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The role of silicone derivatives as additives modifying the lubricity of water

Key words

Lubricants, surfactants, cationic and nonionic silicones, physicochemical and tribological properties.

Słowa kluczowe

Substancje smarowe, związki powierzchniowo czynne, kationowe i niejonowe pochodne silikonów, właściwości fizykochemiczne i tribologiczne.

Summary

Silicone oils are used as lubricants or additives modifying lubricating properties of oil bases. However, those compounds are not water soluble. Therefore, the following silicone derivatives were selected as additives improving the lubricity of water: quaternary diamide polydimethylsiloxane (Quaternium-80) which is a cationic surfactant and an ethoxylated silicone which is a nonionic surfactant (Bis-PEG/PPG-20/20 Dimethicone). Surface activity of the two compounds was high and it was confirmed by surface tension measurements. In this study, motion resistance and wear of steel were determined in the presence of aqueous solutions of selected silicone derivatives as model lubricating substances. The tests were carried out using a T-11 testing apparatus produced by the Institute for Sustainable Technologies in Radom. It has been found that the cationic surfactant considerably decreases motion resistance in comparison with its nonionic equivalent in the low concentration range of the order of a few percent.

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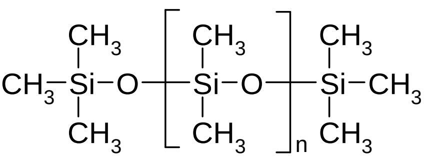
1. Introduction

Lubricants based on silicone oils have been used in lubrication practice for a number of years [1–3]. They exhibit high thermal resistance, low susceptibility to oxidation and are resistant to the action of aggressive chemical agents. They can be used in a wide temperature range of from sub-zero temperatures of the order of about fifty degrees to above-zero temperatures of the order of several hundred degrees Celsius. Silicones are physiologically and biologically neutral. This brief characterisation indicates that the presence of a silicone chain in a molecule makes it possible to formulate silicone-based materials having properties that cannot be obtained using hydrocarbons [1-3].

The object of this investigation are lubricating substances based on water whose poor lubricating properties are modified by surface active compounds used as additives [4-6]. Quaternary diamide polydimethylsiloxane (INCI: Quaternium-80, trade name: Abil Quat 3474, manufacturer: Evonik Chemicals) with positive charges at two quaternary nitrogen atoms was selected for this investigation. The results of physicochemical and tribological tests obtained for aqueous solutions of Quaternium-80 (cationic surfactant) were referred to in an analogous study carried out for a linear silicone polyether (INCI: Bis-PEG/PPG-20/20 Dimethicone trade name: Abil 8832, manufacturer: Evonik Chemicals). The hydrophilic part of this nonionic surfactant was an ethylene oxide chain while a silicone backbone formed the hydrophobic part.

2. Properties of silicones and silicone polyethers

Silicone oils (Formula 1) are clear, tasteless, odourless liquids. They exhibit high resistance to low temperatures (up to -50^0 C) and high temperatures (up to 250^0 C). Their viscosity (from several to as much as a few million mPa·s) depends on their molecular mass and varies slightly with temperature. Silicones are resistant to oxidation and to the action of aqueous solutions of acids, bases, and salts. They do not hydrolyse readily [1, 7, 8].



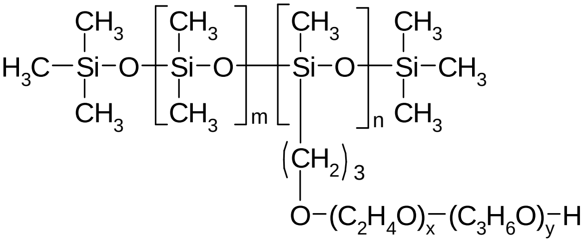
(1)

Structural formula of polydimethylsiloxane
Wzór strukturalny polidimetylosiloksanu

Silicone oils exhibit good wettability of various types of materials. They have considerable hydrophobing properties and are used as antifoaming agents. The compounds are physiologically neutral and safe for the environment [1, 7, 8].

