

Marian W. SUŁEK*, **Marian SZCZEREK****, **Jacek PRZEPIÓRKA*****

PHYSICOCHEMICAL AND TRIBOLOGICAL PROPERTIES OF AQUEOUS SOLUTIONS OF HYDROLYSATE AND HYDROLYSATE WITH SURFACTANTS AS POTENTIAL LUBRICANT BASES

WŁAŚCIWOŚCI FIZYKOCHEMICZNE I TRIBOLOGICZNE WODNYCH ROZTWORÓW HYDROLIZATU JAKO POTENCJALNYCH BAZ SUBSTANCJI SMAROWYCH

Key words: ecological lubricants, water solutions, hydrolysates, surfactants, tribological and physicochemical properties.

Abstract: The study aimed to confirm the hypothesis that aqueous solutions of polymers with surfactants meet the criteria of ecological lubricant bases. An oat hydrolysate was used as the macromolecular substance, and the surfactants were successively: sodium dodecyl sulphate (SDS), Sodium Lauryl Ether Sulfate (SLES), Sodium Lauroyl Sarcosinate (SLS). The research was carried out for two-component solutions (water, hydrolysate) and three-component solutions (water, hydrolysate, surfactant).

In order to document this thesis, tribological tests were performed with a constant and increasing load as a function of time. Stationary tests with loads of 2, 3, and 4 kN confirmed the predictions that active substances in two- and three-component solutions create a lubricating film that transfers high loads with relatively low motion and wear resistance. The stability and durability of the lubricating film were confirmed under the conditions of increasing load at a speed of 409 N/s. An approximately 12-fold increase in the seizing load for the hydrolysate solutions in relation to water was found, and the maximum load value for the T02 tester (7200 N) was achieved. The durability of the lubricating film was mainly determined by the adsorption of the hydrolysate, which was confirmed by physicochemical tests.

Słowa kluczowe: ekologiczne substancje smarowe, wodne roztwory, hydrolizaty, surfaktanty, właściwości tribologiczne i fizykochemiczne.

Streszczenie: Celem pracy było potwierdzenie hipotezy, że wodne roztwory polimerów z surfaktantami spełniają kryteria ekologicznych baz substancji smarowych. Jako substancję wielkocząsteczkową zastosowano hydrolizat owsa, a surfaktantami były kolejno: sodium dodecyl sulfate (SDS), Sodium Lauryl Ether Sulfate (SLES), Sodium Lauroyl Sarcosinate (SLS). Badania przeprowadzono dla roztworów dwuskładnikowych (woda, hydrolizat) oraz trójskładnikowych (woda, hydrolizat, surfaktant).

Aby udokumentować tę tezę wykonano badania tribologiczne przy stałym i wzrastającym w funkcji czasu obciążeniu. Testy stacjonarne przy obciążeniach 2, 3, 4 kN potwierdziły przewidywania, że substancje aktywne w roztworach dwu- i trójskładnikowych tworzą film smarowy, który przenosi wysokie obciążenia przy relatywnie niskich oporach ruchu i zużycia. Stabilność i trwałość filmu smarowego została potwierdzona w warunkach wzrostu obciążenia z szybkością 409 N/s. Stwierdzono około 12-krotny wzrost obciążenia zacierającego dla roztworów hydrolizatu względem wody oraz osiągniętą maksymalną dla testera T02 wartości obciążenia (7200 N). O trwałości filmu smarowego zdecydowała głównie adsorpcja hydrolizatu, co zostało potwierdzone badaniami fizykochemicznymi.

* ORCID: 0000-0001-7114-8238. Cardinal Stefan Wyszyński University in Warsaw, Dewajtis 5 Street, 01-815 Warszawa, Poland.

** ORCID: 0000-0002-1049-7853. Łukasiewicz Research Network – Institute for Sustainable Technologies, Pułaskiego 6/10 Street, 26-600 Radom, Poland.

*** ORCID: 0000-0001-8984-7002. Kazimierz Pułaski University of Technology and Humanities in Radom, Chrobrego 27 Street, 26-600 Radom, Poland.

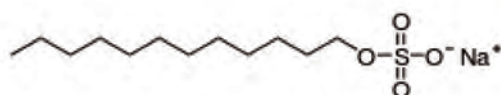
INTRODUCTION

Due to the safety of the natural environment and human health at the workplace, lubricant bases based on raw petroleum materials are limited. In the last century, we started researching new types of lubricant bases based on water solutions of surface active compounds.

The published papers postulated the use of aqueous solutions of surface-active compounds as components of ecological lubricants [L. 1–10]. These pioneering works continued in many scientific and research centres in the field of tribology [L. 18–25]. The results of the laboratory tests carried out allowed us to verify the hypotheses of the mechanisms of action of surfactants under friction conditions. On the other hand, bench and workplace tests confirmed the possibility of their practical applications, mainly as hydraulic and processing fluids [L. 11–17].

The research conducted so far has mainly involved two-component solutions: water and surfactant. This article proposes the study of three-component systems: water, polymer, and surfactant. Hydrolysed oat is the macromolecular component, and the surfactants are three anionic surfactants. Hydrolysate is obtained from renewable raw materials, and its use as a component of cosmetics and food products guarantees its safe use as a component of lubricants. Additionally, the hydrolysate reduces the irritating potential of anionic surfactants present in aqueous solutions. Aqueous solutions of the hydrolysate and hydrolysate with anionic surfactants can be treated as ecological lubricant bases, which do not endanger the environment, even when in direct contact with water or soil. This may take place under operating conditions of the equipment with open friction knots or in the event of equipment failure. In contact with human skin, they do not irritate it, even when the solutions used contain anionic surfactants.

Sodium dodecyl sulfate (SDS)



Rokita's SDS is available under the trade name Rosulfan L.

Research on the application of hydrolysate solutions as ecological lubricants has not been presented in the literature so far. For these reasons, it was necessary to perform comprehensive physicochemical and tribological tests. The results of physicochemical tests indicate a high surface activity of the hydrolysate from two-component solutions. This activity increases when one of the three anionic surfactants (three-component solutions) is added to the hydrolysate solution. Based on the measurements of surface tension and wettability, the high adsorption capacity of solution components on the surface of solids can be predicted. Under frictional conditions, the surface phase can transform into a lubricating film.

Interesting results and correlation between the composition of solutions and the measured physicochemical and tribological characteristics should be expected. The research results can also be expected to stimulate the practical application of these solutions as ecological lubricant bases.

