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Adsorption and anti-corrosion properties od cuttingfluids for shear blades of glass-forming machines

ABSTRACT

The article presents the studies on the adsorption of water-miscible oil-containing cutting fluids on the R6M5 high-speed steel surface. The fluids can be used for the shear blades of drop feeders in glass-forming machines. The dependence of the anti-corrosion and lubricating properties of cutting fluids on their adsorption on steel surfaces is determined. The survey shows the serial G-417 cutting fluid achieves the highest adsorption value and anti-corrosion effect at a volumetric dilution of 1:4000, compared to the experimental cutting fluid based on G-417 at 1:1500. Based on the tests of the experimental cutting fluid at a glass factory, the experimental lubricant has greater operating dilution (1:1300) compared to the G-417 (1:800) at the same initial oil content. The higher lubricity of the new cutting fluid can be explained by the position of the adsorption maximum for the experimental mixture. The research formulates a necessary condition for improved operating characteristics, lubricity, and anti-corrosion properties of a cutting fluid by the selection of emulsifiers and functional additives for the cutting fluid: the proximity of the concentrations for maximum adsorption capacity and operating dilution ranges (1:800 - 1:2000). Electrochemical studies show that both the G-417 and experimental lubricant have anodic mechanism of corrosion inhibition.

Keywords: *Adsorption, cutting fluid, anti-corrosion effect, surface tension, wetting, polarization curves*

1. INTRODUCTION

In the glass bottle production, a stream of molten glass flowing from the drop feeder is cut into the required portions by the glass-cutting shear blades, then the bottles are formed. For proper operation, the shear blades should be sprayed with an aqueous emulsion. For production of the bottles without cutting marks, a cutting fluid is applied. During the treatment, the shear blades should be efficiently lubricated and protected from corrosion, i.e., prepared to a high-quality cutting of the melt drops. In addition, the cutting fluid should be low in consumption, environmentally safe, and easily mixed with water with formation of a stable water emulsion.

There is a wide range of cutting fluids for shear blades. As a rule, a cutting fluid is a mixture of oils and emulsifiers [1–3] or a synthetic composition based on surfactants [4]. Mineral, vegetable or synthetic oils can be used as the components providing lubrication. Mineral oils are usually low-cost, however, they can pollute wastewater and soil [5–7]. As a rule, shear blade cutting fluids based on mineral oils are used at a relatively low dilution (1:100 – 1:500) [1,3], so this cutting fluid type is considered to be uneconomical. The cutting fluids based on synthetic and vegetable oils have better lubricity, they are efficient at dilutions from 1:700 to 1:2000 [2,3] and can be completely biodegradable [3, 8].

During operation, the temperature of the molten glass mass can reach 1200°C [9,10], contributing to increased corrosion of the shear blades. The scratch-like defects on the blown bottles can be formed due to the presence of corrosion products on the blade surface. This can be avoided by introducing corrosion inhibitors into the cutting fluid composition. It should be taken into account, that, as a rule, corrosion resistance of high-speed steel grades is low. High-speed steel contains chromium, vanadium, and molybdenum [11–13]. In these steel grades, the content of chromium, responsible for corrosion resistance, is less than in

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stainless steel. Ethanolamine salts of fatty acids, sarcosinates, phosphate esters, and boric acid esters can be used as efficient corrosion inhibitors for cutting fluids [14,15].

The cutting fluid operates in a dynamic regime, some is continuously washed off and removed with the glass melt and emulsion. Thus, one of the requirements is a good adsorption of the cutting fluid on the blade surface. For improved adsorption, it is necessary to select surfactants that increase adsorption of the cutting fluid in the operating dilutions range.

Perm LLC „NPP Sintez" produces a Gelltex-417 [BW1] [U2] [U3] cutting fluid for shear blades [16]. The dilutions recommended by the manufacturer are in the range 1:800 – 1:1000. The cutting fluid contains mineral oil, vegetable oil and a nonionic emulsifier – oxyalkylated fatty alcohol.

