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## THE EFFECT OF SURFACTANTS WITH STERIC HINDRANCE ON THE PHYSICOCHEMICAL AND TRIBOLOGICAL PROPERTIES OF METALWORKING FLUIDS

### WPŁYW SURFAKTANTÓW Z ZAWADĄ PRZESTRZENNĄ NA WŁAŚCIWOŚCI FIZYKOCHEMICZNE I TRIBOLOGICZNE NOWEJ KLASY CIECZY OBRÓBKOWYCH

**Key words**: metalworking fluids, surfactants, aqueous solutions, tribological properties.

Abstract: In earlier studies, it has been postulated that solutions of surfactants should be used as an original solution

for formulation of Metal Working Fluids (MWF) compositions. The negative feature of some of the fluids was their excessive foamability whose reduction, by introducing hydrophobic foam inhibitors, was limited. Therefore, a synthesis of new oxyalkylated derivatives of 2-ethylhexyl alcohol and sulfosuccinate obtained from this alcohol was planned. Due to steric hindrance, these compounds exhibit low foamability. Aqueous

solutions of these surfactants were subjected to physicochemical and tribological tests.

Słowa kluczowe: ciecze obróbkowe, surfaktanty, wodne roztwory, właściwości tribologiczne.

Streszczenie: W poprzednich pracach postulowano zastosowanie roztworów surfaktantów jako oryginalne rozwiązanie

przy formułowaniu składu MWF. Negatywną cechą niektórych z tych cieczy była nadmierna pianotwórczość, której zmniejszenie przez wprowadzenie hydrofobowych inhibitorów piany, było ograniczone. Dlatego też zaplanowano syntezę nowych, oksyalkilenowanych pochodnych alkoholu 2-etyloheksylowego i sulfobursztynianu otrzymanego z tego rodzaju alkoholu. Ze względu na zawadę sferyczną związki te charakteryzują się niską pianotwórczością. Wodne roztwory tych surfaktantów poddano badaniom fizykochemicznym i tribolo-

gicznym.

#### INTRODUCTION

Materials take on appropriate shapes and sizes due to mechanical working. The process can be divided into three kinds, i.e. turning, milling, and grinding, during which a high amount of energy, mainly in the form of heat, is released which negatively affects, e.g., tribological processes occurring in the friction zone and, as a consequence, this has a negative effect on tool life, surface structure, and the sizes of the material

worked. Metalworking fluids (MWFs) are used in order to remove heat and wear particles out of the friction area and to reduce motion resistance and tool wear.

Depending on their bases, metal working fluids can be divided into oil or water types. A detailed division will be presented in Chapter 2 of this paper. The proposed metalworking fluids based on aqueous solutions of surfactants (surface active agents) cannot be included in any of the classes mentioned. To make the classification clear, they were named surfactant working fluids

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(SWFs). With an increase in applications of aqueous solutions of surfactants in lubrication technology, it is proposed that a new term "surfactant lubricants" (SL) should be introduced.

Our studies on SFS were already intensively carried out in the late 1990s and are now being continued. Aqueous surfactant solutions were successfully modified by the introduction of functional additives which improved functional and physicochemical properties of the fluids produced. As a result of our research, it was possible to achieve a number of scientific goals which have become the subjects of numerous publications, the examples of which are presented in this paper [L. 1–10], and of a number of applications which are patent protected [L. 11–17].

# THE CLASSIFICATION AND CHARACTERISTICS OF BASIC TYPES OF METAL WORKING FLUIDS (MWFS) AND THE ADDITIVES USED

Apart from ensuring the basic functions, i.e. efficient cooling and lubrication, it is necessary to take into account a number of other properties which should characterize metal working fluids, e.g., the removal of chips from the friction zone, washing properties, corrosion prevention, ensuring stability during use and storage, the penetration of the friction surface, and rapid diffusion of components. The effectiveness of these processes depends on particle sizes and viscosity, incombustibility, low foamability, inertness towards the worked material, primarily no metal corrosion, neutral or pleasant smell, and no toxic effect on humans in the workplace and on the natural environment [L. 19].