TEST MATERIALS AND METHODS

Aqueous solutions of hydrolysate and hydrolysate with surfactants as model lubricant bases

Components of solutions

The proposed surfactants: sodium dodecyl sulfate (SDS), Sodium Lauryl Ether Sulfate (SLES), and Sodium Lauroyl Sarcosinate (SLS), were the subject of our research, and their characteristics were presented in the literature [L. 5–7, 10]. This article provides information on these compounds, and the hydrolysates are described in more detail.

Anionic surfactants

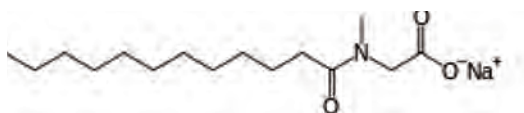
Anionic surfactants are amphiphilic compounds dissociate into an anion and a counterion (sodium cation) in aqueous solutions.

Sodium Lauryl Ether Sulfate (SLES)



Rokita's SLES is traded as Sulforokanol L 370.

Sodium Lauroyl Sarcosinate (SLS)



Schulke's SLS is traded under the trade name Perlasthan L30.

Hydrolysed Oat Protein

As a result of chemical or enzymatic catalysis of proteins, smaller fragments are formed – peptides and amino acids. These products are given to various processes, including drying to obtain a powdered product. They have numerous applications, especially in the food and cosmetics industries, and no side effects have been reported with these applications. For these reasons, they can be treated as safe components of ecological lubricants.

The oat saccharide hydrolysate produced by Croda was used for the tests. They are known as INCI – Hydrolysed Oats. It is a mixture of, among other proteins, amino acids. The commercial product is in the form of a white powder with the trade name Cromoist™ OSD (Croda). It is used in cosmetic products (creams, lotions, conditioners and shampoos). It is compatible with anionic surfactants and reduces their irritating potential. It is a hygroscopic, hydrophilic and water-soluble substance. It does not create foam, and even in solutions with surfactants, it reduces the durability of the created foam (it quenches the foam). The average molecular weight of the hydrolysed oats is 1000 Da. Thus, its molecules are definitely larger than the surfactants used.

An aqueous solution under the trade name Cromoist™025 was used for the tests. The concentration of active compounds (oat proteins, oligosaccharides) is 25%. The initial criterion for using hydrolysates as active ingredients of lubricants was the safety of use, confirmed by using hydrolysates as ingredients in cosmetics and food products, and the formation of a permanent occlusive layer on the surfaces of solids through effective interaction with the surface of solids. It

can be predicted that this layer will transform into a lubricating film. The subjects of the presented research were the remaining physicochemical and tribological properties required for assessing lubricating properties.

Composition of model lubricants

Water is the basic component of the aqueous solutions of the hydrolysate and hydrolysate with individual surfactants (SDS, SLS, SLES). Its percentage ranges from approx. 95 to practically 100%. Distilled water was used for the tests. The tests used a hydrolysate product of the Croda company and under the trade name Cromoist™ 025, which is a 25% aqueous hydrolysate solution. Its concentration in the solution is 1%. Thus, the concentration of the hydrolysate in aqueous solutions is 0.25%. Individual surfactants are added to the aqueous solutions of the hydrolysate: sodium dodecyl sulfate (SDS), Sodium Lauryl Ether Sulfate (SLES), Sodium Lauroyl Sarcosinate (SLS), so that their final concentrations are respectively: 10-3, 10-2, 10-1 1, 2, 3, 4, 5%. The solutions were made by weight. 0.1% of SDS and SLES hydrolysate solutions were unstable. Physicochemical and tribological measurements were not performed for these concentrations.

The results of the physicochemical and biological tests are presented in **Figs. 1–10**. The following designations of water and solutions were adopted:

- Water – **H₂O**,
- an aqueous solution of the hydrolysate (two-component solution) – **HO**,
- an aqueous solution of the hydrolysate with a surfactant (three-component solution) – **HO SUR**,
- aqueous solutions of hydrolysate with sodium dodecyl sulfate (SDS) (three-component solutions) **HO SDS**,
- aqueous solutions of the hydrolysate with Sodium Lauryl Ether Sulfate (SLES) (three-component solutions) **HO SLES**,
- an aqueous hydrolysate solution from Sodium Lauroyl Sarcosinate (SLS) (ternary solutions) **HO SLS**.

Apparatus and research methods

Physicochemical tests

The aqueous solutions of the hydrolysate and the hydrolysate with surfactants (SDS, SLS

and SLS) were characterised by the results of stability, surface tension, wettability, viscosity and foam formation tests. These methods have been described in the literature and our publications. Therefore, signalling information will be presented. The results of physicochemical measurements are presented in **Figs. 1–4**. They are arithmetic means from three independent measurements.

Stability

The solutions were visually inspected, which consisted in observing the changes in colour and clarity of solutions stored alternately in reduced (5°C) and increased (60°C) and subjected to centrifuge tests. The SDS and SLS hydrolysate solutions were unstable at 0.1% concentration. The remaining solutions were stable, and the remaining physicochemical tests were performed on them at the temperature of 20°C.

Surface tension (σ)

The measurements were made with the peel-off method on the Lauda TD1C apparatus, and the results are shown in **Fig. 1**.

Contact angle (Θ)

The wettability of the steel surfaces (52100 steel) was determined by measuring the contact angle with the solutions with a camera and a microscope. They were coupled with a computer equipped with a data processing system. The results are shown in **Fig. 2**.

Kinematic viscosity (ν)

The procedure was based on the PN-81/c-04011 standard, and the measurements were made using an Ubbelode capillary viscometer. The results are shown in **Fig. 3**.

Foaming

Measurements of the solutions to foam formation were performed with the modified Ross Miles method (PN ISO 696: 1994 P). The foaming capacity and durability of the foam were determined (**Fig. 4**).

Tribological investigations

The tribological tests were carried out using a four-ball apparatus (Tester T02) manufactured at the Institute of Łukasiewicz Research Network – Institute of Sustainable Technologies in Radom (PN – 76/C – 04147) [**L. 26**]. Two

types of tests were performed: with constant and linearly increasing load. The results presented in **Figs. 5–10** are arithmetic means from three independent measurements.

Constant load test

Tribological tests were carried out for three different loads: 2, 3, and 4 kN. At a constant speed of 200 rpm, the test duration was 900 seconds. Wear and resistance to motion were determined for each of the three different loads. The measure of wear was the diameter of the wear marks measured after the end of the test and expressed in millimetres (d) (POLAR reflection microscope – PZO Warszawa). The measure of the resistance to motion was the coefficient of friction (μ) determined based on the measured moment of friction forces (MT). The results are shown in **Fig. 5**.

Tests with a linearly increasing load (friction tests)

The seizure tests were carried out with a linearly increasing load with a speed of 409 N/s, a load range from 0 to 7.2 kN and a spindle speed of 500 rpm.