A laboratory sample based on the G-417 was developed, some emulsifiers, corrosion inhibitors and bactericidal additives were introduced into the G-417 composition [17]. Modification of the G-417 cutting fluid was carried out for improvement of its consumer characteristics – anti-corrosion protection of the shear blades, increasing the blade service life, cutting fluid resistance to bacterial contamination. Present study is aimed at:

- revealing the emulsifier effect on the adsorption of the initial and experimental cutting fluids on the surface of R6M5 steel;
- establishing the dependence of anti-corrosion effect on the amount of adsorbed cutting fluid at various concentrations;
- determination of the relationship between the cutting fluid adsorption and operating dilution range;
- research of the mechanism of the corrosion inhibition of the lubricants.

2. EXPERIMENTAL

To improve the anti-corrosion effect, a corrosion inhibitor from among amines and a phosphorus-containing anionic surfactant were added to the G-417 cutting fluid. These additives were selected, assuming that the combination of amine and phosphorus-containing compounds can provide an efficient corrosion protection due to the synergistic action of the inhibitors [18]. In addition, the presence of ionic surfactants contributes to stability of the aqueous cutting fluid emulsion [19, 20]. A novel sample was designated as ES (experimental sample). Table 1 shows the compositions of the prototype and novel cutting fluids [19].

Table 1. Compositions of G-417 and experimental sample.

Cutting fluid	Components
G-417	A mixture of mineral and vegetable oils (75-85%), non-ionic emulsifier (15-25%)
ES	A mixture of mineral and vegetable oils (75-85%), non-ionic emulsifier (15-25%), amine type corrosion inhibitor (2%), anionic emulsifier (3%), bactericidal additive (1%)

The percentage of mineral and vegetable oils in the cutting fluid is not disclosed, however, it is the same in the G-417 and ES. Thus, the cutting fluid compositions differ only in the content of the emulsifiers and functional additives.

2.1. Adsorption characteristics of the cutting fluids

To evaluate the effect of emulsifiers and additives on the cutting fluid adsorption on the steel surface, the surface tension of the cutting fluid emulsions and the contact angle of the cutting fluid emulsions on steel were determined in the dilution range of 1:8000 – 1:200. Surface tension σ and contact angle Θ were measured using a Kruss DSA25 drop shape analyzer. The hanging drop and sessile drop methods were used [21 – 23]. The adsorption value was calculated by the formula [24, 25]:

$$\Gamma_{S-L} = \frac{1}{RT}\frac{d(\sigma_{L-G}\cos\Theta)}{d(\ln C)} \quad (1)$$

where Γ_{S-L} – adsorption at the solid-liquid interface, σ_{L-G} – surface tension at the liquid-gas interface, Θ – contact angle; *C* – cutting fluid concentration (dimensionless).

The cutting fluid concentration was calculated by formula:

$$C = \frac{V_{lubricant}}{V_{water}} \quad (2)$$

where $V_{cutting\ fluid}$ – the volume of cutting fluid required for emulsion preparation, V_{water} – the volume of water.

Equation (1) can be written as:

$$\Gamma_{S-L} = \frac{\cos\Theta}{RT}\frac{d(\sigma_{L-G})}{d(\ln C)} + \frac{\sigma_{L-G}}{RT}\frac{d(\cos\Theta)}{d(\ln C)} \quad (3)$$

That is, the parameters, determining the cutting fluid adsorption, are the surface tension of its aqueous emulsion and wetting of steel surface by the cutting fluid emulsion. These parameters can be varied by changing the composition, and, at the same time, the type of adsorption isotherm is likely to be changed as well.

2.2. Gravimetric tests

The anti-corrosion effect is determined according to the GOST 9.506-87 state standard (Russian Federation) [26]. The household drinking water was used as a corrosive medium. The gravimetric measurements were carried out at room temperature. When corrosion occurs at elevated temperatures, a continuous dark coating, or patina, can be formed on the samples, and the weighing is not accurate. The corrosion parameters of steel at various cutting fluid concentrations are assumed to be more accurate when conducting the corrosion tests at room temperature. This is important for the relationship between the cutting fluid anti-corrosion effect and its adsorption on the steel surface to be determined.

For the gravimetric tests, the R6M5 steel plates were used with dimensions of 30*20*2 mm. The elemental composition of carbon steel is as follows: C (< 0.9), Si (< 0.5), Mn (< 0.5), Cr (< 4.4), W (< 6.5), Mo (< 5.3), V (< 2.1) and Fe (remainder). The samples were subjected to a corrosive medium for 24 hours. Gravimetric corrosion parameters were calculated by the formula:

$$K = \frac{\Delta m}{S \times t} \quad (4)$$

where *K* – corrosion rate (g/m^2*h); Δm – weight difference of the samples before and after tests, g; S – surface area of the samples, m^2; t – exposure time of the samples in a corrosive medium, h.

