. In fact, the real contact between bodies occurs only in a limited number of small areas on the surfaces (Figure 1).

![Figure 1. Schematic illustration of contact during sliding friction](image1)

![Figure 2. Components of sliding friction](image2)

Figure 1 shows (a) body contact with an ideally flat surface and stress distribution (b) real contact, which includes: ideal surface - 1, real surface - 2, elastic deformation region - 3 and plastic deformation, region - 4. The size of the contact area increases with increasing load. On the tops a connection may occur, thus creating resistance to relative motion. In the specialized literature [16] a relation was derived for the coefficient of friction, according to the equation (1):

$$F_t = A_{mech} \cdot \tau_s = \mu F_N$$

(1)
where:  \( F_t \) [N] – frictional force acting against the direction of movement;
\( A_{mech} \) [mm\(^2\)] – actual contact area of the firm connection;
\( \tau_s \) [MPa] – shear strength of the material;
\( F_N \) [N] – load force;
\( \mu \) [-] – coefficient of friction.

In the case of sliding friction three basic components can be observed. The ratio of each component depends on the type of material pairs, the friction conditions (material properties of pairs of movements, surface roughness, presence of a lubricant etc.) and the time stage of the mutual movement.

The following mechanisms are applied when friction occurs (Figure 2):
- Friction due to adhesion between the surface roughness;
- friction due to striations caused by the presence of fine particles arising from the wear surface of friction due to deformation of the surface roughness;
- friction due to the deformation of the surface roughness. [17, 18]

2. Materials and Methods

2.1. Evaluation of tribological tests

The basis of tribological measurements is the “ball-on-disc” testing method. The measurement involves the injection of fixed attachments of a test piece (“ball”) in the form of balls (Figure 3) of the chosen material with a defined force to drive (test sample). An essential part is the friction sensor. The coefficient of friction between the unit and the disc is determined during the test measurement. [7]

![Figure 3. Schematic representation of the contact with the sample.](image)

![Figure 4. CETR UMI Multi-Specimen Test System.](image)

The coefficient of friction was determined using a CETR UMI Multi-Specimen Test System tribometer (Figure 4) and the groove of the tribological test was evaluated by a (LM) Zeiss AXIO Imager M2 direct light optical microscope with a fully motorized stage configuration for observations in reflected light (Figure 5) and a Dektak™ XT mechanical profilometer (Figure 6) from BRUKER.

Tribological testing (EN1071-13:2010) was conducted by using a ball made from Si₃N₄ with a diameter of 6.350 mm, with a constant load of 10 N at room temperature and humidity of 40 ± 2 %.

The material of the disc was steel 16MnCr5 - EN 10084-94, EN 84-70 with a polished surface and a roughness of Ra 0.01µm. The radius of the circle along the "ball" body was moving was 12 mm and the coefficient of friction was measured using a 5% solution of process fluids with a volume of 100 ml.

The use of a light-optical microscope allows the microscopic objects and structures to be observed and analyzed in reflected light at magnifications from 25x to 1000x. Preparation of the samples for analysis using the optical microscope in reflected light first involves grinding and then polishing. The
contrast of the images is obtained based on the individual structural reflexivity, different phases or due to the surface topography. The intensity of reflected light is proportional to $\cos\varphi$, where $\varphi$ is the angle between the sample surface and the incident light beam. [19]

Figure 5. Light optical microscope.  

Figure 6. Dektak™ XT mechanical profilometer.

A recording of images from a light optical microscope is obtained using a CCD camera. Software can then be used to archive, analyse and modify the scanned data. The aim of the software data analysis is to process visual information, eliminate random errors and extract typical features characterising the image [19, 20]. Optical microscopy allows structures to be displayed very fast using various contrast methods, e.g. phase contrast, polarization, fluorescence, Hoffman modulation contrast or Nomarski differential interference contrast [21].

