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The impact of natural nanoaditiv on the tribological and chemical properties of process fluids

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Abstract: *When using cooling and lubricating process fluids (PF), a contamination occurs, due to the technological process. These contaminations have a negative effect on decreasing the fluids lifespan and changes in their functional attributes. That can be strongly expressed not only by inappropriate actions of the fluid during the technological process, but also increased economic costs. Using natural fillers in a form of nanoparticles has a high efficiency due to their high chemical and biological activity. Using nanoparticles is one of the ways to inhibit bacteria and improve biological, chemical and technological stability of the process fluids. Not less important are technological attributes of the process fluids, especially their tribological and anti-adhesion behavior. Main goal of the tribology is to ensure, that the relative motion of two surfaces is happening with the least energy and material loss. Lifespan of the water miscible fluids is one of the main factors defining the fluid quality.*

Keywords: *process fluids (PF), nanoaditives, biological activity, machining, friction.*

1. Introduction

1.1 Machining technology

Machining technology is still a fast developing branch, either the area of machine-tools, or the area of cutting tools and last but not least the area of process media. At the present moment the basic substances are natural and synthetic hydrocarbons, synthetic esters, plant esters, polyglycols or mixtures of these substances and water as a basic additive component. [1 – 3]

A large amount of PF is being used in the manufacturing processes. In case of particle technology PF affect mainly friction on the contact areas between the tool and the work-piece, mechanics of the particles, topography and stabilization of the machined surface. Good process fluid must show anticorrosive attributes, must not create gooey and sticky deposits and must not cause changes on the metal surface. [4 - 7]

1.2 Process fluid from the standpoint of ecology and health

Requirements of the European Union are specifically directed towards greening and abiding of health norms during the work with PF.

Modern PF, meeting with their composition the newest European health, safety and ecological requirements present an important part of the manufacturing process and are one of the basic pre-condition for safe working environment. [8, 9]

Application of the environmentally acceptable PF is one of the basic problems of machining. For specific cases of utilization, it is important to avoid negative effects, for example increased costs, effects on the surface with heat or deformation. PF based on oil usually contain chlorine, phosphorus and sulfur additives. In emulsions, besides basic oils there is a whole range of additional additives, including solutions causing skin problems (e.g. eczema). From the standpoint of ecology and economy, we can therefore assess them as dangerous to the environment and health.

The implementation of any solution into the machining process always comes with increased costs and whole range of additional problems from the standpoint of ecology, hygiene, and also from the technical and technological point of view. In terms of economy there is a high emphasis on efficient ways to use PF. [4, 5, 8]

The effects of PF, direction towards greening and methodology for testing of new ecological PF are an important part of the machining process. Use, maintenance, lifespan and then disposal leads to economic and ecologic problems.

Main trends for greening are:

- dry machining (machining without the fluid);
- decreased number of additional substances;
- alternative substances of ecological type;
- multifunctional oils;

- use of PF with less emissions;
- replacing the emulsions with oils etc.

The development of new technologies and the improvement of PF effects go hand in hand with the effort for greening and decreased costs. The greening and environment protection is primary; therefore it is necessary to delve into this matter and design new strategies and solutions to specific problems.

1.3 The production of PF

At the moment the manufacturers of fluids produce PF so they are the most resistant to bacteria. This is achieved by a balanced ratio of mineral oils, emulsifier, amines, esters, anticorrosion inhibitors etc. and by adding bactericide, with the goal to inhibit the formation of bacteria.

Water miscible PF differentiate into synthetic, partially-synthetic and mineral.

- Synthetic fluids

They don't contain mineral oils, therefore don’t contain emulsifiers necessary to bind oil to water, they are not emulsions but solutions. These solutions are generally less susceptible to bacteria formation.

- Partially-synthetic fluids (emulsions)

Contain from 10 to 50% of mineral oil and emulsifiers. They are moderately susceptible to bacteria formation.

- Mineral fluids (emulsions)

Contain from 50 to 80 % of mineral oils, therefore higher concentration of emulsifiers. They are the most susceptible to bacteria formation.