The protective effect *Z* was calculated by the equation:

$$Z = \frac{K_1 - K_2}{K_1} \times 100\% \quad (5)$$

where K_1 – corrosion rate in an uninhibited medium (without cutting fluid), g/m^2·h; K_2 – corrosion rate in the cutting fluid emulsion, g/m^2·h.

After removing of corrosion products, the sample surface images were acquired using an Olympus BX51 optical microscope at 1000x magnification.

2.3. Electrochemical study of the corrosion inhibition by the cutting fluids

The mechanism of the anti-corrosion effect of the lubricants was studied by the method of polarization curves. The curves were recorded using a P-8 potentiostat-galvanostat with a potential sweep rate of 1 mV/s. The working electrode was made of R6M5 steel and had an area of 1 cm^2. A silver chloride electrode was used as a reference electrode, and a platinum electrode was used as an auxiliary electrode. The volumetric dilution of the lubricant was 1:1000. To determine the mechanism of the protective action of lubricants, the inhibition coefficients of partial corrosion reactions were calculated using the formula:

$$\gamma_{a,c} = \frac{i_{blank\,(a,c)}}{i_{lubricant(a,c)}} \quad (6)$$

where $i_{blank(a,c)}$ – corrosion current density in “blank” water (without lubricant), $i_{lubricant\ (a,\ c)}$ – corrosion current density in lubricant emulsion; “a” and “c” refer to anodic and cathodic reactions, respectively.

The corrosion current *i* was calculated using the CView2 program by extrapolating the linear sections of the polarization curves. The electrochemical protective effect *z* was calculated by the formula:

$$z = \left(1 - \frac{i}{i_{blank}}\right) \times 100\% \quad (7)$$

where *i* – corrosion current in lubricant emulsion, i_{blank} – corrosion current in water.

3. RESULTS AND DISCUSSION

Introduction of the additives results in a significant increase in the cutting fluid surface activity compared to the G-417. This is reflected in a more pronounced steepness of the falling branch on the surface tension isotherm (Fig. 1). In addition, a surface tension value of 30 mN/m is achieved at lower cutting fluid concentrations. This may be due to the synergistic effects, usually observed in the systems containing surfactants of various classes [27, 28].

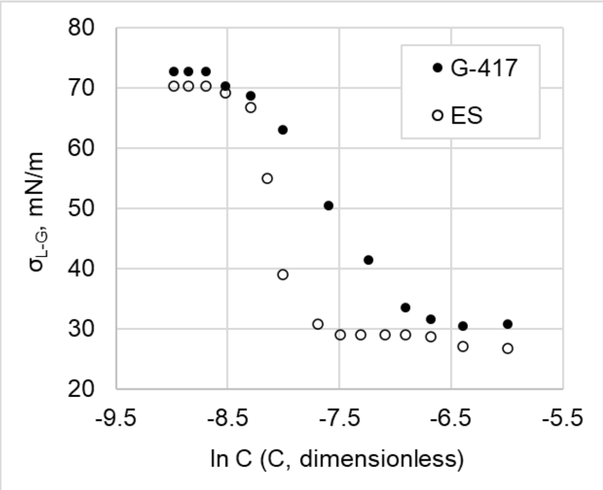

Figure 1. Surface tension isotherms

Wetting isotherms of the cutting fluids have a similar shape (Fig. 2). The surface contact angle decreases with increasing cutting fluid concentration in the emulsion, this wetting pattern being typical for many surfactants [29 – 31]. However, in the case of the experimental sample, the slope of the isotherm is lower compared to G-417. At dilutions less than 1:1800 (ln *C* > -7.5), the contact angle value for the experimental sample is close to constant. In a high dilution range (ln *C* < -8.5), the wetting of the steel surface by the experimental cutting fluid emulsion is somewhat better than by the G-417 emulsion.