It is practically impossible to select a metalworking fluid base which would satisfy all the functions listed above. Therefore, packages of additives improving physicochemical and functional properties of MWFs are introduced. Thus, the composition of metalworking fluids is complex, and the choice of components is a result of advanced analyses of the functions of MFSs and the safety of both humans in workplaces and the natural environment.

#### Oil bases

Various kinds of oils can be used – both natural and synthetic [L. 20]. The most important ones are vegetable oils, petroleum products, and naphthenic and paraffin oils. Vegetable and animal oils were historically the first ones used. In view of their composition variability, they were replaced with petroleum products. Oils have very good lubricating properties. They result from the formation of a stable lubricant film even at high loads and temperatures. The film separates the mating surfaces. Due to high viscosity and relatively small viscosity variations as a function of pressure and temperature,

they can be used at high working speeds. The materials worked are mainly steel, and, to a lesser extent, nonferrous metals, as in the case of copper and its alloys, oils may cause corrosion. Vegetable oils are favoured due to their high degree of biodegradability. On the other hand, they readily undergo ageing emitting malodorous substances. Generally, oils have an adverse effect on the natural environment

#### Water bases

Water-based metalworking fluids are divided into two kinds: solutions and emulsions. Water has a number of advantages (eco-friendliness, fire resistance, high thermal conduction, non-toxicity, general availability, low price), but water-based metalworking fluids also have numerous disadvantages (corrosivity, low boiling point, evaporative power and low viscosity). Water lubrication is important in view of environmental and product compatibility. Therefore, water as a base can find potential applications in the food, biomedical, and pharmaceutical industries. The essential limitations in its application are low viscosity and an unfavourable dependence of viscosity on pressure and temperature. As a result, water is squeezed out of the friction zone, which causes direct contact of microasperities and an increase in motion resistance and wear and, at higher loads, may result in seizure.

#### Solutions

This class of metalworking fluid bases comprises solutions of polar hydrophilic compounds in water. It is assumed that lipophilic compounds and emulsifiers do not appear in the solutions. An example of a solution composition is as follows: pH buffer (5%), corrosion inhibitors (10%), extreme—pressure additives (9%), and water (70%). The solutions frequently contain from 15 to 60 different chemical compounds which may have a negative or even a toxic effect on human health. As an example, boric acid, amines, and chlorinated products may cause cancer of the skin, scrotum, larynx, pancreas, and bladder. Thus, although water satisfies ecological criteria, the solutions may adversely affect human health and the natural environment.

# Emulsions, microemulsions, nanoemulsions of the o/w type

They are produced on the basis of water (continuous phase) and oil (dispersed phase) [L. 22]. Individual emulsion types differ in the degree of dispergation of the oil phase and, as a result, in the stability which increases with a decrease in oil particle sizes. Optically, emulsions are usually milky (light scattering, Tyndall effect), while micro and nanoemulsions are transparent. Water contained in emulsions ensures good cooling properties, whereas oil ensures good lubrication. Amphiphilic compounds which surround oil "droplets"

to protect them against flocculation are used to ensure emulsion stability. As commercial products, emulsions are concentrates which are diluted directly before use to obtain oil concentrations of 3 to 10 wt %. Even the most highly dispersed emulsions differ from aqueous solutions in the structures formed and action mechanism. Under friction conditions, there occurs phase\_inversion and oil is a continuous phase of the emulsion being formed on the friction surface. This can explain high lubrication efficiency. The o/w emulsion is to "transfer" the oil phase to the friction zone and transform into w/o emulsions. The emulsifier's job is not only to ensure the emulsion's stability but also the re-emulsification of the oil present on the surface in the form of droplets [L. 23–25].

## Additives modifying properties of metalworking fluids

Modern metalworking technologies should provide high efficiency by increasing the speed of the process while ensuring the proper quality and accuracy of the surface machined. The bases offered, regardless of their type, do not guarantee satisfying these requirements. Therefore, metalworking fluid bases are usually enriched with certain types of additives in the form of packages consisting of various groups of compounds. They can be generally divided into antiseizure additives (EP – extreme pressure), antiwear additives (AW), friction

modifiers (FM), emulsifiers, biocides, foam inhibitors, corrosion inhibitors, and antifogging additives (AF). The selection of additives modifying the properties of metalworking fluid bases is essential. Additive packages are mixtures of chemical compounds and are targeted at specific bases and technical and technological solutions. Synergistic behaviour of individual compounds should be preferred while antagonistic behaviour should be excluded. The additives mentioned are applied primarily in oil bases, emulsions, and solutions. Some of them can have a negative impact on human health.