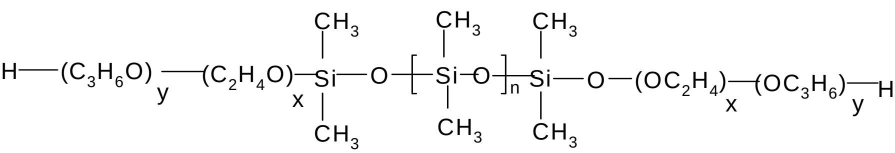
Lubricant films can break and be squeezed out of the friction zone by external loads under friction conditions. This is more likely in the case of a metal/metal contact, but less likely in the case of metal/plastic or plastic/plastic contacts [2].

An attempt has been made in this study to apply silicone derivatives that, apart from the hydrophobic part, would have a hydrophilic part [9]. These derivatives retain the properties of silicones but, additionally, show affinity for water and hydrophilic surfaces [7–8]. The compounds having such properties are silicone glycols, also called silicone polyethers, polyether polysiloxanes or PEG/PPG Dimethicone (Formulas 2 and 3).



(2)

Structural formula of comb-like silicone glycol
Wzór strukturalny glikolu silikonowego o budowie grzebieniowej



(3)

Structural formula of block silicone glycol
Wzór strukturalny glikolu silikonowego o budowie blokowej

Silicone polyethers are a group of nonionic surfactants. They are capable of forming micelles in solutions but, in contradistinction to hydrogen-based surfactants, their surface activity is higher [7-8].

Surface activity, solubility, and miscibility with solvents and other constituents can be modified at the stage of the synthesis of the compounds. In order to obtain the desired properties, the compounds are assigned an appropriate structure, an organosilicone chain length, and the lengths of ethylene oxide (PEG) and propylene oxide (PPG) chains. An increase in the number of PEG groups leads to an increase in water solubility, and an increased number of PPG groups increase solubility in nonpolar media [1].

The application of silicone glycols as additives modifying lubricating properties of water is interesting [9]. Aqueous solutions of silicone glycols (c = 1 - 80%) and "pure" compounds (c = 100%) were suggested as model lubricants. The effectiveness of lubricating substances was tested based on the estimation of motion resistance and antiwear properties.

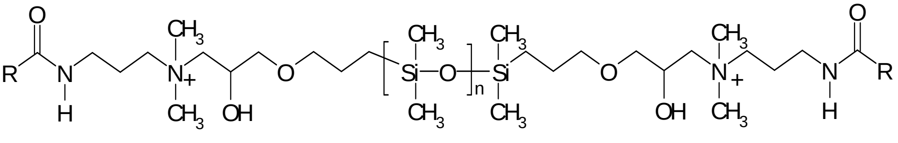
Based on the tests carried out at constant loads (10 and 50 N) and using a ball-on-disc tribosystem (T-11 testing apparatus), it was shown that there was no decrease in motion resistance and wear at low concentrations of polyethers (1, 4, 10%) [9]. It can even be stated that the quantities tend to increase slightly relative to water. Friction conditions change dramatically in the case of the concentrations of the order of forty percent, where the value of μ drops as much as nearly fourfold. The character of $\mu(c)$ changes at both 10 N and 50 N loads is similar. The lowest μ values (as low as 0.07) were observed for pure compounds at both 10 N and 50 N. Such low motion resistance indicate fluid friction in which friction couple surfaces are fully separated by a lubricant film. The results of the tests conducted at 10 and 50 N showed that the wear of friction couples decreased with concentration of the compounds. The lowest wear was observed in the case of pure compounds (wear scar diameters were even more than threefold smaller than those for water) [9].

3. Structure and surface activity of selected silicone derivatives

As mentioned above, silicone polyethers (nonionic surfactants) efficiently modify lubricity of water at the concentrations of forty percent. However, at the concentrations of several percent, the effect of the additive is modest and it is even possible to observe an increase in motion resistance and wear [9].