The Dektak™ XT mechanical profilometer comes into direct contact with the surface of the sample tip. A load must be selected according to the type of sample to prevent the mechanical damage (scratching) of samples if the sample is soft and the force is disproportionately large. During the measurement the sample is placed on a substrate and is in direct contact with the tip. The inequalities on the surface of the sample are registered by the tip which performs a linear movement, and the samples move relatively to the stationary tip. In the contact mode the mechanical profilometer scans the shape of the surface in contact with a diamond tip, which has the size of a few micrometres; thereby it is possible to study the surface morphology of the horizontal plane with the size from a hundred micrometres to tens of millimetres [7].

2.2. Use of natural fillers in the form of nanoparticles

When using cooling and lubricating process fluids contamination due to technological process occurs.

Figure 7. SEM images of Silicon dioxide (SiO₂) nanoparticles.  

Figure 8. SEM images of Titanium dioxide (TiO₂) nanoparticles.
This has a negative impact on the reduction of their lifespan and also changes their functional properties. Bacterial attacks also have an impact on the quality of process fluids. The resistance of process fluids to bacterial attack determines the resulting lifespan of the fluid. The nanoparticles may be added to reduce the presence of bacteria and fungi, and if this occurs, prevent their spreading.

The aim of the modification of industrially supplied process fluids is to increase their biological stability even after long-term use. The experiment was performed at the Institute for Nanomaterials, Advanced Technology and Innovation, Technical University of Liberec (TUL), Czech Republic. Two standard supplied process fluids labelled PF 1 and PF 2 were used in the experiment.

Nanoparticles of silicon dioxide SiO$_2$ and titanium dioxide TiO$_2$ (Figure 7 and Figure 8) were added to the process fluids and subsequently tribological tests were carried out and the technological and biological stability of the processes were evaluated.

![Figure 9.](image1)

**Figure 9.** Particles of ascorbic acid (C$_6$H$_8$O$_6$) from a Sky Scan 1272 micro-tomograph device.

![Figure 10.](image2)

**Figure 10.** SEM images of silver nitrate (AgNO$_3$) nanoparticles.

Both process fluids were modified by the addition of silver nitrate (AgNO$_3$) and ascorbic acid (C$_6$H$_8$O$_6$). Ascorbic acid (Figure 9) was chosen for the purpose of improving antimicrobial and antioxidant activity and also to reduce the metallic silver nanoparticles from the silver nitrate solution (Figure 10). Variants of process fluids were prepared: with the addition of silver only and with the addition of silver and ascorbic acid. Reduction of silver nanoparticles from silver nitrate was carried out using UV radiation. UV irradiation was performed in a closed chamber using a high performance halogen metal vapour lamp with a combination of metal halides generating strong radiation in the UVB range (280 - 315 nm) and especially in the UVA range (315 - 380 nm). Reduction of silver nanoparticles resulted in a change in colour of the tested process fluids.

### 3. Experimental results

The effects of adding a nanoadditive to the process fluids on their tribological behaviour were evaluated by comparing the frictional properties and wear-resistant material for tribology. The friction coefficients without and after adding the nanoadditives to a 5% solution were evaluated as well as the tribological wear of the material after the experiment.

#### 3.1. Evaluation of friction and wear using process fluid 1

Process fluid 1 is a water miscible high-performance cooling lubricant based on mineral oils. The examined PF 1 contains a high proportion of polar additives, during processing it has long-term stability and provides excellent corrosion protection.

The tribological results are shown in Figure 11 (left), where we can see a comparison of the friction coefficient of the pure 5% PF 1 solution and solutions with added nanoparticles (NPs) of Silicon dioxide (SiO$_2$), Titanium dioxide (TiO$_2$), Silver nitrate (AgNO$_3$) and Ascorbic acid (C$_6$H$_8$O$_6$), marked as Ag$^+$AA NPs in the Fig. 11. Rating of ball wear was performed according to standard EN1071-
13:2010, friction pair were ball of Si\textsubscript{3}N\textsubscript{4} and steel 16MnCr5-EN 10084-94, EN 84-70, results are shown in Figure 11 (right).