Some of the additives mentioned above can also be used in surfactant working fluids (SWFs). Due to their specific composition and form, new kinds of compounds which would satisfy the assumed requirements should be planned as SWF additives. Based on our\_studies, it can be assumed that properly selected surfactants can satisfy a number of functions of additives. In this way, the number of additives will be lower and it will be easier to select appropriate chemical compounds.

#### **EXPERIMENTAL RESULTS**

The subjects of research are metalworking fluids (MWFs) based on surfactant solutions. This paper presents experimental results for solutions of three compounds denoted symbolically by P4, P8, and P16 (**Table 1**).

**Table 1. Surfactants used** Tabela 1. Stosowane surfaktanty

Mark	Description
P4	EHP1E9-DMC propoxypolyethoxylate of 2-ethylhexyl alcohol 1 mole of propylene oxide / 9 moles of ethylene oxide DMC (Double Metal Cyanide) catalyst.
P8	EHP3E9-DMC – propoxypolyethoxylate of 2-ethylhexyl alcohol 3 moles of propylene oxide / 9 moles of ethylene oxide DMC (Double Metal Cyanide) catalyst.
P16	EHP3E3-DMC-SS – sulfosuccinate derivatives produced on the basis of polyoxyalkylates of 2-ethylhexyl alcohol 3 moles of propylene oxide / 9 moles of ethylene oxide DMC (Double Metal Cyanide) catalyst.

Structurally, the first two compounds differ substantially from the third one. P4 and P8 are oxyalkylates of 2-ethylhexyl alcohol and nonionic surfactants. P16 is a sulfosuccinate derivative of this alcohol and an anionic surfactant. The aim of such a choice of these compounds was to show the effect of the kind of surface active agents (nonionic and anionic) on selected physicochemical and tribological properties.

The concentrations of surfactant solutions were determined gravimetrically. Eight solutions with the following percentage concentrations:  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$ ,  $10^{-0}$ ,  $1x10^{0}$ ,  $2x10^{0}$ ,  $3x10^{0}$ ,  $4x10^{0}$ , and  $5x10^{0}$  were prepared for individual surfactants. The measurement points marked in **Figs. 1–6** are arithmetic means from three

independent measurements. The measure of error was the standard deviation of the arithmetic mean calculated according to Student t distribution for the confidence level of 90%. The methods of physicochemical and tribological studies were repeatedly described in literature [L. 18]; therefore, only basic information on the procedures will be given and the importance of the determined quantities for the production and evaluation of working fluids will be described.

#### The characteristics of aqueous surfactant solutions

By planned selection of surfactants, it is possible to shape, to a large extent, the required characteristics of aqueous solutions, such as surface activity, rheology, density, foamability, and the solubilization capacity of functional components. This paper presents the measurement results of the following physicochemical quantities: surface tension, wettability, foamability, viscosity, density, pH, stability, and clarity.

#### Surface tension

The effect of these structures on surface tension ( $\sigma$ ) was measured by means of the ring tear-off method using the TD1C Lauda tensiometer at 25°C. The results are given in **Fig. 1**.

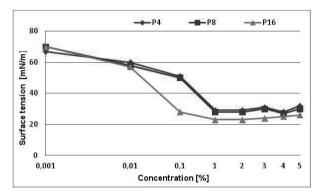


Fig. 1. Relation between surface tension  $(\sigma)$  of aqueous solutions of sulfosuccinate derivatives as a function of their concentration

Rys. 1. Zależność napięcia powierzchniowego (σ) wodnych roztworów pochodnych sulfobursztynianów w funkcji ich stężenia

The value for water equals 72 mN/m, while, for solutions of the compounds, it decreases with an increase in concentration. A significant change in the value of surface tension can be observed in the concentration range of 10<sup>-2</sup> to 10<sup>0</sup> %, and then it stabilizes at the level of 20 to 30 mN/m. It is a substantial (even over threefold) decrease relative to water which points to the high surface activity of the surfactants studied. The lowest values were obtained for surfactant P16 solutions which, for the concentration range discussed, reach 23 do 26 mN/m. These values are comparable to the surface tension values for the most surface active compounds. Additionally, a distinct decrease in surface tension can be seen in the  $10^{-2} - 10^{-1}\%$  concentration range, which indicates a possible adsorption layer formation already at these concentrations.