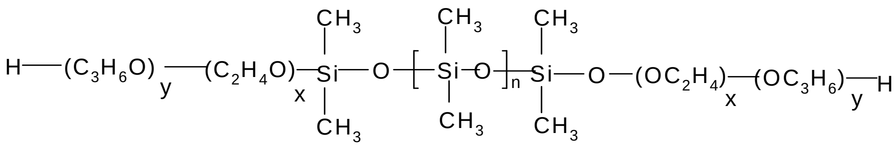
In view of the beneficial properties of silicones and their derivatives, as well as the concentration range in which the additives are used (of the order of 1%), an attempt was made to search for other silicone derivatives that would be effective at low concentrations.

The analysis of literature data and our own research indicates that the formation of the surface phase is connected not only with the hydrophobic effect but also with the interactions of molecules with the solid surface [4, 10]. In the case of nonionic surfactants, these are hydrogen bonds and also weak dispersive interactions. They may not be strong enough to produce the surface phase that, under friction, transforms into a lubricant film having high resistance to mechanical and thermal loads. Therefore, an ionic surfactant (a cationic organosilicone compound) was selected for the studies as an additive to water. Its structure is presented below (see Formula 4).


(4)

Structural formula of Quaternium-80
Wzór strukturalny Quaternium-80

There are two positively charged quaternary nitrogen atoms at the ends of the silicone chain. The results obtained for the solutions of this compound will be referred to as solutions of silicone glycol (INCI: Bis-PEG/PPG-20/20 Dimethicone) that, just like Quaternium-80, is linear and having ethylene oxide and propylene oxide chains at the end of the silicone chain (Formula 5).


(5)

Structural formula of Bis-PEG/PPG-20/20 Dimethicone
Wzór strukturalny Bis-PEG/PPG-20/20 Dimethicone

Surface activity of the solutions of both compounds (Formulas 4 and 5) was compared. Its measure was surface tension (σ) determined by means of the ring detachment method (Lauda Tensiometer TD1) (Fig. 1). The measurements were made for aqueous solutions of the compounds with the concentrations of 0.001-5% - Quaternium-80 and 0.01-10% - Bis-PEG/PPG-20/20 Dimethicone.

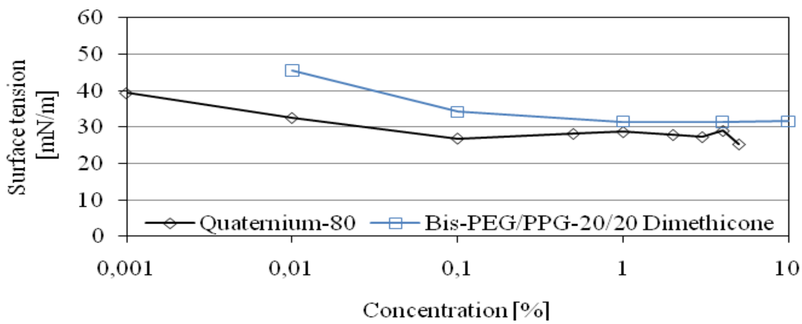


Fig. 1. Dependence of surface tension on concentration of aqueous solutions of Quaternium-80 and Bis-PEG/PPG-20/20 Dimethicone. The value of surface tension for water is about 72 mN/m
Rys. 1 Zależność napięcia powierzchniowego od stężenia wodnych roztworów Quaternium-80 oraz Bis-PEG/PPG-20/20 Dimethicone. Wartość napięcia powierzchniowego wody ok. 72 mN/m

The differences found can be interpreted as a result of stronger interactions of the ionic surfactants with the surface.

Viscosity is one of the more important quantities that may affect tribological properties of a lubricating substance. Therefore, viscosity of the solutions as a function of additive concentration was compared just before the tribological tests. The studies were carried out using aqueous solutions of silicones of the same concentrations as those used in surface tension measurements. The results are given in Fig. 2.