The following values were determined:

- seizing load (P_{\downarrow}) – pressure above which the boundary layer is broken, resulting in a rapid increase in the moment of frictional forces,
- seizure load (P_{oz}) – load at which the moment of friction forces exceeded the value of $10 \text{ N} \cdot \text{m}$,
- limit seizure load (p_{oz}), which was calculated from the following relationship:

$$p_{oz} = 0,52 \frac{P_{oz}}{d^2} \quad (1)$$

Moreover, measurements of the ball wear trace were carried out in the direction parallel and perpendicular to the direction of friction. The mean of these two measurements was the dose value. A Polar reflection microscope, produced by PZO-Warsaw (Poland), was used.

EXPERIMENTAL RESULTS

Physicochemical properties of aqueous solutions of hydrolysate and hydrolysate with surfactants

The physicochemical properties of aqueous solutions of the and hydrolysate with one of the three anionic surfactants (SDS, SLES and SLS) were characterised by: stability, surface tension, wettability, foam formation, density and reaction).

Stability

The stability was confirmed by the temperature tests and the centrifugal test (centrifugal force) as described in Chap. 2.2. Only 0.1% of SDS and SLS solutions were unstable. Research is ongoing to clarify these anomalies. Physicochemical and tribological tests were performed only for stable solutions.

Surface tension (σ)

The surface tension is a measure of the surface activity of solution components. The measurement methodology is described in Chapter 2.2. Measurements of σ values were performed for water (σ_{H_2O}), 0.25% aqueous hydrolysate (σ_{HO}) and aqueous hydrolysate solutions (0.25%) with individual surfactants (SDS, SLES, SLS) (σ_{HOSUR}) for concentrations: 0.001, 0.01, 0.1, 1, 2, 3, 4, 5% (only for stable solutions) and the results are shown in **Fig. 1**.

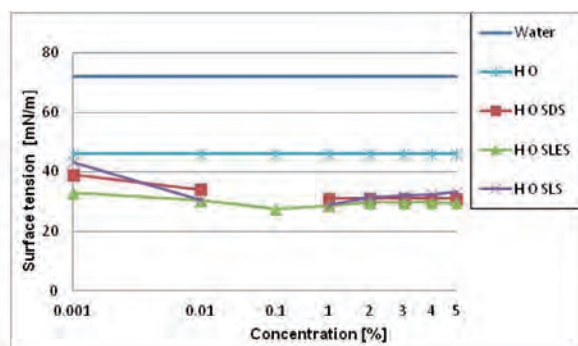


Fig. 1. Dependence of surface tension as a function of surfactant (SDS, SLES, SLS) concentration in aqueous solutions: surfactant and hydrolysed oats. $\sigma_{H_2O} = 72$ mN/m, $\sigma_{HO} = 46$ mN/m

Rys. 1. Zależność napięcia powierzchniowego w funkcji stężenia surfaktantów (SDS, SLES, SLS) w wodnych roztworach surfaktantów i hydrolyzatu owsa. $\sigma_{H_2O} = 72$ mN/m, $\sigma_{HO} = 46$ mN/m

The value of σ for water and 0.25% of the aqueous solution of the hydrolysate were 72 mN/m and 46 mN/m, respectively. As a result of introducing the hydrolysate into the water, a significant decrease in the surface tension value by approx. 36% was found. It indicates the high adsorption capacity of the hydrolysate molecules on the surface of the solid, which results in the possibility of creating an adsorption layer. Introducing any surfactant to the aqueous hydrolysate solution causes a further decrease in the value of σ from the lowest concentrations of these compounds (0.001%). The greatest decrease in the surface tension of the hydrolysate

solutions with surfactants is observed at the lowest concentration (0.001%) for the solution with: SDS – 7 mN/m, SLES – 13 mN/m, SLS – 3 mN/m. For higher surfactant concentrations ($C > 1\%$), the values of σ are comparable within the error limits and assume the values for the following solutions: SDS – approx. 31 mN/m, SLS – <28, 29> mN/m, SLES – <29.34> mN/m.

When summarising, it can be stated that surfactant solutions with a concentration of 0.001% are the most effective in reducing surface tension. After exceeding this concentration, the stabilisation of the σ value is observed, possibly a slight increase within the experimental error. The lowest values of surface tension were measured for SLES hydrolysate solutions. For a concentration of 0.001%, the decrease in surface tension in relation to the SDS and SLS solution is, respectively, about two and more than four higher. These results can be interpreted based on the existence of ethylene oxide groups in the SLES molecule capable of forming hydrogen bonds with the hydrolysis products.

Both the solutions of the hydrolysate and the hydrolysate with surfactants achieve low values of surface tension, which proves the high activity of the components of the solutions.

Wettability

The measure of wettability is the contact angle (Θ). A decrease in contact angle corresponds to an increase in wettability; conversely, an increase in contact angle corresponds to a decrease in wettability. The relationship between the contact angle and the concentration of surfactants is shown in **Fig. 2**.

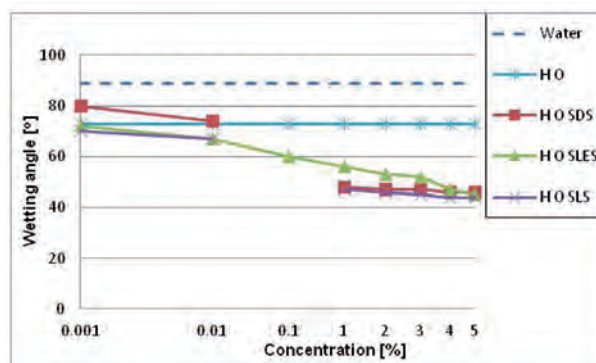


Fig. 2. Dependence of wetting angle as a function of surfactant (SDS, SLES, SLS) concentration in aqueous solutions: surfactant and Hydrolysed oats. $\Theta_{H_2O} = 89^\circ$, $\Theta_{HO} = 73^\circ$

Rys. 2. Zależność kąta zwilżania w funkcji stężenia surfaktantów (SDS, SLES, SLS) w wodnych roztworach surfaktantów i hydrolyzatu owsa. $\Theta_{H_2O} = 89^\circ$, $\Theta_{HO} = 73^\circ$

The contact angle of 52100 steel with distilled water is 89° and 0.25% with 73° hydrolysate solution. Thus, a significant drop in value (approx. 18%) after the introduction of the hydrolysate is observed. Quantitative changes in surface tension and wettability as a function of surfactant concentration are different. A relatively large decrease in the value of σ , already at a concentration of 0.001%, is not observed in the case of changes in the contact angle. For the lowest concentration of 0.001% surfactant, the value of Θ increases for SDS and SLS solutions to 80° and 77° , respectively, and for SLES solutions, it drops by 1° . Therefore, at the lowest concentrations, the solutions of these surfactants show comparable or lower wettability compared to 0.25% aqueous solutions the hydrolysate. Definitely, lower values are observed for concentrations of $\geq 1\%$ so that at the highest concentration (5%), comparable values of Θ from the range $\langle 44^\circ, 46^\circ \rangle$ for all tested solutions are obtained. On average, SLES solutions show the highest wettability.