#### Surface wettability

Wettability is an important quantity characterizing interactions of surfactants with the surface. An increase in wettability improves lubrication and thus metalworking. Contact angles were determined using the "sitting drop" method at 25°C. The results are given in **Fig. 2**.

The measure of wettability was the contact angle  $(\Theta)$  whose decrease indicated an increase in wettability.

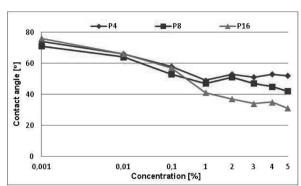


Fig. 2. The dependence of the contact angle for a bearing steel surface with aqueous solutions of sulfosuccinate derivatives as a function of their concentration

Rys. 2. Zależność kąta zwilżania powierzchni stali łożyskowej wodnymi roztworami pochodnych sulfobursztynianów w funkcji ich steżenia

**Figure 2** shows that the angle value decreases monotonically as a function of an increasing surfactant concentration. In the case of the lowest concentrations, the  $\Theta$  value is close to the value determined for water; whereas, for the 1% concentration, the value obtained was in the 41 – 49° range. Lower  $\Theta$  values ca. 40° can be observed for the P16 compound. In the case of concentrations of over 1%, solution wettability stabilizes with a slight falling tendency. The gradations of wettability of solutions for the concentrations of > 1% can be shown by means of the following inequality:

Solutions of the P16 compound show distinctly higher wettability in the range of higher concentrations (>1%).

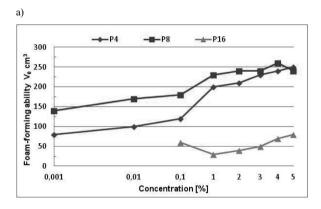
#### Foamability

One of the drawbacks of applications of SWFs was their excessive foam formation in aqueous solutions. The presence of foam both in the bulk phase and in the surface phase of working fluids is a disadvantage. Air bubbles may disturb liquid flow and cause the formation of a heterogeneous lubricant film in the friction zone. The cavitation phenomenon may occur under high loads. Cavitation disturbs friction conditions and results in micro-damage of the surfaces of tools and the material worked.

Foam inhibitors have been used in order to significantly reduce the amount of foam in surfactant working fluids. This work offers a different approach consisting in introducing a new type of surfactants with low foamability in aqueous solutions. This group includes surface active agents with branched alkyl chains. Preliminary tests confirmed these assumptions. The steric hindrance, connected with a branched alkyl chain in alcohol, considerably reduces the foamability of

this type of surfactants in water. 2-ethylhexyl alcohol was selected as a starter to obtain amphiphilic compounds with a branched chain. The alcohol was ethoxylated and propyloxylated. Oxyalkylates with various shares of ethylene oxide and propylene oxide and a sulfosuccinate derivative were obtained.

Foam-forming ability was measured using the Bikerman method [Bikerman J.J., 1973, Foams, New York, Springer-Verlag, p. 337] at a constant air flow through a given solution. The volume of foam was measured in cm<sup>3</sup> after 1 minute  $(V_1)$  and after 10 minutes  $(V_{10})$  after its formation and the results are given in **Fig. 3**.