When using PF (emulsion) a contamination occurs with very negative impact on lifespan and changes in lubrication and cooling attributes. That can strongly affect the functioning of the fluid during machining process and greatly increase financial costs. Therefore it is very important to frequently observe the emulsion and adjust their attributes. The contamination is usually caused in praxis by these basic effects:

- Contamination by fluids (foreign oils),
- Solid particles (dust, particles),
- Biological contamination (bacteria).

The best prevention while using fluids is quality care and clean environment. The basis for longest lifespan of process fluids is to maintain the right concentration of fluids, then removal of foreign oils from the fluid surface, maintaining the cleanliness of fluids, fluid filtration through filtration textile and prevention of fluid contamination by organic contaminants (cigarette butt, apple core, particles of food, etc.). Last but not least we can achieve long lifespan by using the right PF.

2. Fluid lifespan

The PF lifespan is influenced by:

- water quality used for fluid preparation;
- the composition of the mixture;
- contamination during the machining process and fluid maintenance;
- bacterial infection of the fluid etc.

First on the list in lifespan degradation of PF is bacterial infection of the fluid. It is the resistance of the PF against bacterial infection that decides the total lifespan of the fluid.

Bacteria that infect PF are mostly anaerobic, that means they reproduce mostly during the absence of oxygen. The foods for these bacteria are mostly emulsifiers, sulphonates, fatty alcohols, inhibitors of corrosion and other organic additives.

2.1 Biocide additives

The purpose of biocide additives is to protect the fluid itself from a biological attack by bacteria of fungi. Other problem they solve is the protection of an operator from spores and endotoxins, these independently living organisms would create. Biocides itself are usually classified as significantly dangerous additives. Increased ratio of these additives can lead to prolonged PF lifespan, on the other hand increase possibility of allergic reaction in people working with the fluid. . [6, 8, 10]

At the moment nanotechnology is one of the most discussed technologies. Ions of metals are a method, already for some time used, to combat bacteria in the environment.

The other important factor influencing the PF lifespan is the contamination with solid particles during the machining process. Besides the organic contamination in PF, there is a large amount of solid particles created during machining process. Number of these particles in a given fluid depends especially on anti-adhesive and tribological attributes of the PF. Research of the contamination impact must be conducted in laboratory conditions for these reasons:

- identification of the impact of used water on solution attributes;
- keeping precise concentrations of PF solution;
- precise identification of the PF solution contamination by particles;
- observation of PF evaporation during the process;
- precise preparation of solutions for biological and chemical evaluation of the PF contamination impact by various concentrations of solid particles. [8, 9]

3. Mechanism of friction pairs

The development of high-tenacity materials, modernization of measuring methods in the area of material science and long-term experience with the workings of high tech units show, that surface treatment significantly influences their lifespan and reliability. With the growing intensity of machining processes, with increases in cutting speeds, the heat range during machining also increases. Most often analyzed parameters are surface density and hardness. Besides these analyzed parameters the tribological attributes of the new functional surface are also analyzed frequently, then corrosion, fatigue resistance or inclination to broadening of flaws. [3 - 6]

Mechanism of friction is defined as a resistance against relative motion of two bodies in the area of their contact. The friction force F depends on the coefficient of friction μ and the load L [3]. The description of friction and the introduction of this concept dealt with Coulomb (1799). The basic relationship is known as Coulomb's law:

$$\mu = \frac{F_t}{F_p} \qquad (1)$$

F_t - Frictional force acting against the direction of movement;
F_p - Pressing force acting perpendicular to the direction of movement;
μ - Coefficient of friction.

Slippery friction happens when two bodies get into mutual contact and start moving on each other. The size of the contact area increases with the increased load. A joining may happen at the tips; therefore a resistance against relative motion occurs.

In case of slippery friction, it is possible to observe three basic components. Ratio of individual components depends on the type of material pair, conditions for friction (attributes of the material pair, way of the motion, surface roughness, use of lubricant etc.) and a time stage of the relative motion.

- friction by adhesis between surface unevenness;
- friction by striation, caused by fine particles created during the attrition of the surface, which is cause by unevenness of the surface;
- friction caused by deformation or surface unevenness.