Based on the obtained results, it can be concluded that the tested solutions moisten the steel surface well, especially when, in addition to the hydrolysate, there is a surfactant in them.

Kinematic viscosity (ν)

The determined value of the water viscosity is $0.91 \text{ mm}^2/\text{s}$, and a hydrolysate solution is $0.97 \text{ mm}^2/\text{s}$. An increase in surfactant concentration causes a monotonic increase in viscosity. The highest concentration (5%) amounts to a few per cent (Fig. 3).

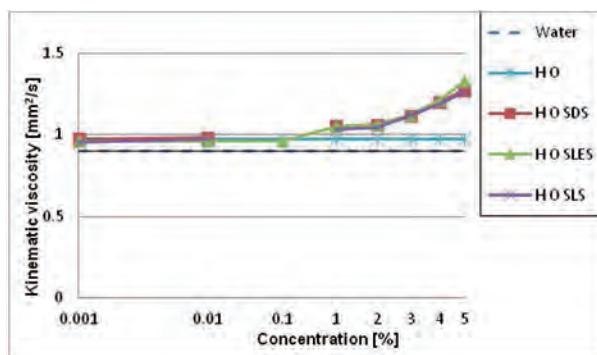


Fig. 3. Dependence of kinematic viscosity as a function of surfactant (SDS, SLES, SLS) concentration in aqueous solutions: surfactant and Hydrolysed oats. $\nu_{\text{H}_2\text{O}} = 0.91 \text{ mm}^2/\text{s}$, $\nu_{\text{HO}} = 0.97 \text{ mm}^2/\text{s}$

Rys. 3. Zależność lepkości kinematycznej w funkcji stężenia surfaktantów (SDS, SLES, SLS) w roztworach wodnych: surfaktantów i hydrolyzatu owsa. $\nu_{\text{H}_2\text{O}} = 0,91 \text{ mm}^2/\text{s}$, $\nu_{\text{HO}} = 0,97 \text{ mm}^2/\text{s}$

These changes can be attributed to the interaction of surfactants with the hydrolysate and the formation of aggregates with larger spatial dimensions.

Foaming (V_0, V_{10})

The measurement method is presented in Chap. 2.2 and the results in Fig. 4.

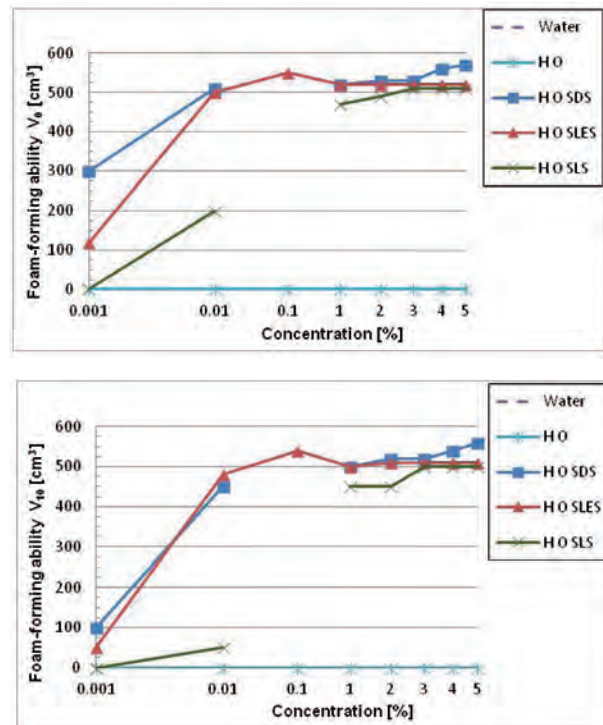


Fig. 4. Dependence of foam formation as a function of surfactant (SDS, SLES, SLS) concentration in aqueous solutions: surfactant and Hydrolysed oats. $V_{0, \text{HO}} = 0$, $V_{10, \text{HO}} = 0$

Rys. 4. Zależność powstawania piany w funkcji stężenia surfaktantów (SDS, SLES, SLS) w wodnych roztworach surfaktantów i hydrolyzatu owsa. $V_{0, \text{HO}} = 0$, $V_{10, \text{HO}} = 0$

The foam volume for the hydrolysate solution, both immediately after measurement (V_0) and after 10 minutes (V_{10}), is equal to zero. This is important because these solutions, when used as lubricants, do not require the use of foam inhibitors. The introduction of surfactants into aqueous solutions of the hydrolysate causes an increase in the volume of V_0 and V_{10} to about 500 cm^3 . Thus, unexpectedly high values of V_{10} in relation to V_0 are observed, indicating the foam's relatively high durability. Therefore, the aqueous solutions of the hydrolysate with surfactants require the use of foam inhibitors until reaching the value of 300 cm^3 immediately after generating the foam and 50 cm^3 after 10 minutes from generating the foam.

Density

The density of 0.25% of the hydrolysate solutions was 1 g/cm^3 and was comparable to that of water. After adding surfactants, the density increased by about 6% and was practically independent of the concentration and type of surfactants. These results indicate an increase in packing, practically independent of the surfactant's type and concentration.

Reaction

The pH of the water was 6.8, and the aqueous solution of the hydrolysate was 5.0. The introduction of surfactants to the hydrolysate solutions caused an increase in pH from 6.2 (0.001%) to 8.1 (5%) for SDS solutions and from 5.2 (0.001%) to 8.2 (5%) for SLS. On the other hand, for the hydrolysate solutions with SLES, the pH decreased from 5.2 (0.001%) to 4.8 (5%). The increase in pH for the surfactant solutions with the hydrolysate compared to the hydrolysate solution is related to the anionic nature of the surfactant. The different trend of changes for SLES solutions results from the neutralising effect of ether groups in the molecule of this compound.

Tribological properties of model lubricants

Constant load tests (2, 3, 4 kN)

At constant loads (2, 3, 4 kN), the coefficients of friction (μ) were measured, and after the completion of the tests, the diameter of the wear marks (d). The results are shown in Figs. 5 and 6, and they are arithmetic means from 3 independent measurements.

Coefficient of friction (μ)

The results of the measurements of the friction coefficients at constant loads are shown in Fig. 5.