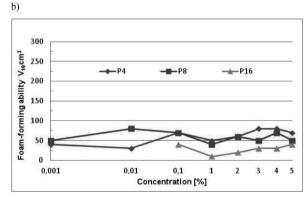


Fig. 3. The dependence of foam volume  $(\Theta)$  after 30s  $(V_1)$  (Fig. 3a) and 10 min  $(V_{10})$  (Fig. 3b) created as a result of the flow of air through the aqueous solutions of surfactants P4, P8, P16

Rys. 3. Zależność objętości piany  $(\Theta)$  po 30 s  $(V_1)$  (rys. 3a) i 10 min  $(V_{10})$  (rys. 3b) wytworzonej w wyniku przepływu powietrza przez wodne roztwory surfaktantów P4, P8, P16

In the concentration range considered ( $10^{-3} - 5x10^{0}$ %), one can observe an increase in the volume of foam produced after one minute ( $V_1$ ) with an increase in concentration, particularly for P4 and P8 surfactant solutions, which, at the highest concentrations, reached the  $V_1$  values from 200 to 250 cm<sup>3</sup>. The solutions of the P8 compound show higher  $V_1$  volumes (**Fig. 3a**). After 10 minutes, the P4 and P8 solutions yield lower foam volumes, below 80 cm<sup>3</sup>. The volumes of foam after

10 minutes after its formation (V<sub>10</sub>) are comparable for various concentrations of the two compounds. A considerably lower foam formation is observed in the case of P16 solutions for which the V, values do not exceed 80 cm $^3$  and the  $V_{10}$  values are lower than 40 cm<sup>3</sup> (Fig. 3b). Additionally, in the case of three lowest concentrations, foam volumes after 1 and 10 minutes are immeasurably small and have not been presented in the diagrams (Fig. 6). The 1% solutions of P16 formed a low volume of foam (30 cm<sup>3</sup>) also after 30 seconds. These results can be related to solutions of other surfactants without the steric hindrance. For example, foam volumes of typical anionic surfactants – sodium laureth sulfate (SLES) and sodium dodecylbenzene sulfonate (SDBS) are 450 and 420 cm<sup>3</sup> after 1 minute and 450 and 400 cm<sup>3</sup> after 10 minutes, respectively.

#### Stability and clarity

The evaluation of stability and homogeneity of the solutions was carried out by means of the following tests:

- Storage: The solutions were stored at room temperature for two weeks.
- Thermal shock: The solutions were stored alternately at lowered (5°C) and increased temperatures (40°C).
- Resistance to mechanical loads: The solutions were exposed to centrifugal force in a centrifuge (4000 rpm) for 10 minutes at 5, 23 and 40°C.

Only stable and transparent solutions were used in further studies. In view of the predicted applications, the stability of solutions was essential as any changes in the structure of liquids under working processes should be excluded.

#### Viscosity, density, pH

Kinematic viscosity was determined using an Ubbelohde viscometer at 25°C. It increased to a small degree with an increase in the concentration of surfactants, ca. 15%, on average, in the whole concentration interval. Similar variation tendencies were observed in the case of density. The pH values ranged from approximately 6.0 to about 6.5.

#### **Tribological investigations**

High water concentrations (up to about 95%) were needed to satisfy the criteria for coolants. High thermal conduction, a high value of heat of vaporization and also low viscosity of the solutions allow for effective heat removal from the material worked and from wear products (chips). The other very important characteristic of working fluids is their lubricity, particularly at high loads. Therefore, a load range from 0 to 7.2 kN under concentrated contact (T02 four-ball tester) was selected for the tribological tests. The measurement method was described in numerous publications [L. 18] and will not be discussed in this paper.

The following tests were carried out:

- At constant loads (2, 3, 4 kN) for which friction coefficients (μ) and wear (d) were determined; and,
- At a linearly increasing load (409 N/s) in the range of 0 to 7.2 kN. (The dependence of friction torque (M<sub>T</sub>) was determined as a function of increasing load and it was used to determine the P<sub>t</sub>, P<sub>oz</sub>, d, and p<sub>oz</sub> quantities discussed below in this chapter.)

#### Tests at constant load (2, 3, 4 kN)

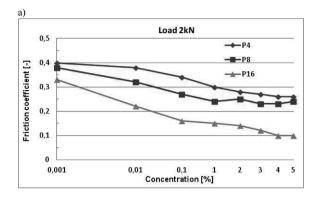
The measurement results are given in **Figs. 4** and **5**. They can be divided into two parts: those dealing with the dependence of friction coefficient on concentrations of individual surfactants (**Fig. 4**) and analogous dependencies of average wear scar diameters (d) (**Fig. 5**).