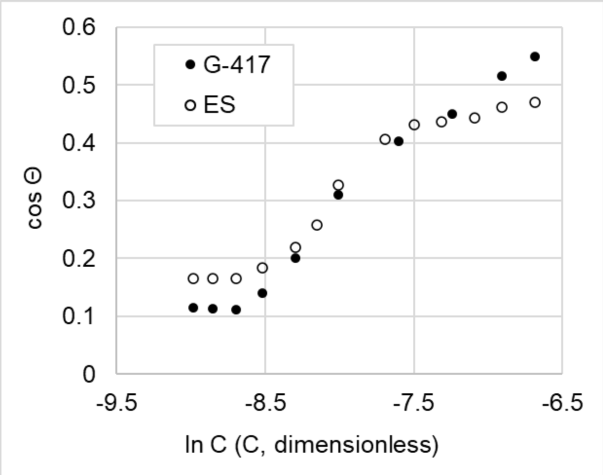

Figure 2. Wetting isotherms

The adsorption curves pass maximum at a dilution of 1:4000 and 1:1500, for G-417 and ES, respectively (Fig. 3). For the relationship between the adsorption value and protective effect to be established, the gravimetric tests were carried out at the cutting fluid dilution ranges corresponding to the adsorption and desorption branches of the isotherm, and, finally, at the dilution in the adsorption maximum (Table 2).

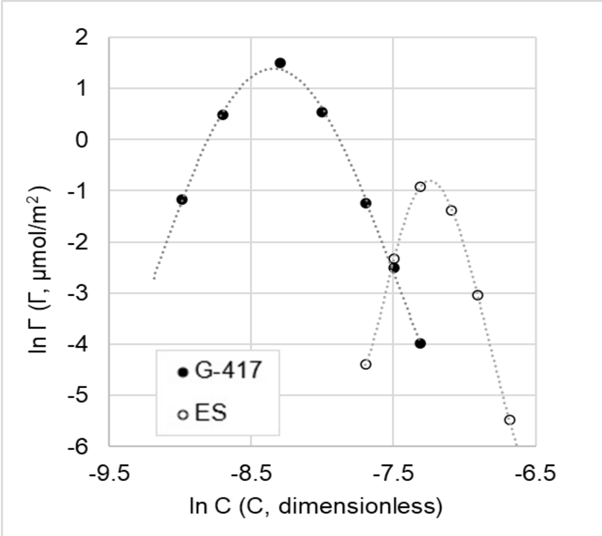

Figure 3. Adsorption isotherms. For ease of comparison, the curves are presented in logarithmic coordinates

Table 2. Adsorption and anti-corrosion effect of G-417 and ES cutting fluids

Cutting fluid	Dilution	$C*10^4$	Γ, μmol/m^2	K, g/m^2*h	Z, %
G-417	1:6000	1.67	1.62	0.039	45
	1:4000	2.50	4.48	0.028	61
	1:3000	3.33	1.71	0.055	24
	1:1000	10	0.02	0.048	33
ES	1:2000	5.00	0.04	0.021	71
	1:1500	6.67	0.40	0.016	79
	1:1000	10	0.01	0.017	76
Blank	-	-	-	0.072	-

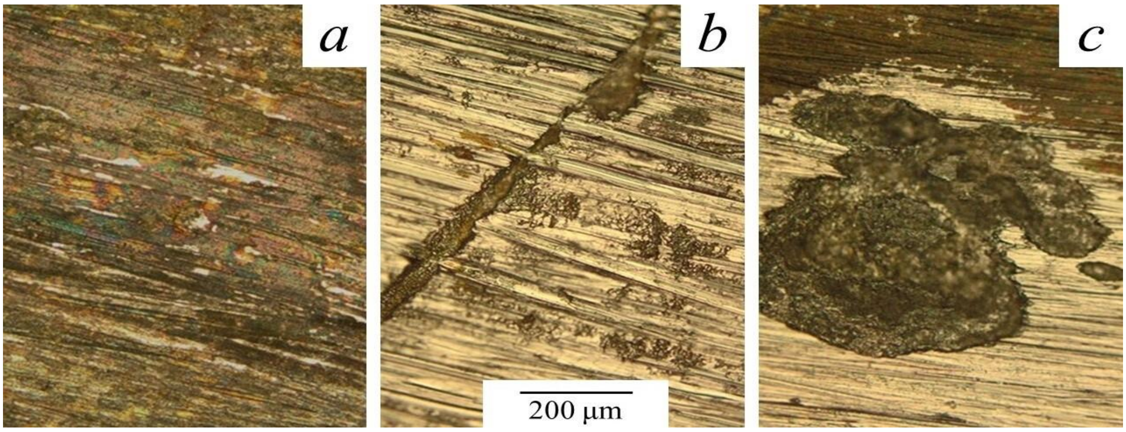

Figure 4. Steel surface images after removing of the corrosion products, corrosive media – G-417 emulsions, dilutions: a) 1:6000, b) 1:4000, c) 1:3000; zoom x1000