At the load of 2 kN, the value of μ for water was 0.47. At higher loads, the system seizes. No seizure was observed for the 0.25% hydrolysate solution, and the friction coefficients at successive loads were 0.21 (2 kN), 0.19 (3 kN) and 0.18 (4 kN). In terms of errors, they are comparable with the observed slight downward trend. These results indicate the ability of the hydrolysate to create a durable lubricating film that does not deteriorate even under a load of 4 kN. For aqueous solutions of the hydrolysate with individual surfactants, a decrease in the value of μ is observed for the lower concentrations of surfactant, and for $c \geq 1\%$,

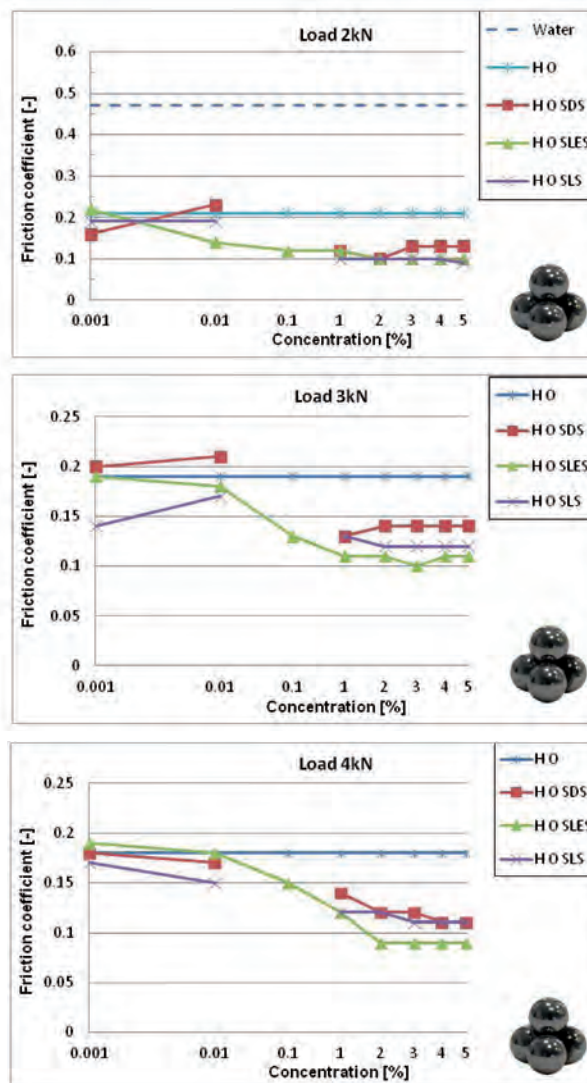


Fig. 5. Dependence of friction coefficient as a function of surfactant (SDS, SLES, SLS) concentration in aqueous solutions: surfactant and Hydrolysed oats. $\mu_{\text{H}_2\text{O}, 2\text{KN}} = 0.47$, $\mu_{\text{H}_2\text{O}, 3\text{KN}} - \text{seizes}$, $\mu_{\text{H}_2\text{O}, 4\text{KN}} - \text{seizes}$, $\mu_{\text{HO}, 2\text{KN}} = 0.21$, $\mu_{\text{HO}, 3\text{KN}} = 0.18$, $\mu_{\text{HO}, 4\text{KN}} = 0.18$

Rys. 5. Zależność współczynnika tarcia w funkcji stężenia surfaktantów (SDS, SLES, SLS) w wodnych roztworach surfaktantów i hydrolyzatu owsa. $\mu_{\text{H}_2\text{O}, 2\text{KN}} = 0,47$, $\mu_{\text{H}_2\text{O}, 3\text{KN}} - \text{zatarcie}$, $\mu_{\text{H}_2\text{O}, 4\text{KN}} - \text{zatarcie}$, $\mu_{\text{HO}, 2\text{KN}} = 0,21$, $\mu_{\text{HO}, 3\text{KN}} = 0,18$, $\mu_{\text{HO}, 4\text{KN}} = 0,18$

the values of μ are comparable for a given load. From the analysis of the results, 1% surfactant concentration can be assumed as optimal due to the achievement of practically the lowest values of the friction coefficients.

Resistances to motion for three-component solutions for specific surfactant concentrations are comparable, which is especially visible for $c \geq 1\%$. However, solutions with different surfactants differ in friction coefficient values. The highest μ values

are taken by solutions with SDS, then by SLS, and the lowest by SLES. These differences, however, are slight, especially for $c \geq 1\%$.

Wear

The measure of wear is the measured diameter of the wear marks (d). The measurement results are presented in Fig. 6. The individual points are the arithmetic mean of three independent measurements.

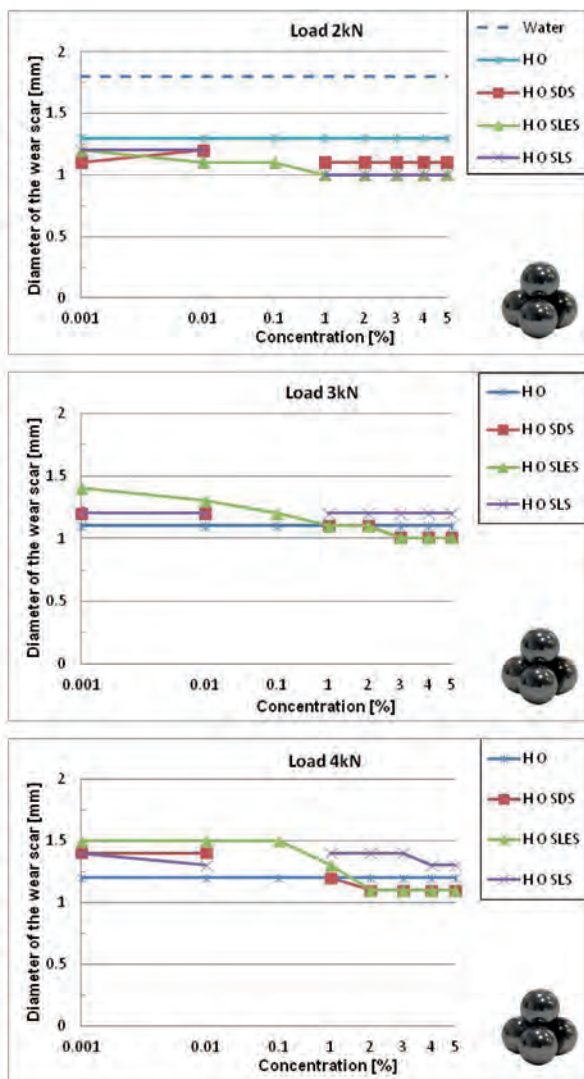


Fig. 6. Dependence of wear scar diameter as a function of surfactant (SDS, SLES, SLS) concentration in aqueous solutions: surfactant and Hydrolysed oats. $d_{H_2O, 2KN} = 1.8$ mm, $d_{H_2O, 3KN}$ – seizures, $d_{H_2O, 4KN}$ – seizures, $d_{HO, 2KN} = 1.3$ mm, $d_{HO, 3KN} = 1.1$ mm, $d_{HO, 4KN} = 1.2$ mm