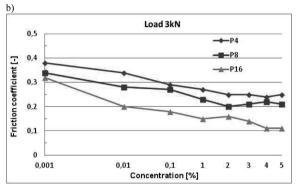
#### Friction coefficient (µ)

The determined friction coefficient values as a function of concentrations of surfactants are given in Fig. 4.

Lubricating properties of water are insufficient. Tests for water can be carried out only at the lowest load (2 kN) on a four-ball tester. The determined value of friction coefficient (2 kN) is 0.47, and the wear scar diameter is 1.8 mm. These values are higher even in comparison with the values for solutions with the lowest concentrations of surfactants. At higher loads, the M<sub>T</sub> value exceeded 10 Nm which is the highest allowable value. The system which reached that value is treated as if it underwent seizure. At the load of 4 kN, the system with P16 solutions seized only at the lowest concentration (0.001%), P8 at the concentrations of 0.001 and 0.01%, and P4 at 0.001, 0.01, and 0.1%. It follows from this analysis that solutions of the P16 compound have the highest load-carrying capacity at low and high concentrations.

The values of friction coefficients as a function of surfactant concentration decrease for all solutions (Fig. 4). In the case of the solutions of the compounds predicted for working fluids (>1%), friction coefficients depend on load to a small degree. In the case of the P4 solutions with the concentration of >1%, friction coefficients range from 0.24 to 0.28 with an observed decreasing tendency as a function of increasing concentration (Fig. 4). Analogous variability can be observed for P8 solutions. For > 1% concentrations, the values of  $\mu$  do not practically depend on load and they range from 0.20 to 0.24. Although this range exceeds the measuring error, the differences are not really significant. Such P16 solutions do not display major changes with an increase in concentration (>1%). Although we can observe seizure at the lowest concentration, the impact of load is limited in the 0.001 to 0.1% concentration range. At the two highest concentrations, these solutions display minimal friction coefficients (0.10 - 0.11). The dependence of friction coefficient on the kind of





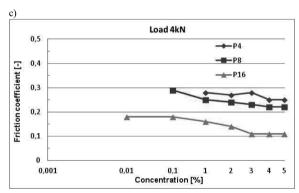


Fig. 4. Friction coefficient (μ) as a function of concentration of sulfosuccinates (P4, P8, P16) in their aqueous solutions for the loads of 2 kN (Fig. 4a), 3 kN (Fig. 4b) and 4 kN (Fig. 4c). Tribological tester T02, spindle speed of 200 rpm, test time of 900 s

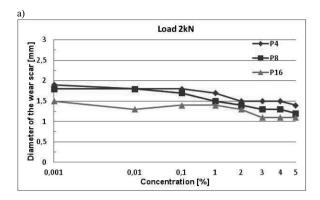
Rys. 4. Zależność współczynnika tarcia (μ) od stężenia sulfobursztynianów (P4, P8, P16) w ich wodnych roztworach dla obciążeń 2 kN (rys. 4a), 3 kN (rys. 4b) i 4 kN (rys. 4c). Tester tribologiczny T02, prędkość obrotowa wrzeciona 200 obr./min, czas testu 900 s

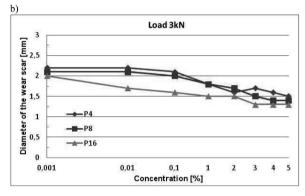
surfactant for the whole range of concentrations can be expressed by the following inequality:

$$\mu(P4) > \mu(P8) > \mu(P16)$$
.

#### Wear (d)

Wear values (d) demonstrate lower dynamics of changes as a function of concentration in comparison with analogous changes in the coefficient of friction (Fig. 5).





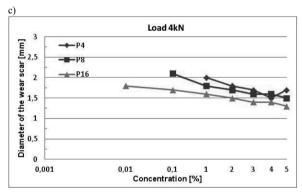


Fig. 5. The dependence of wear scar diameter (d) on the concentration of sulfosuccinates (P4, P8, P16) in their aqueous solutions for the loads of 2 kN (Fig. 5a), 3 kN (Fig. 5b) and 4 kN (Fig. 5c). Tribological tester T02, spindle speed of 200 rpm, test time of 900 s

Rys. 5. Zależność średnicy śladu zużycia (d) od stężenia sulfobursztynianów (P4, P8, P16) w ich wodnych roztworach dla obciążeń 2 kN (rys. 5a), 3 kN (rys. 5b) i 4 kN (rys. 5c). Tester tribologiczny T02, prędkość obrotowa wrzeciona 200 obr./min, czas testu 900 s

The  $\mu$  value decreased even fivefold relative to water, whereas d decreased 1.5-fold. Besides, the mean d value is an arithmetic mean of three averaged d values directed perpendicularly to each other. Therefore, the measuring error connected with the determination of wear scar diameters was estimated as 0.05 mm, and the results were recorded with the accuracy of one decimal place.