4. Experiments

4.1 Chemical composition of process fluids

In the experimental part were evaluated chemical composition used in process fluids with the designation PF 1 and PF 2. It was made a basic measurement how to determinate the chemical composition of process fluid´s concentrates was made by using the static method HS-GS-MS (Head Space-Gas Chromatography-Mass Spectrometry). Process fluid (PF 1) consists mainly of oxygenated organic compounds types of glycols and higher alcohols, which are not part of the process fluid (PF 2). The exception is 4.4 - dimethyl oxazolidine. From a toxicological point of view the PF 1 does not contain substances that have carcinogenic or mutagenic properties. For process fluid PF 1 can be stated that there is no major negative impact on the human body.

Process fluid (PF 2) contains a methylene chloride, which is toxic to the human body. It has demonstrated carcinogenic effects and thus is associated with a number of risks to human health. Dichloromethane is metabolized in the body to produce a carbon monoxide. As a consequence, increases the level of carboxyhemoglobin in the blood and thus reduces the capacity of blood to transfer oxygen to induce respiratory problems, headaches and dizziness. Other hazardous substance is 1.4-dioxane. The process fluid is toxic by inhalation and it is also referred to as a probable carcinogen. Formamide, trimethylsilanol and octametyhcyclotetrasiloxan belongs to the group of substances which have a toxic effect on reproduction.

4.2 Using natural fillers in the form of nanoparticles

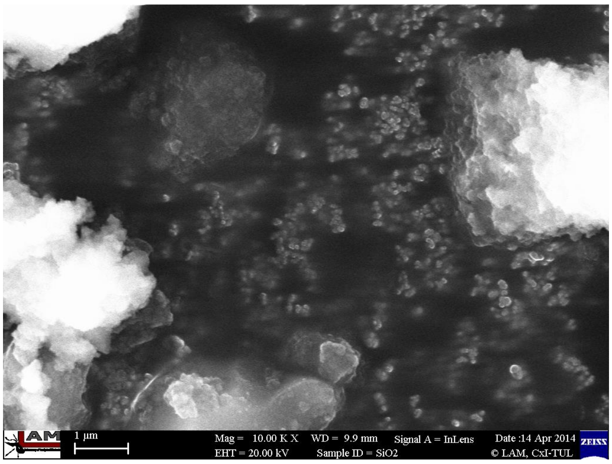

Figure 1 Nanoparticle SiO_2

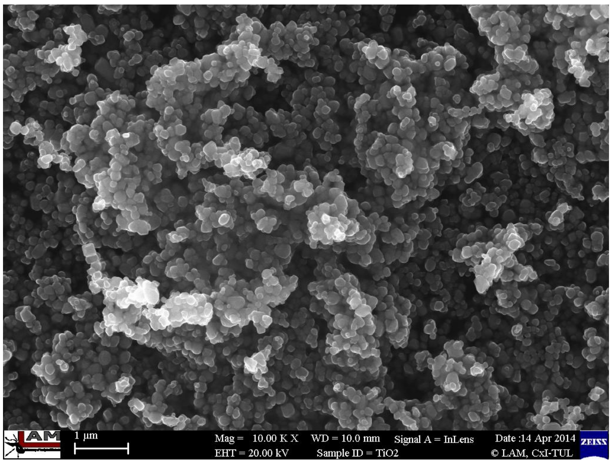

Figure 2 Nanoparticle TiO_2

The use of natural fillers in a form of nanoparticles has a high efficiency due to their high chemical and biological activity. The use of nanoparticles is probably the way to dispose of bacteria and improve a biological, chemical and technological stability of the fluids. [11, 12]

Suitable alternative for development of antimicrobial solutions is to synthetized metal nanoparticles, the biocide attributes (especially nanoparticles based on silver). Nanoparticles with dimensions smaller than 100nm have larger surface area so they can interact easier and in higher rate with the biological material.

Nanoparticles SiO_2 and TiO_2 (Figure 1 and Figure 2) were added to the process fluids and subsequently were carried out tribological tests and evaluations of the technological and biological stability of processes.

4.2 Evaluation of tribological tests

Tribology evaluates attributes that influence interaction of surfaces, environment and the body during their relative motion. It includes processes of influence on the line between solid, fluid and gaseous state of units. The main goal of tribology is to ensure the relative motion of two surfaces happens with the least energy and material loss. Tribological attributes describe most of all the coefficient of friction and wear. [3 - 6] During the research of friction mechanism and effects we look at the system comprised of two units and their contact areas and a substance, which is between contact areas and close environment, as a tribological system.