Rys. 6. Zależność średnicy śladów zużycia w funkcji stężenia surfaktantów (SDS, SLES, SLS) w wodnych roztworach surfaktantów i hydrolizatu owsa. $d_{H_2O, 2KN} = 1,8$ mm, $d_{H_2O, 3KN}$ – zatarcie, $d_{H_2O, 4KN}$ – zatarcie, $d_{HO, 2KN} = 1,3$ mm, $d_{HO, 3KN} = 1,1$ mm, $d_{HO, 4KN} = 1,2$ mm

For water as a lubricant, the system does not seize only for a load of 2 kN, for which the value of the diameter of the wear marks is 1.8 mm. Seizure occurs for higher loads (3, 4 kN). Hydrolysate solutions do not seize even under the highest loads. The d values for the three loads are 1.3, 1.1 and 1.2 mm, respectively. The influence of the load on wear is small and unfocused. The reason for the low resistance and wear of the hydrolysate solutions may be the formation of a permanent lubricating film on the friction surfaces, which effectively protects the friction surface against wear.

For a load of 2 kN, three-component solutions with surfactant (SDS, SLES, SLS) achieve lower d values than two-component solutions, but the differences are not large 0.1, 0.2 mm. For higher loads (3 and 4 kN), the wear correlations for three-component solutions are more complicated. The value reduction in relation to the hydrolysate solutions is observed for higher concentrations ($c \geq 1\%$, except for SLES solutions for which the consumption is higher than the hydrolysate solution).

Hydrolysate solutions are characterised by low consumption, decreasing slightly with increasing load. The measured diameters of the wear marks are, on average, over 30% smaller than for water with a load of 2 kN. These results show a significant effect of the hydrolysate even at extremely high pressures (3, 4 kN). The effect of lowering the consumption after introducing the surfactant is insignificant, and even for the addition of SLS, an increase in consumption is observed for higher loads (3, 4 kN).

Tests with a linearly increasing load (409 N/s)

Based on changes in the friction force moment (M_T) as a function of the linearly increasing load, the following measurements were determined directly from the measurements: seizure load (P_t), seizure load (P_{oz}) and wear mark diameter (d_{oz}). The wear mark's diameter is determined by measuring its diameter in the perpendicular and parallel directions and then calculating the average of these measurements.

On the other hand, the value of p_{oz} is a composite quantity, and it was calculated from the formula 1. For these reasons, the quantity p_{oz} is burdened with a relatively large error because it is the sum of the error in determining P_{oz} , especially the d_{oz} , present in the square.

Seizure load (P_t)

Seizure load is defined as the pressure value at which there is a significant increase in the moment of frictional forces, and it can be treated as a load which destroys the lubricating film. The P_t value was determined based on three independent experiments, and the mean values are presented in Fig. 7.

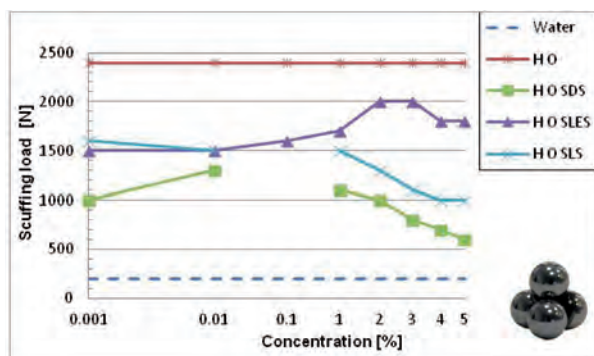


Fig. 7. Dependence of seizing load as a function of surfactant (SDS, SLES, SLS) concentration in aqueous solutions: surfactant and Hydrolysed oats. $P_{t, H_2O} = 200$ N, $P_{t, HO} = 2400$ N

Rys. 7. Zależność obciążenia zacierającego w funkcji stężenia surfaktantów (SDS, SLES, SLS) w wodnych roztworach: surfaktantów i hydrolizatu owsa. $P_{t, H_2O} = 200$ N, $P_{t, HO} = 2400$ N

P_t values for the hydrolysate solutions were equal to 2400 N, which is a value 12 times higher than for water (200 N). Such high values indicate that a permanent lubricating film forms on the friction surfaces, and it is insensitive to the highly unfavourable conditions in the test with a linearly increasing load.

For three-component solutions with the participation of individual surfactants, a decrease in the P_t value is observed, and thus a reduction in the durability of the film formed. Solutions demonstrate the most favourable properties with SLES, which for high concentrations (3.4%) reach P_t values equal to 2000 N. The dependence of P_t on concentration is not monotonic, which indicates a complicated mechanism of lubricating film formation. For the other two surfactants, these values are much lower. For higher concentrations ($c \geq 1\%$), the P_t values for SLS solutions are in the range from 1500 N (1%) to 1600 N (5%) and for solutions with SDS from 1500 N (1%) to 1000 N (5%).

The presented research results show that aqueous solutions of the hydrolysate, as model

lubricants, show the ability to create a durable lubricating film. The anionic surfactant introduced into these solutions lowers the P_t value, which indicates that the structure of the lubricating film underwent unfavourable changes.

Seizure load (P_{oz})

The aqueous solutions of the hydrolysate showed a very high seizure load (7.2 kN) (Fig. 8).

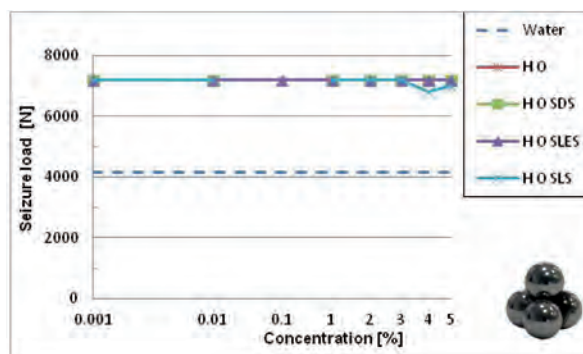


Fig. 8. Dependence of seizure load as a function of surfactant (SDS, SLES, SLS) concentration in aqueous solutions: surfactant and hydrolysed oats. $P_{oz, H_2O} = 4150$ N, $P_{oz, HO} = 7200$ N

Rys. 8. Zależność obciążenia zatarcia w funkcji stężenia surfaktantów (SDS, SLES, SLS) w wodnych roztworach: surfaktantów i hydrolizatu owsa. $P_{oz, H_2O} = 4150$ N, $P_{oz, HO} = 7200$ N

It is the highest value allowed for the type of tester used – T02. The value of the moment of friction forces corresponding to this load reaches the maximum value of $10 \text{ N} \cdot \text{m}$; when exceeded, the drive system is automatically disconnected, and the measurement is interrupted. There was no adverse effect of lowering the p_{oz} value after adding the surfactants. Only solutions with SLS were observed for the highest concentrations (4.5%), a decrease in the value of p_{oz} to the level of 6800 and 7000 N. This is a slight decrease, which, however, indicates no positive effects of introducing surfactants into the aqueous solutions of the hydrolysate.