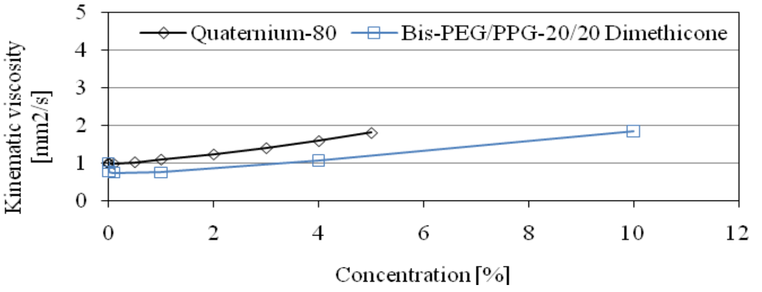


Fig. 2. Dependence of kinematic viscosity on concentration of aqueous solutions of Quaternium-80 and Bis-PEG/PPG-20/20 Dimethicone
Rys. 2. Zależność lepkości kinematycznej od stężenia wodnych roztworów Quaternium-80 oraz Bis-PEG/PPG-20/20 Dimethicone

The values of viscosity coefficients are so low in the concentration ranges used that they will not affect tribological properties of the lubricants tested.

4. Tribological properties

The evaluation of tribological properties was carried out for 1-5% aqueous solutions of Quaternium-80 and 1–10% aqueous solutions of Bis-PEG/PPG-20/20 Dimethicone. The measurements were made for 3 loads (10, 30, and 50 N) to determine the coefficient of friction (μ) and wear scar diameter (d). The methods presented in the literature [11] were applied. For tribological measurements steel samples (ŁH15) were used. Ball of the diameter equal to 0.5" was used as a sample. The disc of the diameter equal to 25 mm, surface roughness Ra = 0.16 μm was used as a counter-sample.

The solutions of cationic surfactants have lower friction coefficients than water, which is the base of the model lubricants analysed (Fig. 3).

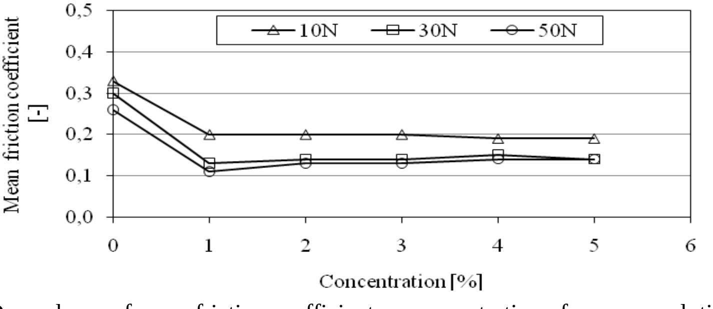


Fig. 3. Dependence of mean friction coefficient on concentration of aqueous solutions of Quaternium-80. Tribological test, T-11 testing apparatus, steel ball-steel disc couple, test duration 900 s, sliding velocity 0.1 m/s, radius 10 mm, loads 10, 30 and 50 N
Rys. 3. Zależność średniego współczynnika tarcia od stężenia wodnych roztworów Quaternium-80. Badanie tribologiczne, aparat T-11, skojarzenie kulka stalowa–tarcza stalowa, czas testu 900 s, prędkość poślizgu 0,1 m/s, promień 10 mm, obciążenia 10, 30 oraz 50 N

After using Quaternium-80 in the lowest concentration (c = 1%) μ values were even 2 times lower in comparison to water, as a base. Further growth of cationic silicone concentration generally didn`t cause changes in the μ values. The reason of changes could be related with Quaternium-80 surface activity (Fig. 1) and the possibility of micells appearance in water solutions.