![Figure 11. Coefficient of fiction and wear of balls (Si\textsubscript{3}N\textsubscript{4}) in the process fluid PF1 without/with nanoparticles.](image)

With the help of the optical microscope several important parameters for wear can be evaluated, e.g. size of wear beads, which are shown in Figures 12 and 13 (top left of the figure).

![Figure 12. Mechanical profilometer: 3D image of profile on the disk after tribology - clean solution and optical microscopic images of wear of the ball.](image)

![Figure 13. Mechanical profilometer: 3D image of profile on the disk after tribology - nanoadditive Silicon dioxide (SiO\textsubscript{2}) and optical microscopic images of wear of the ball](image)
Information on the volume of spalled material can be obtained using a Dektak XT™ mechanical profilometer, Figures 12 and 13, which shows the wear when using the unmodified process fluid and process fluid with nanoparticles Silicon dioxide (SiO₂). The relevant software enables the measured values to be sorted using Gauss’ law along the investigated profile and offers the possibility of sorting values in a histogram according to their frequency. The wear rate of the friction pair of two parts provides information on the friction properties of the media used under specific conditions (Figure 11 right - wear of ball Si₃N₄ without/with nanoparticles).

3.2. Evaluation of friction and wear using process fluid 2

Process fluid 2 is a semi-synthetic, water-miscible high-performance cooling lubricant based on mineral oils. The examined fluid PF 2 contains a high proportion of polar additives containing boron and bactericide; it has long-term stability and provides excellent corrosion protection.

The tribological results are shown in Figure 14 (left), where the coefficient of friction using a 5% solution of pure PF 1 is compared with solutions with the addition of nanoparticles (NPs) of silicon dioxide (SiO₂), titanium dioxide (TiO₂) Silver nitrate (AgNO₃) and ascorbic acid (C₆H₈O₆), marked as Ag+AA NPs in the Fig. 14. Rating of ball wear was performed according to standard EN1071-13:2010, friction pair were ball of Si₃N₄ and steel 16MnCr5-EN 10084-94, EN 84-70, results are shown in Figure 14 (right).

Several important parameters for wear can be evaluated using the optical microscope, e.g. size of wear beads, shown in Figures 15 and 16 (top left of the figure).

![Figure 14: Coefficient of friction and wear of balls (Si₃N₄) in the process fluid PF2 without/with nanoparticles.](image-url)

![Figure 15. Mechanical profilometer: 3D image of profile on the disk after tribology - clean solution and optical microscopic images of wear of the ball.](image-url)
Information on the volume of spalled material can be obtained using the Dektak XT™ mechanical profilometer, Figures 15 and 16, which shows the wear when using the unmodified process fluid and process fluid with nanoparticles Silver nitrate (AgNO₃) and Ascorbic acid (C₆H₈O₆). The relevant software enables the measured values to be sorted using Gauss’ law along the investigated profile and offers the possibility of sorting values in a histogram according to their frequency. The wear rate of the friction pair of two parts provides information on the friction properties of the media used under specific conditions (Figure 14 right - wear of ball Si₃N₄ without/with nanoparticles).

![Figure 16. Mechanical profilometer: 3D image of profile on the disk after tribology - nanoadditive Silver nitrate (AgNO₃) and Ascorbic acid (C₆H₈O₆) and optical microscopic images of wear of the ball.](image)

### 3.3. Chemical composition of process fluids

In the experimental part the chemical composition of the process fluids PF 1 and PF 2 was evaluated. The chemical composition of the process fluid concentrates was determined using the static method HS-GS-MS (Head Space-Gas Chromatography-Mass Spectrometry). Process fluid (PF 1) consists mainly of oxygenated organic compound types of glycols and higher alcohols, which are not part of the process fluid PF 2. PF 1 contains methylene chloride, which is toxic to the human body and has been proven to have carcinogenic effects; it is also associated with a number of risks threatening human health. Dichloromethane is metabolized in the body to form carbon monoxide, consequently increasing the carboxyhemoglobin level in the blood and thus reducing the capacity of the blood to carry oxygen to induce respiratory distress, headache and dizziness. Other hazardous materials, components of PF1, are 1.4 - dioxane, dimethylformamide, trimethylsilanol and octamethycyclotetrasiloxan belonging to the group of substances with proven toxic effects.