The high P_{oz} for two- and three-component solutions is determined by forming a permanent lubricating film by the hydrolysate under frictional conditions, and it effectively prevents seizure.

The diameter of the wear pattern (d_{oz})

The hydrolysate solutions are characterised by relatively low consumption (Fig. 9).

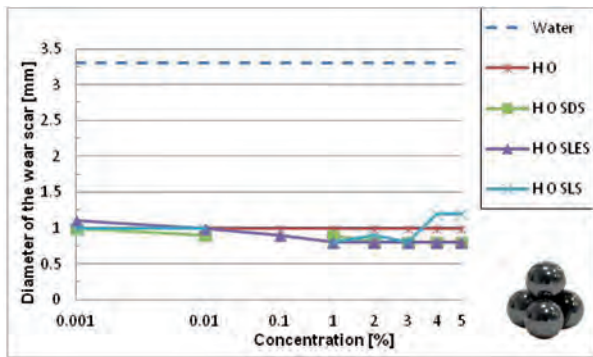


Fig. 9. Dependence of wear scar diameter (d_{oz}) as a function of surfactant (SDS, SLES, SLS) concentration in aqueous solutions: surfactant and hydrolysed oats. $d_{oz, H_2O} = 3.3$ mm, $d_{oz, HO} = 1.0$ mm

Rys. 9. Zależność średnicy śladu zużycia (d_{oz}) w funkcji stężenia surfaktantów (SDS, SLES, SLS) w wodnych roztworach surfaktantów i hydrolizatu. $d_{oz, H_2O} = 3,3$ mm, $d_{oz, HO} = 1,0$ mm

The diameter of the signs of wear ($d_{oz} = 1.0$ mm) is more than three times smaller than that of water (3.3 mm). After the introduction of individual surfactants, the d_{oz} decreases, reaching average values of $d_{oz} \leq 1.0$ mm. Slightly higher d_{oz} values were noted for higher SLS concentrations, which are 1.2 mm (4 and 5%).

Seizure limit load (p_{oz}).

The seizure limit load indicates the ability of the tribological system to withstand high loads. The calculated values of p_{oz} (Eq. 1) for the tested solutions are shown in **Fig. 10**.

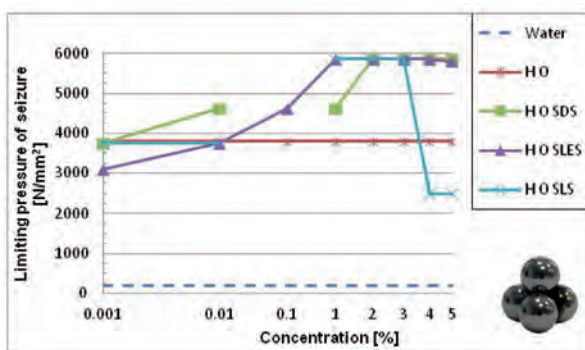


Fig. 10. Dependence of limiting seizure pressure as a function of surfactant (SDS, SLES, SLS) concentration in aqueous solutions: surfactant and Hydrolysed oats. $p_{oz, H_2O} = 200$ N/mm², $p_{oz, HO} = 3800$ N/mm²

Rys. 10. Zależność granicznego obciążenia zatarcia w funkcji stężenia surfaktantów (SDS, SLES, SLS) w wodnych roztworach: surfaktantów i hydrolizatu owsa. $p_{oz, H_2O} = 200$ N/mm², $p_{oz, HO} = 3800$ N/mm²

In binary hydrolysate solutions, the p_{oz} value equals approximately 3,800 N/mm². It is approx. 19 times higher than for water. Additionally, the presence of one of the surfactants (SDS, SLES, SLS) increases the p_{oz} value, which for higher concentrations ($c > 1\%$) gets a value close to 6000 N, which means over 1.5 times increase in relation to the hydrolysate solution. This results from lower values of the wear mark diameter with a constant P_{oz} (7200 N) value for SDS and SLES solutions. For 4 and 5% SLS solutions, it is a consequence of the increase in d_{oz} and decrease in P_{oz} .

The high load carrying capacity of the two- and three-component solutions is high, making it possible to use them as lubricant bases at extremely high pressures.

SUMMARY AND CONCLUSIONS

A broad spectrum of physicochemical and tribological tests was performed to evaluate aqueous solutions of the hydrolysate (two-component solutions) and the hydrolysate with individual surfactants (three-component solutions) as potential lubricant bases. The starting point was the safety of the environment and people at the workplace. This requirement was met because the surfactants used are used in cosmetic products, and the hydrolysate is used in food and cosmetic products. Additionally, the hydrolysate reduces the irritating effect of the anionic surfactants used.

The basic research is tribological tests, the aim of which is to document that adding additives (hydrolysate, surfactants) to water favourably changes the lubricating properties of water. Tribological measurements have documented this thesis on the T02 Tester under the conditions of constant load (2, 3, 4 kN) and the load increases over time, with the speed of 409 N/s. Both types of tests clearly indicate the high lubricity of the solutions and the possibility of using them as ecological lubricants.

Under high and constant load conditions, seizure does not occur for two- and three-component solutions, while water is already seized at 3 kN. The friction coefficients for these loads are in the order of several hundredths, and the diameter of the wear marks is approx. 1 mm. The test results with the linearly increasing load confirm the high lubricity of the tested solutions in relation to water. The solutions exhibit seizure load approx. 12 times higher than that determined for water. The seizure

load assumes the maximum value for the T02 Tester, which is 7.2 kN. The average diameter of the wear marks is over three times lower than that of water. The calculated limit load of seizure is 29 times higher than for water.

In general, the assessment of two and three-component solutions as model lubricants is positive. The lubricity of these solutions is many times higher than that of water, which indicates the possibility of potential practical applications. For specific applications, the performance characteristics should be additionally determined. One of them has already been designated, and it is foaming. It turns out that the hydrolysate solutions can be used directly, and the hydrolysate-surfactant solutions require the use of a foam inhibitor.