It follows explicitly from **Fig. 5** that wear scar diameters decrease with an increase in the concentration of surfactants at all loads. The solutions show relatively low d values even at the highest load (4 kN). The values

are even about 30% lower for 4 kN compared to water at the 2 kN load. It can thus be claimed that the surfactant solutions used are bases which are characterized by relatively low wear values. With the measuring method used, out of the three surfactants, the P16 compound turned out to be the most effective one in wear reduction. For the whole concentration range, wear can be presented by means of the following inequality (Fig. 5):

$$d(P4) > d(P8) > d(P16)$$
.

It is hard to determine which of the solutions have the most favourable antiwear properties under real metalworking conditions. Based on the results obtained, it can be said that the P16 solutions displayed the highest efficiency in decreasing wear.

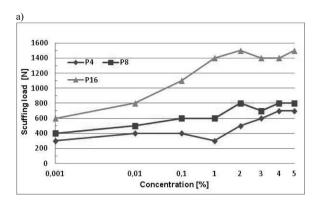
#### Tests at linearly increasing load

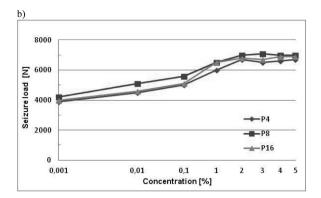
The tests are carried out under specific conditions. Load changes from 0 to 7.2 kN within about 18 seconds at the speed of 409 N/s. The conditions can be treated as extreme. Based on the analysis of the dependence of friction torque ( $M_T$ ) as a function of time, it is possible to determine scuffing load ( $P_t$ ), seizure load ( $P_{OZ}$ ), wear scar diameter at the highest load at which the system does not undergo seizure ( $d_{OZ}$ ), and the limiting pressure of seizure ( $p_{OZ}$ ).

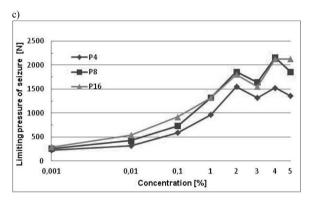
#### Scuffing load (P)

According to a general interpretation, below scuffing load, the system is characterized by the conditions of hydrodynamic or boundary friction. After exceeding the P<sub>t</sub> value, mixed friction begins. The P<sub>t</sub> values for the solutions of the three surfactants are given in **Fig. 6**.

The P value for water is 200 N. Surfactant solutions have a higher seizing load value which increases with an increase in surfactant concentration (Fig. 6b). A detailed analysis indicates that the pace of increase is different in various concentrations intervals. Above the concentration of 0.01%, there occurs a higher P. increase, particularly in the case of P16 solutions which at higher concentrations (3-5%) reach the highest value of about 1500 N. This value is 7.5-fold higher than the one for water. Lower P, values were determined for P8 and P4 solutions. The P8 values were higher for the highest concentrations by about 200 N. These values are fourfold (P8) and threefold (P4) higher, respectively, in relation to water. Such high scuffing load values indicate that, in the presence of solutions, a lubricant film forms on mating surfaces. In the case of P16 solutions, this film, to the least degree, undergoes destruction under conditions of rapid load increase and high pressure values achieved. The different behaviour of the solutions of the three surfactants can be interpreted on the basis of different properties of anionic compounds (P16) and nonionic compounds (P4, P8).