As it has already been mentioned in Chapter 2, motion resistance for a nonionic surfactant (Bis-PEG/PPG-20/20 Dimethicone) are relatively high, comparable and even higher than those observed in the presence of water (Fig. 4).

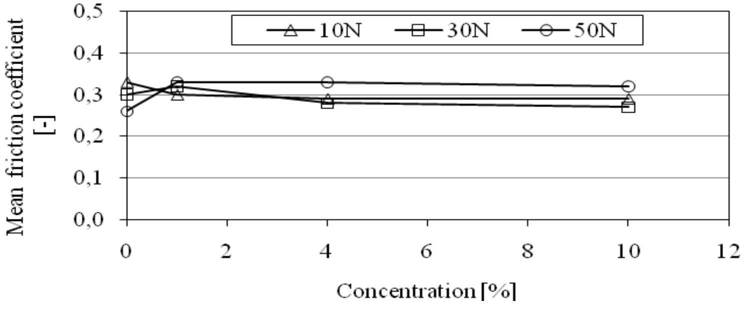


Fig. 4. Dependence of mean friction coefficient on concentration of aqueous solutions of Bis-PEG/PPG-20/20 Dimethicone. Tribological test, T-11 testing apparatus, steel ball-steel disc couple, test duration 900 s, sliding velocity 0.1 m/s, radius 10 mm, loads 10, 30 and 50 N
Rys. 4. Zależność średniego współczynnika tarcia od stężenia wodnych roztworów Bis-PEG/PPG-20/20 Dimethicone. Badanie tribologiczne, aparat T-11, skojarzenie kulka stalowa–tarcza stalowa, czas testu 900 s, prędkość poślizgu 0,1 m/s, promień 10 mm, obciążenia 10, 30 oraz 50 N

In the case of all the concentrations and loads, the μ values are higher than threefold for Bis-PEG/PPG-20/20 Dimethicone solutions than for Quaternium-80 (Figs 3 and 4). The largest changes in the μ value as a function of Quaternium-80 concentration can be observed up to 1%. Above this concentration, the coefficient of friction stabilises within the measurement error limits (0.01). Another tendency observed is a drop in the μ value with an increase in load. The drop is quite considerable with the load change from 10 to 30N but less so with the 30 to 50N change (Fig. 3). The maximum decrease in the μ value for individual loads (10, 30, 50N) relative to water is 1.6, 2.3, and 2.4, respectively. Thus, at moderately high loads (10-50N) the lowest decrease was observed for 10N, while the decreases for 30 and 50N are comparable and higher than those for 10N.

The analysis of Fig. 5 indicates that the action efficiency of Quaternium-80 as an antiwear additive is low.

Wear scar diameters (d) obtained after applying Quaternium-80 range from 0.58 to 0.70 mm (see Fig. 5), and thus they are larger for the model lubricants proposed than for water (d = 0.50 - 0.57). The results may indicate chemical wear resulting from the reaction of ionic surfactants with the steel surface.