The basis of tribological measurements is testing method “ball-on-disc”. The measurement involves the injection of fixed attachments of the test piece (“ball”) in the form of balls of the chosen material 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.

The coefficient of friction was determined using tribometer CETR UMI Multi-Specimen Test System (Figure 3) and groove of the tribological test was evaluated by mechanical profilometer Dektak – XT (Figure 4) from the BRUKER company.

Figure 3 CETR UMI Multi-Specimen Test System

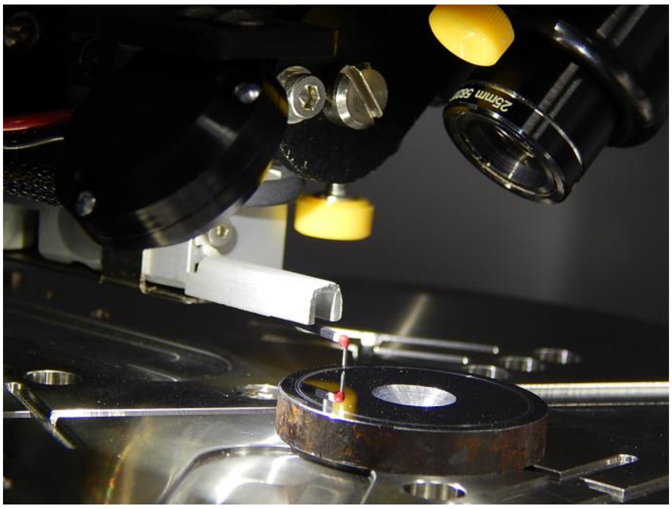

Figure 4 Mechanical profilometer Dektak – XT

Tribological testing (EN1071-13:2010) was conducted by using a ball made from Si_3N_4 with a diameter of 6.350 mm, with a constant load of 10 N at room temperature. The material of disc was steel 16MnCr5 - EN 10084-94, EN 84-70 with a polished surface with roughness of Ra 0.01μm. The radius of the circle along which the moving unit was 13 mm and measuring the coefficient of friction was carried out by using a 5% solution of process fluids with a volume of 100 ml.