PF 2 is mainly composed of oxygenated organic compound types of glycols and higher alcohols, which are not part of the process fluid PF 1. From a toxicological point of view, PF 2 does not contain substances that have carcinogenic or mutagenic properties and causes no major negative impact on the human body.

### 3.4. Evaluation of biological tests

The addition of SiO₂ and TiO₂ nanoparticles to PF1 caused a reduction in cell number, even after 120 days of the experiment the number of cells did not change significantly, while in the second sample PF2 the number of cells increased. SiO₂ and TiO₂ nanoparticles in PF 1 have a long-term effect on reducing bacterial multiplication.

The addition of AgNO₃ nanoparticles into the process fluids caused a reduction in cell numbers even after 70 days of the experiment and the number of cells further decreased. AgNO₃ nanoparticles have a long-term effect on reducing bacterial multiplication.
The addition of ascorbic acid into the sample causes additional inhibition of the bacterial strain of *E. Coli*. The most significant biocidal effect of AgNO$_3$ was observed in PF 2. After two months of exposure the effect of the AgNO$_3$ nanoparticles in the studied samples was still observed resulting in reduced respiratory activity compared to the control sample (23% of the *E. Coli* strain).

4. Discussion
The use of natural fillers in the form of nanoparticles is highly efficient due to their high chemical and biological activity. The use of nanoparticles is one method for inhibiting bacteria and improving the biological, chemical and technological stability of the fluids.

Tribological tests were conducted in both process fluids under the same conditions. It has been shown that the addition of silver nitrate and ascorbic acid in a 5% aqueous solution of PF 1 has a positive effect on reducing the coefficient of friction during the tribological process (Figure 11). Adding nanoadditives in the form of nanoparticles leads to a faster stabilization of the tribological process under certain experimental conditions, which is a very important factor when machining. The rate of wear of the friction pair after adding nanoadditives to the solution PF 1 did not lead to significant changes.

For process fluid 2 the values of the coefficient of friction using a 5% solution with the addition of nanoadditives TiO$_2$, SiO$_2$ and silver nitrate with ascorbic acid had no effect on the tribological properties (Figure 14). Adding nanoparticles of silver nitrate with ascorbic acid resulted in a significant reduction in the depth of material being removed, and furthermore to an increase in the groove width. For nanoadditives TiO$_2$ and SiO$_2$ it resulted in a decrease of groove width, even more significantly when using the solution of TiO$_2$ nanoparticles.

5. Conclusion
The tribological tests (Figure 11 and Figure 14) show that the addition of nanofillers SiO$_2$ and TiO$_2$ has no negative effect on the coefficient of friction during the tribological process. For PF 1 it resulted in a stabilization of the values of friction coefficient using a 5% solution with the addition of nanoaddatives SiO$_2$, TiO$_2$ and silver nitrate with ascorbic acid. In process fluid 2 the values of the coefficient of friction using a 5% solution with the addition nanoadditives TiO$_2$, SiO$_2$ and silver nitrate with ascorbic acid had no effect on the tribological properties. The measured values are close to the values registered in the tribology of the pure 5% solution.

The biological experiments demonstrate the positive impact of the use of nanoadditives. Suppression of bacterial proliferation was achieved by using nano - SiO$_2$ 35 ÷ 69%, nano-silver nitrate 60 ÷ 90% and nano - silver nitrate with ascorbic acid and 70 ÷ 90%, where significant toxic effects were observed in the bacterial strain of *E. Coli*.

The manufacturing process with process fluids has to be in accordance with European Union requirements that are specifically focused on environmental and health and safety standards. The addition of natural nanoadditives is one possible way of improving the PF properties and compliance with EU requirements.

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