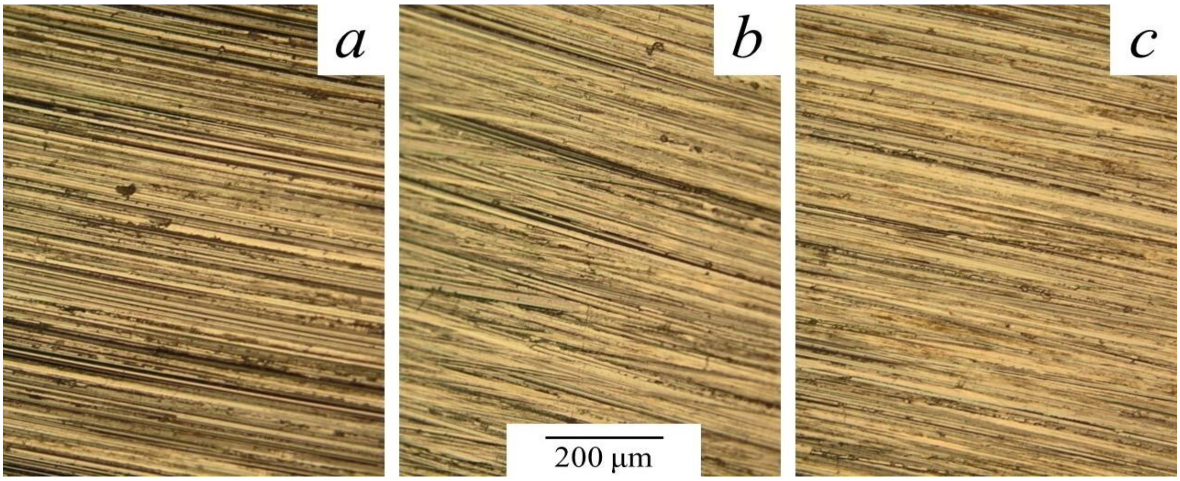

Figure 5. Steel surface images after removing of the corrosion products, corrosive media – ES emulsions, dilutions: a) 1:2000, b) 1:1500, c) 1:1000; zoom x1000

For both cutting fluids, the highest anti-corrosion effect was observed at the dilutions near the adsorption maximum, which correlates with the behavior of adsorption-type corrosion inhibitors [32 – 34]. However, the G-417 adsorption maximum lies within a high dilution range, and at these dilutions the cutting quality is unsatisfactory. In contrast to the G-417, the ES adsorption maximum is near the concentration range, suitable for an efficient cutting.

At the same time, for the experimental cutting fluid, the anti-corrosion effect is less dependent on the adsorption value in the dilution range of 1:2000 – 1:1000 than in the case of the G-417 cutting fluid in the dilution range of 1:6000 – 1:3000. This fact can be explained by the presence of the efficient corrosion inhibitors in the ES composition.

According to the tests of the experimental cutting fluid at Roslavl Glass Factory, the novel composition provides an efficient cutting at a dilution of 1:1300, and the G-417 was used there before at a dilution of 1:800. Thus, the lubricity of the novel cutting fluid is higher than that of the G-417, the oil content being the same. The improved lubricity of the experimental cutting fluid is probably due to the higher adsorption values in the operating dilution range.

Thus, for the anti-corrosion effect and lubricity of a cutting fluid to be improved, the adsorption maximum should be shifted to the concentration range providing an efficient cutting. This can be achieved by selection of appropriate wetting agents, emulsifiers, corrosion inhibitors, and functional additives.