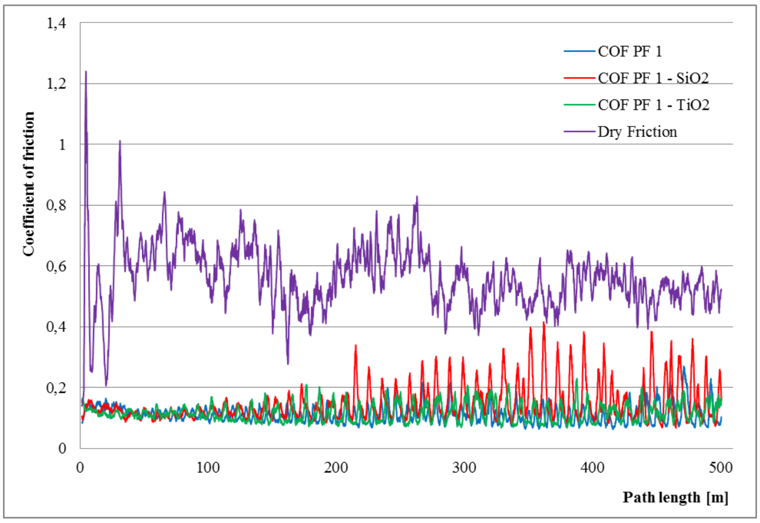

Figure 5 Coefficient of friction PF 1

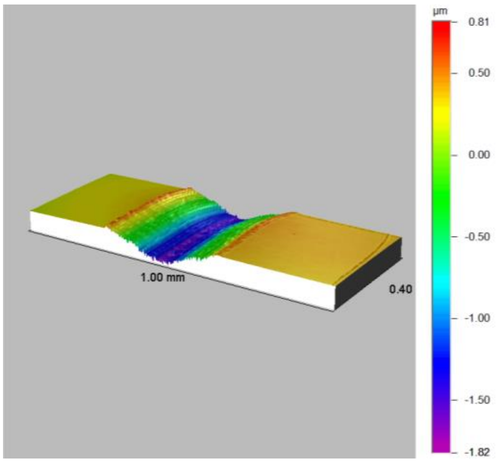

Figure 6 3D profile PF 1 after tribology

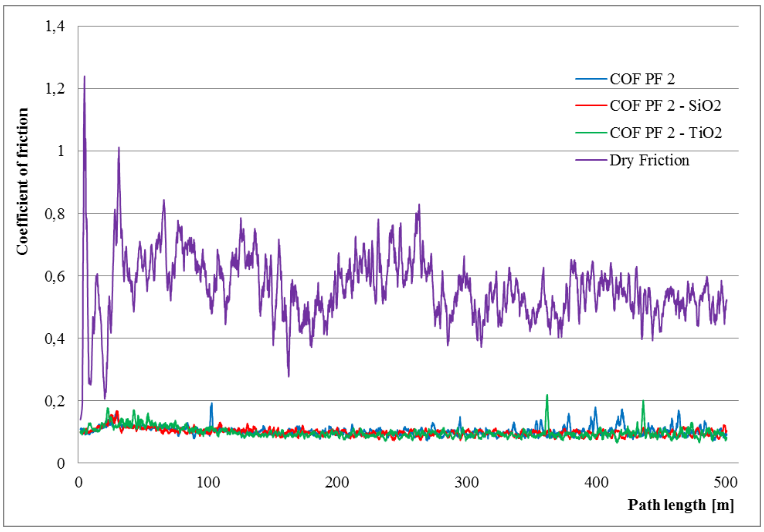

Figure 7 Coefficient of friction PF 2

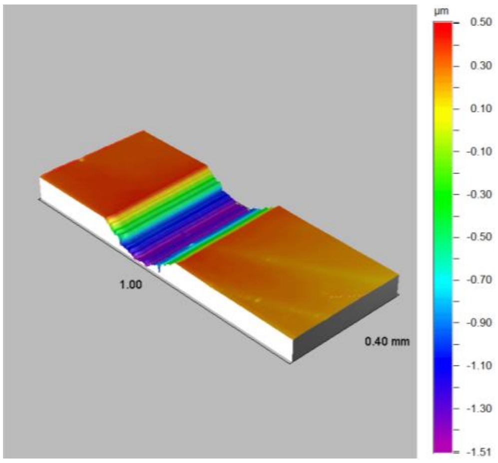

Figure 8 3D profile PF 2 after tribology

4.3 Evaluation of biological tests

4.3.1 Assessment respiratory activity of bacterial populations

Assessment respiratory activity of bacterial populations was implemented on the device Columbus Instruments Micro-Oxymax Data, Sampling time: 6 minutes; Gas Units: *mg*.

Methodology, preparation and assessment samples:

To test the metabolic activity of the bacterial population was used a respirometry method (evaluation O_2, CO_2, CH_4). Samples were prepared in accordance with the standard DIN EN ISO 9408 (Water quality). To the reagent bottles (100 ml) were dosed 20 ml of the sample. In these intervals was measured a gas concentration. During the five days of measurement was no significant evaporation of the sample.

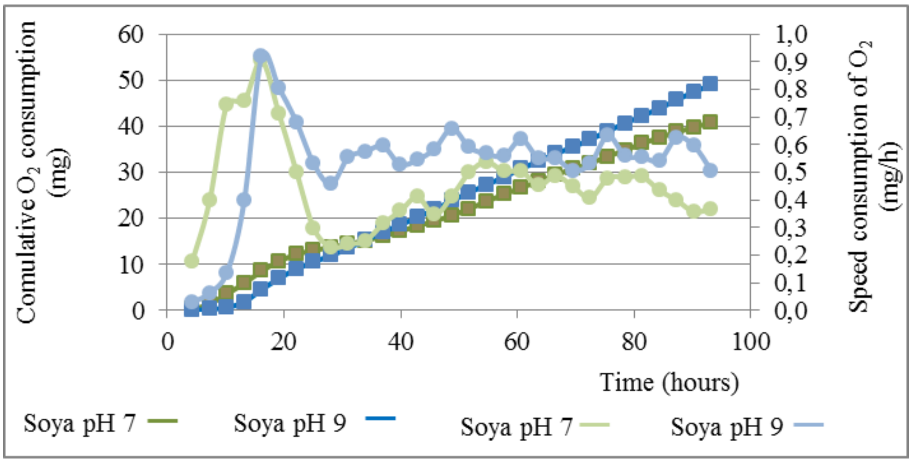

Figure 9 Control measurements

Control measurements of respiration *E. Coli* to soy broth carried out by assumption. In the course of about 90 hours was consumed about 45 mg O_2, the average rate of oxygen consumption is under "normal conditions" in the control measuring 0.5 mg O_2/hour.