The interpretation of the obtained results of the tribological tests was based on the measurements of the surface tension and wettability of the ternary solutions. They show that the activity of the hydrolysate from aqueous solutions is high and increases with the addition of surfactant. It can be assumed that the hydrolysate forms complexes with individual surfactants in the bulk and surface

phases. The structure and concentration of the complexes formed in the surface phase determine the adsorption layer's formation and the lubricating film's friction conditions.

The results of physicochemical and tribological tests were interpreted in terms of the high activity of the solution components, their mutual interaction, and the formation of a lubricating film on the surfaces of friction pairs. They are an excellent starting point for supplementing the proposed databases with additives conditioning the achievement of functional properties for specific engineering applications.

Acknowledgements

The test results were obtained, among others, as part of implementing the following Research and Development Projects carried out at the Radom University of Technology, headed by prof. Marian Włodzimierz Sułek: "Development of the composition and production technology of a new generation of cutting fluids" and "New generation hydraulic fluids for mechanised mining supports".

REFERENCES

1. Sułek M.W., Bocho-Janiszewska A.: The Effect of Metal 8-Hydroxyquinolates as Lubricant Additives on the Friction Process. *Tribol. Lett.* 2003, 15, pp. 301–307.
2. Wasilewski T., Sułek M.W.: Paraffin oil solutions of the mixture of sorbitan monolaurate–ethoxylated sorbitan monolaurate as lubricants. *Wear* 2006, 261, pp. 230–234.
3. Sułek M.W., Wasilewski T.: Tribological properties of aqueous solutions of alkyl polyglucosides. *Wear* 2006, 260, pp. 193–204.
4. Sułek M.W., Bocho-Janiszewska A.: The effect of ethoxylated esters on the lubricating properties of their aqueous solutions. *Tribol. Lett.* 2006, 24, pp. 187–194.
5. Sułek M.W., Bąk-Sowińska A.: Aqueous Solutions of Surfactants in Materials Engineering of Tribological Systems. In *Surfactants in Tribology, Volume 4*; Informa UK Limited: Colchester, UK, 2014; pp. 239–258. *Materials* 2020, 13, 5812 19 of 20.
6. Sułek M.W., Wasilewski T., Kurzydłowski, K.J.: The Effect of Concentration on Lubricating Properties of Aqueous Solutions of Sodium Lauryl Sulfate and Ethoxylated Sodium Lauryl Sulfate. *Tribol. Lett.* 2010, 40, pp. 337–345.
7. Sułek M.W., Bąk-Sowińska A.: 10. Chapter in the Monograph "Surfactants in Tribology", "Aqueous Solution of Surfactants in Materials Engineering of Tribological Systems"; Biresaw G., Mittal K.L., Eds.; CRC Press: Boca Raton, FL, USA, 2014; Volume 4, pp. 239–258.
8. Sułek M.W., Hreczuch W., Przepiórka J., Adach A.: Solutions of Water Sterically Specific Surfactants as Model Ecological Cutting Fluids. *Tribology* 2018, 271, pp. 87–95.
9. Sułek M.W., Przepiórka J., Kulczycki A., Hreczuch W.: The Effect of Surfactants with Steric Hindrance on the Physicochemical and Tribological Properties of Metalworking Fluids. *Tribology* 2020, 290, pp. 75–84.

10. Sułek M.W., Bąk-Sowińska A, Przepiórka J.: Ecological Cutting Fluids, *Materials* 2020, 13, pp. 5812–5832.
11. Przondo J., Sułek M.W., Sas W.: Concentrate for the Preparation of Cutting Fluids and Non-Emulsion Hydraulic Fluids. Patent No. 208,951, 30 June 2011.
12. Pernak J., Walkiewicz F., Sułek M.W., Wasilewski T.: Multifunctional Grease Containing Ionic Liquids. Patent No. 215,892, 10 April 2013.
13. Sułek M.W., Bąk A., Wasilewski T., Wachowicz J., Pytlik A.J.: Flame-Retardant Water-Based Hydraulic Fluid. Patent No. 218,550, 5 March 2014.
14. Sułek M.W., Bąk A., Wasilewski T., Wachowicz J., Pytlik A.J.: Flame-Retardant Water-Based Hydraulic Fluid. Patent No. 218,551, 5 March 2014.
15. Sułek M.W., Bąk A., Wasilewski T., Wachowicz J., Pytlik A.J.: Flame-Retardant Water-Based Hydraulic Fluid. Patent No. 218,566, 25 February 2014.
16. Sułek M.W., Wasilewski T., Piotrowska U., Seweryn A.: Cooling—Lubricating Liquid for Metalworking. Patent No. 225,734, 2 December 2016.
17. Sułek M.W., Wasilewski T., Sas W., Piotrowska U.: Cooling and Lubricating Liquid for Metal Processing. Patent No. 221,760, 17 June 2015.
18. Botan A., Joly L., Fillot N., Loison C.: Mixed Mechanism of Lubrication by Lipid Bilayer Stacks. *Langmuir* 2015, 31, pp. 12197–12202.
19. Benedicto E., Rubio E.M., Carou D., Santacruz C.: The Role of Surfactant Structure on the Development of a Sustainable and Effective Cutting Fluid for Machining Titanium Alloys. *Metals* 2020, 10, p. 1388.
20. Ma L., Zhang C., Liu S.: Progress in experimental study of aqueous lubrication. *Chin. Sci. Bull.* 2012, 57, pp. 2062–2069.
21. Chen W., Amann T., Kailer A., Rühle J.: Macroscopic Friction Studies of Alkylglucopyranosides as Additives for Water-Based Lubricants. *Lubricants* 2020, 8, p. 11.
22. Han T., Zhang, C., Luo J.: Macroscale Superlubricity Enabled by Hydrated Alkali Metal Ions. *Langmuir* 2018, 34, pp. 11281–11291.
23. Klein J.: Hydration lubrication. *Friction* 2013, 1, 1–23.
24. Brinksmeier E.D., Huesmann-Cordes A.G., Herrmann C.: Metalworking fluids—Mechanisms and performance, *CIRP Annals—Manufacturing. Technology* 2015, 64, pp. 605–628.
25. Schwarz M., Dado M., Hnilica R., Veverková D.: Environmental and Health Aspects of Metalworking Fluid Use. *Pol. J. Environ. Stud.* 2015, 24, pp. 37–45.
26. Piekoszewski W., Szczerek M., Tuszyński W.: The action of lubricants under extreme pressure conditions in a modified four-ball tester. *Wear* 2001, 249, pp. 188–193.