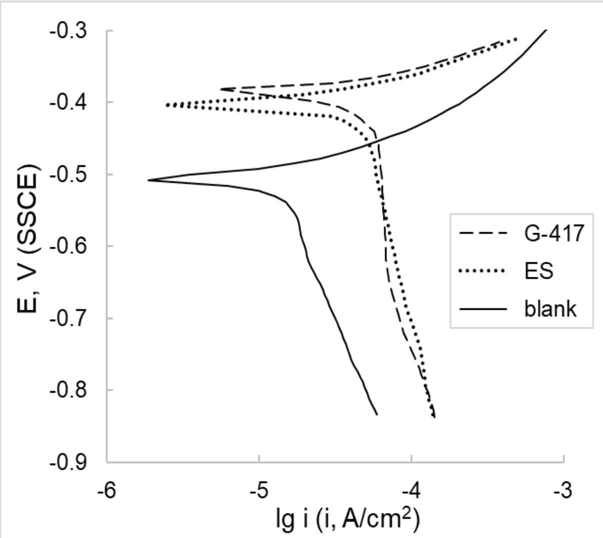

Figure 6. Polarization curves, 70°C, tap water

Table 3. Electrochemical characteristics of R6M5 steel by 70°C

Lubricant	E_0, V	i, μA/cm^2	z, %	γ_a (E = -0.35 V)	γ_c (E = -0.65 V)
-	-0.501	12	-	-	-
G-417	-0.369	58	-	3.7	0.4
ES	-0.419	11	8	3.2	0.3

The given polarization curves indicate that both studied lubricants have anodic mechanism of corrosion inhibition. Lubricants decrease the corrosion rate for the anodic process but increase cathodic corrosion rate. Addition of the lubricant to the corrosive medium shifts the corrosion potential towards positive values. Corrosion current density for G-417 turned out to be higher than for "blank" experiment, this contradiction with the results of gravimetric tests can be explained by shorter time of the electrochemical experiment.

4. CONCLUSIONS

1. The adsorption and anti-corrosion properties of the cutting fluids for the shear blades of glass-forming machines were studied.

2. A novel cutting fluid based on the serial G-417 product was developed. It can be used in greater dilutions compared to the prototype, due to its higher adsorption on steel surface at operating dilution, when compared to the G-417.

3. Among other factors, an insufficient anti-corrosion effect of the G-417 product could be attributed to its low adsorption values on steel surface at operating dilution.

4. To improve the lubricating and anti-corrosion properties of a cutting fluid, its adsorption in the operating concentration range should be increased. This can be achieved by a proper selection of the cutting fluid components.

5. Studied lubricants have anodic mechanism of corrosion inhibition.

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IZVOD

ADSORPCIJSKA I ANTIKOROZIONA SVOJSTVA TEČNOSTI ZA REZANJE NA MAŠINAMA ZA FORMIRANJE STAKLA

U radu su prikazane studije o adsorpciji tečnosti za rezanje koje se mešaju sa uljem i sadrže ulje na površini brzoreznog čelika R6M5. Tečnosti se mogu koristiti za smicanje sečiva kapalnih hranilica u mašinama za formiranje stakla. Utvrđena je zavisnost antikorozivnih i podmazujućih svojstava tečnosti za sečenje od njihove adsorpcije na čeličnim površinama. Istraživanje pokazuje da serijska tečnost za sečenje G-417 postiže najveću vrednost adsorpcije i antikorozivni efekat pri zapreminskom razblaženju od 1:4000, u poređenju sa eksperimentalnom tečnošću za sečenje na bazi G-417 u 1:1500. Na osnovu ispitivanja eksperimentalne tečnosti za sečenje u fabrici stakla, eksperimentalno mazivo ima veće radno razblaživanje (1:1300) u poređenju sa G-417 (1:800) pri istom početnom sadržaju ulja. Veća mazivost nove tečnosti za sečenje može se objasniti položajem adsorpcionog maksimuma za eksperimentalnu smešu. Istraživanje je formulisalo neophodan uslov za poboljšanje radnih karakteristika, mazivosti i antikorozivnih svojstava tečnosti za sečenje izborom emulgatora i funkcionalnih aditiva za tečnost za sečenje: blizina koncentracija za maksimalni kapacitet adsorpcije i radni opseg razblaživanja (1 :800 - 1:2000). Elektrohemijske studije pokazuju da i G-417 i eksperimentalno mazivo imaju anodni mehanizam inhibicije korozije.
Ključne reči: *Adsorpcija, tečnost za sečenje, antikorozivni efekat, površinski napon, vlaženje, polarizacione krive*

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