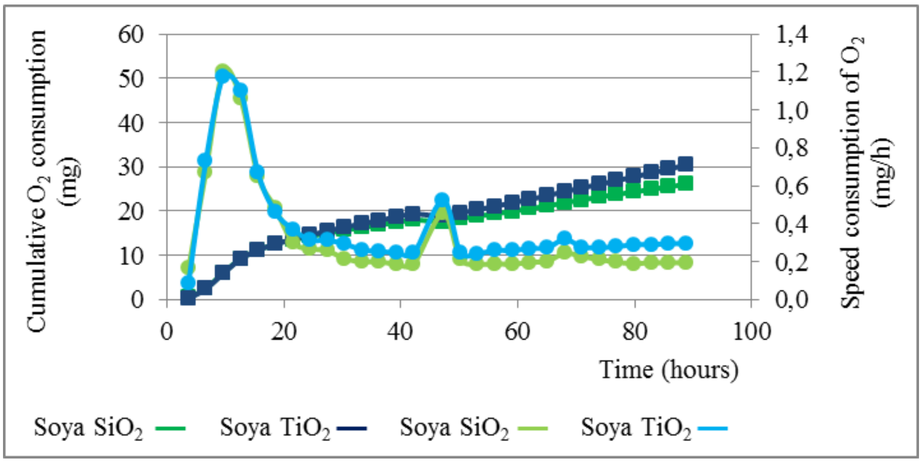

Figure 10 Measurement clean fillers

When measuring the net filler (pure nanoparticles placed in a soy broth) was to determine the toxicity of nanoparticles themselves to a bacterial strain of *E. Coli*. The bacteria grew in all samples (samples SiO_2 and TiO_2 were very balanced). In the course of about 90 hours were consumed about 26 and 30.5 mg O_2 (samples gradually SiO_2, TiO_2). The average rate of oxygen consumption during measurement of nanoparticles is successively 0.29 and 0.34 mg O_2/hour. The results show that for samples SiO_2 and TiO_2 bacterial respiratory activity was inhibited by about 40%.

4.3.2 Measurement of process fluids with a modified pH 7

A modified process fluids with a pH 7 showed significantly higher respiratory activity than the process fluid with the initial pH 9 (higher values of respiration correspond to significant contamination with bacteria). During machining there is a reduction of pH (the lower value) and respiratory activity of the cells will grow. The bacterial strain E. coli with the process fluid will multiply exponentially and process fluid may lose the desired properties.