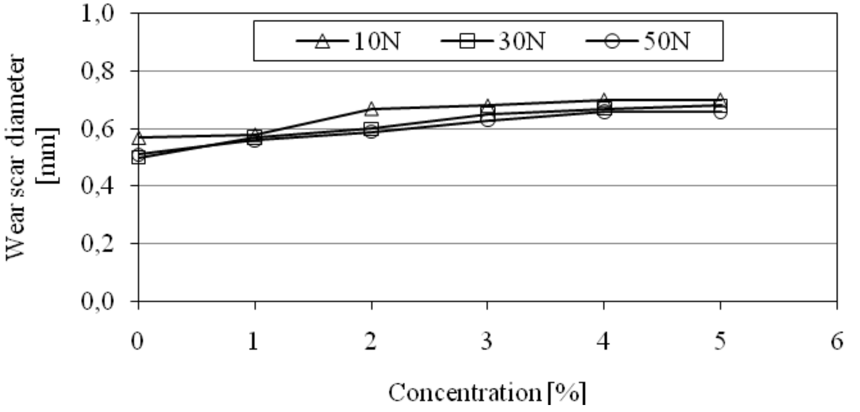


Fig. 5. Dependence of wear scar diameter on concentration of aqueous solutions of Quaternium-80. Tribological test, T-11 testing apparatus, steel ball-steel disc couple, test duration 900 s, sliding velocity 0.1 m/s, radius 10 mm, loads 10, 30 and 50 N
Rys. 5. Zależność średnicy skazy kulki od stężenia wodnych roztworów Quaternium-80. Badanie tribologiczne, aparat T-11, skojarzenie kulka stalowa–tarcza stalowa, czas testu 900 s, prędkość poślizgu 0,1 m/s, promień 10 mm, obciążenia 10, 30 oraz 50 N

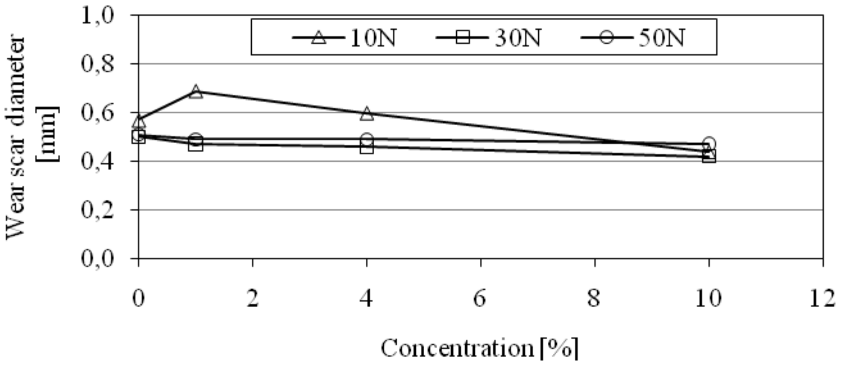


Fig. 6. Dependence of wear scar diameter on concentration of aqueous solutions of Bis-PEG/PPG-20/20 Dimethicone. Tribological test, T-11 testing apparatus, steel ball - steel disc couple, test duration 900 s, sliding velocity 0.1 m/s, radius 10 mm, loads 10, 30 and 50 N
Rys. 6. Zależność średnicy skazy kulki od stężenia wodnych roztworów Bis-PEG/PPG-20/20 Dimethicone. Badanie tribologiczne, aparat T-11, skojarzenie kulka stalowa–tarcza stalowa, czas testu 900 s, prędkość poślizgu 0,1 m/s, promień 10 mm, obciążenia 10, 30 oraz 5 0N

Nonionic surfactants exhibit slightly better antiwear properties (Fig. 6). Wear of the balls decreases slightly as a function of increasing concentration of an additive relative to wear observed when water is used as a base. The maximum drop in the d value of the solutions relative to water is several percent (4% solutions).

5. Summary

Organosilicone compounds possess a number of interesting physicochemical properties that form the basis for their application as active constituents of lubricating substances. Silicones are, however, insoluble in water and that considerably limits their application range. Therefore, the subjects of this study are water-soluble silicone polymers [9]. Used as additives, they show high efficiency only in the case of high concentrations of the order of forty percent. As additives modifying tribological properties of bases, they are used primarily at the concentrations of the order of several percent, and an attempt was made to find silicone derivatives which would improve tribological properties in this concentration range.

The silicone selected for the investigation was an ionic one (Quaternium-80) and the investigation results were referred to water as a base and to aqueous solutions of a nonionic silicone (Bis-PEG/PPG-20/20 Dimethicone). The analysis of the results obtained indicates that, for the ball-disc tribosystem (T-11 testing apparatus) and loads of above 10 N, the ionic surfactant considerably affects a reduction in the coefficient of friction both relative to water (about twofold) and relative to the nonionic silicone solutions (about threefold). Wear, however, is comparable or even higher than the one for water.