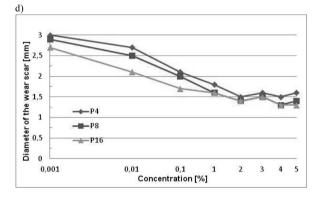


Fig. 6. Relation of scuffing load ((Fig. 6a), seizure load (Fig. 6b), limiting pressure of seizure (Fig. 6c), and the ball's wear scar diameter (Fig. 6d) as a function of sulfosuccinates concentration (P4, P8, P16) in their aqueous solutions. Tests were performed with an increasing load at a speed of 409 N/s and a spindle speed of 500 rpm

Rys. 6. Zależność obciążenia zacierającego (Rys. 6a), obciążenia zatarcia (Rys. 6b), granicznego obciążenia zatarcia (Rys. 6c), średnicy śladu zużycia kulki (Rys. 6d) od stężenia sulfobursztynianów (P4, P8, P16) w ich wodnych roztworach. Test przy narastającym obciążeniu z szybkością 409 N/s, prędkość wrzeciona 500 rpm

Variations in scuffing load as a function of surfactant kind can be expressed by means of the following inequality:

$$P_{1}(P4) > P_{1}(P8) > P_{1}(P16)$$
.

Seizure load (P , )

Seizure load is equivalent to the highest allowable friction torque (10 N·m) for this tribometer.

The tendencies of variations in the  $P_{OZ}$  (b) values for solutions of various surfactants are similar (Fig. 6b). Starting at the concentration of about 0.01%, a rise occurs in the pace of  $P_{OZ}$  value increase; and for  $c \ge 2\%$ , it takes constant values ( $\pm 100~\rm N$ ). The character of the observed changes in  $P_{OZ}$  (Fig. 6b) corresponds well with the changes in surface tension and wettability, which points to a significant role of adsorption of surface active agents at the interface. In the case of the highest concentrations, the solutions show practically the highest values comparable with the maximum load at which the device shuts off ( $M_{T_{max}} = 10~\rm N \cdot m$ ). Although the differences between the solutions of various compounds are not really large, it is possible for

practically all concentrations to establish the following gradation of changes:

$$P_{OZ}(P16) > P_{OZ}(P8) > P_{OZ}(P4)$$
.

Wear scar diameter (d<sub>a</sub>)

Wear scar diameters were measured at the lowest registered load. The results obtained are given in **Fig. 6d**. The value of  $d_{oz}$  is 3.3 mm for water at the load of 0.2 kN above which seizure occurred. In the case of the solutions, wear scar diameter values decreased with an increase in surfactant concentrations reaching the lowest values at the highest concentrations. The analysis of  $d_{oz}(c)$  dependences (**Fig. 6d**) indicates different paces of changes. The highest decrease can be observed in the 0-0.1% concentration range. Above 0.2%,  $d_{oz}$  takes approximately constant values for various solutions. The gradations of wear changes for various compounds can be illustrated using the following inequality:

$$d_{0z}(P16)>d_{0z}(P8)>d_{0z}(P4)$$
.

Limiting pressure of seizure (p<sub>a</sub>)

Limiting pressure of seizure can be calculated using the following equation:

$$p_{oz} = 0.52 \frac{P_{oz}}{d_{oz}^2} \qquad \left[ \frac{N}{mm^2} \right]$$

The  $p_{oz}(c)$  dependence is shown in **Fig. 6c**. For the C> 0.01% concentrations, one can observe a practically monotonic increase in  $p_{oz}$  as a function of increasing concentration (**Fig. 6c**). The highest values of limiting pressure of seizure are observed for P16 solutions followed by P8 and P4. The changes can be presented by means of the following equation:

$$p_{oz}(P16) > p_{oz}(P8) > p_{oz}(P4)$$
.

The highest  $p_{oz}$  values are obtained in the case of the solutions with the highest concentrations. They take the following values: 1.4 kN (P4), 1.9 kN (P8), and 2.1 kN (P16).

#### **SUMMARY**

Based on our investigations **[L. 1–17]** and the results presented in this paper, it has been found that aqueous surfactant solutions can act as good ecological bases for working fluids. The aim of this paper was to examine solutions of the compounds which would display low foam formation ability. Attention was paid to compounds with steric hindrance containing branched alkyl chains. 2-ethylhexanol was selected as a starter and, using it as a base, about 20 compounds were synthetized of which 2 oxyalkylates (P4, P8) and 1 sulfosuccinate (P16) were selected (**Table 1**).

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