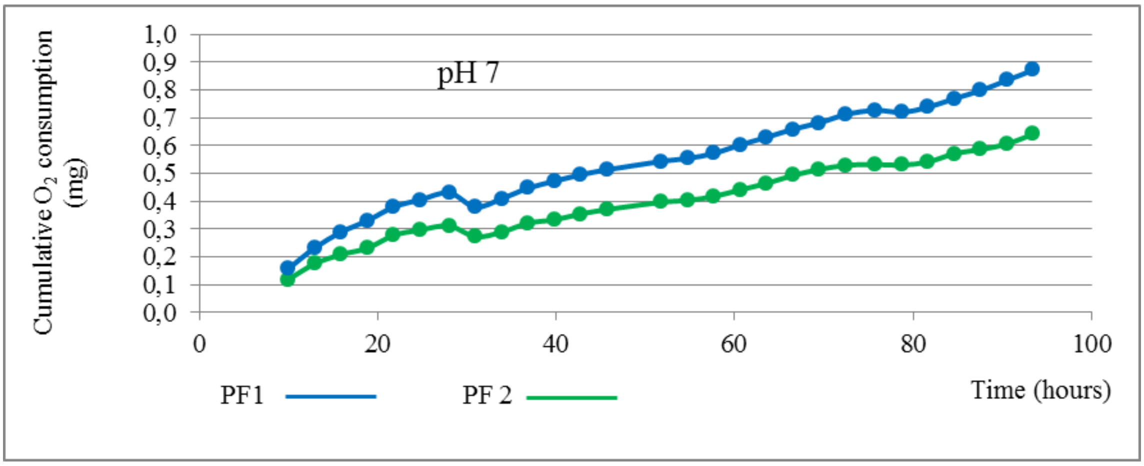

Figure 11 Process fluids with a modified pH 7

When measuring the respiratory activity is the process fluid (PF 2) suitable for pH 7 and least suitable for other applications is PF 1. However, the difference between all the observed samples was almost within the measurement error.

When measuring the respiratory activity is the process fluid (PF 1) suitable for pH 9 and least suitable for other applications is PF 2.

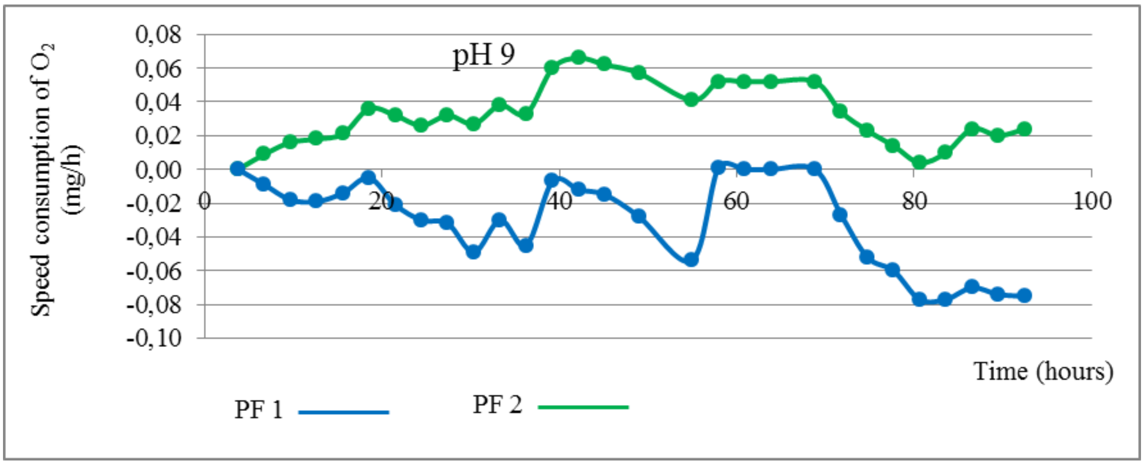

Figure 12 Process fluids with untreated pH 9

In the course of 90 hours was consumed about 0.7 mg O_2 (value for each process fluids does not much differ). The average rate of oxygen consumption is approximately 0.0078 mg O_2/hour (by approximately 98% lower relative to a control measurement).

5. Conclusion

By comparing the chemical composition of process fluids can be concluded that liquid PF 1 does not contain substances that have a major impact on human health or the environment. Process liquid PF 2 contains substances that have carcinogenic effects on the human body and ingested or enters airways can lead to a person's death.

Biological tests show that the measurement of pure filler (pure nanoparticles placed in a soy broth) was the strain of *E. Coli* showed no significant effect of the nanoparticles (no toxicity, inhibition or increased mortality). For samples of SiO_2 and TiO_2 bacterial respiratory activity was inhibited by about 40%.

Bacteria are not able to adapt to the environment of process liquids in the composition, although the pH of the sample is reduced to pH 7 Process fluid adjusted at pH 7 showed a slightly higher activity than the respiratory process fluid with the initial pH 9.

Tribological tests (Figure 5 and Figure 7) shows that addition of nanoparticles SiO_2 and TiO_2 have a negative effect on the friction coefficient during the tribological process. For PF 1 was no change of coefficient of friction by using a 5% solution with the addition of TiO_2 nanoaditive. For liquid PF 2 value of the coefficient of friction by using a 5% solution by adding nanoaditive ofp SiO_2, closer to the ground state. Process liquid PF 2 has better friction characteristics, but contains substances that have an adverse effect on the human body.

Manufacturing process liquids must be in compliance with the requirements of the European Union that are specifically directed towards ecological and compliance with health standards at work with process fluids.

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