The beneficial effect of the ionic silicone additive on the reduction in motion resistance can be explained by stronger, compared to the nonionic surfactant, interactions with the steel surface; whereas, high wear can be attributed to the chemisorption of additives.

The application of silicone water solutions as lubricants is predicted in friction pairs were leakage or human skin contact may appear, and in machines used in cosmetic industry, pharmaceutic and household products manufacturing.

Acknowledgments

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References

[1] Rościszewski P., Zielecka M.: Silikony – właściwości i zastosowanie, Wydawnictwo Naukowo-Techniczne, Warszawa, 2002.
[2] Capporiccio G., Cann P.M., Spikes H.A.: Additives for fluorosilicone oils at high temperature, Wear, 193, 1996, 261-268.
[3] Ni S.C., Kuo P.L., Lin J.F.: Antiwear performance of polysiloxane-containing copolymers at oil/metal interface under extreme pressure, Wear, 253, 2002, 862-868.
[4] Sułek M.W.: Wodne roztwory surfaktantów w inżynierii materiałowej systemów tribologicznych, Wydawnictwo Instytutu Technologii Eksploatacji, Radom, 2009.

[5] Sułek M.W, Wasilewski T., Influence of critical micelle concentration (CMC) on tribological properties of aqueous solutions of alkyl polyglucosides, Tribology Transaction, 52, 2009, 12-20.
[6] Sułek M.W., Wasilewski T., Zięba M.: Tribological and physical-chemical properties aqueous solutions of cationic surfactants, Industrial Lubrication and Tribology, 2010, 62/5, 279-284.
[7] Hill R.: Silicone surfactants, Marcel Dekker, New York, 1999.
[8] Maciejewski H., Marciniec B.: Polietery silikonowe. Synteza, właściwości, zastosowania, Przemysł Chemiczny, 2(82), 2006, 138-141.
[9] Sułek M.W., Zięba M., Polietery silikonowe jako efektywne dodatki modyfikujące właściwości smarne wody, Tribologia, 3/2009, 226, 247-256.
[10] Nagatani N., Fukuda K., Suzuki T.: Interfacial behaviour of mixed systems of glycerylether-modified silicone and polyoxyethylene-modyfied silicone. Journal of Colloid and Interface Science, 234, 2001, 337-343.
[11] Piekoszewski W., Szczerek M., Wulczyński J: Urządzenie typu trzpień-tarcza do badań tribologicznych w podwyższonych temperaturach, Tribologia, 5-6, 1997, 826-832.

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Rola pochodnych silikonów jako dodatków modyfikujących właściwości smarne wody

S t r e s z c z e n i e

Oleje silikonowe są stosowane jako substancje smarowe względnie dodatki modyfikujące właściwości smarowe baz olejowych. Związki te wykazują jednak brak rozpuszczalności w wodzie. Dlatego jako dodatki poprawiające smarność wody wytypowano rozpuszczalne w wodzie pochodne silikonowe. Są nimi: czwartorzędowy diamidopolidimetylosiloksan (Quaternium-80), zaliczany do surfaktantów kationowych oraz oksyetylenowany silikon, należący do grupy niejonowych związków powierzchniowo czynnych (Bis-PEG/PPG-20/20 Dimethicone). Aktywność powierzchniowa obydwu związków w wodzie jest wysoka i została potwierdzona przez pomiar napięcia powierzchniowego. W prezentowanej pracy wyznaczone zostały opory ruchu i zużycie stali w obecności wodnych roztworów wybranych pochodnych silikonowych, jako modelowych substancji smarowych. Testy prowadzono za pomocą aparatu T-11, wyprodukowanego przez Instytut Technologii Eksploatacji w Radomiu. Stwierdzono, że w zakresie niskich stężeń, rzędu kilku procent, kationowy surfaktant zdecydowanie zmniejsza opory ruchu w stosunku do jego niejonowego odpowiednika.