Study of anti-corrosion and adsorption properties of novel synthetic cutting fluids for the glass container industry

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Abstract

In present paper development of a synthetic cutting fluid for glass forming machines has been described. The cutting fluid is designed for lubricating and cooling of the drop feeder shear blades. An experimental sample composition is based on a commercial lubricant and additives, commercially available in Russia. During the research, a number of prototypes have been obtained. The sample with the maximum anti-corrosion effect to the R6M5 high-speed steel has been selected. For both the selected prototype and commercial lubricant, adsorption and anti-corrosion behavior has been studied. Anti-corrosion tests have been carried out in a circulating corrosive medium. Electrochemical properties have been studied by the polarization curves method. Isotherm of the adsorption of the lubricant on the R6M5 steel surface has been calculated using surface tension and wetting angle data. In both cases an anodic mechanism of corrosion inhibition has been established, the experimental cutting fluid being more efficient than the commercial one in terms of anti-corrosion effect in distilled and tap water. At dilutions above 1:1000, the experimental cutting fluid is characterized by higher adsorption values on the steel surface compared to the prototype. Tests of the new cutting fluid at a glass container plant showed that it can be used at the same dilution as the commercial cutting fluid – 1:1000. Thus, the lubricity of the experimental sample is comparable to that of the commercial product, which can be explained by the similar adsorption values of both cutting fluids on the shear blade surface at working dilution.

Introduction

During the operation of a glass-forming machine, the liquid glass mass, flowing from the drop feeder, is cut into the portions (drops) by special blades. Then from these glass drops

hollow glassware is manufactured. For continuous operation of the feeder shear blades, constant cooling and lubrication of the shear blades with an aqueous cutting fluid emulsion are required. The cutting fluid must provide an efficient cutting of the glass melt at low working concentrations, prevent corrosion of the blades. In addition, it should be non-toxic and ecologically safe.

There is a wide range of cutting fluids for shear blades. Cutting fluids can contain mineral, vegetable or synthetic oils. Vegetable oils have such advantages over mineral oils as higher lubricating properties, non-toxicity, and biodegradability. These oils can be produced from renewable resources. However, vegetable oils are often characterized by low thermal stability [1]. During operation, the feeder shear blades heat up, and vegetable oils are oxidized with formation of deposits on the blades [2]. Synthetic oils are more oxidation-resistant than vegetable oils, however, they are less biodegradable [3]. Some synthetic components of cutting fluids for the shear blades can be based on vegetable oils. At the same time, these products have high thermal stability [4], so the formation of solid deposits on the blades is avoided. Currently, there is a research trend for the development of environmentally friendly and biodegradable cutting fluids [5–7], so the cutting fluids for shear blades, based both on synthetic and natural components is a promising direction.

A working dilution range for shear blade cutting fluids is usually from 1:700 to 1:2000, this value being significantly higher than the one recommended for water-miscible cutting fluids used in metalworking. To prepare a cooling emulsion, a reservoir can be used, from which the emulsion is supplied to the shears [8], or more modern spray systems (for example, offered by Graphoidal Developments [9]) that provide automatic mixing of the cutting fluid with water immediately before the emulsion is supplied to the shears. The emulsion supply system must not be clogged due to the cutting fluid. Clogging can be triggered by a bacterial contamination of the emulsion [8] or by the interaction of fluid components with water hardness ions [4]. As a rule, shear lubricants based on mineral and vegetable oils are recommended for use in softened water [10], while synthetic cutting fluids can be used in water of any hardness [11].

The LLC "NPP Sintez" produces a Gelltex-425 (G-425) cutting fluid for shear blades [12]. A nonionic surfactant, an ester of a fatty acid and polyalkylene glycol, is the main component of this fluid, responsible for a lubricating effect. The cutting fluid also contains another non-ionic surfactant – an amine-type corrosion inhibitor, and a bactericidal additive. The G-425 fluid is designed for use in water of any hardness, it is biodegradable. The working dilution range of this fluid is 1:800–1:1300.

The corrosion inhibitor used in this cutting fluid is imported and has no analogues in Russia, which increases the product cost. Present paper is devoted both to the development of a novel synthetic cutting fluid without imported components in the composition and to the study of its anti-corrosion and adsorption properties. The G-425 was used as a prototype.

Materials and Methods

The component of the G-425 cutting fluid, polyalkylene glycol ester, was chosen as the base for the new synthetic fluid composition. This choice was dictated by the component availability in Russia and its sufficient water solubility. Thus, the only difference of the novel fluid from the prototype is the corrosion inhibitor composition. Various nitrogen-, sulfur-, and phosphorus-containing surfactants produced in Russia are studied as corrosion inhibitors. The benzalkonium tris(pentafluoroethyl)trifluorophosphate (BA-FAP) was obtained by methathesis reaction using HFAP acid. The main criterion for the inhibitor selection is the corrosion resistance of high-speed steel in presence of the novel cutting fluid. This parameter was evaluated by the gravimetric method.

The cutting fluid components were weighed, mixed in a glass beaker and stirred until a homogeneous liquid was formed. The compositions were tested for resistance to freezing and thawing in a freezer at −20°C. After freezing and thawing, the sample must be homogeneous, no separation or sedimentation should be observed.

Working emulsions of cutting fluids for shear blades must be stable for at least 24 h. During this period, no clots or drops of a non-emulsified fluid should be formed in the emulsion. So, emulsions of the test fluid compositions were prepared in dilutions of 1:1000 and 1:200. The emulsions should be homogeneous within 24 h.

The anti-corrosion effect was determined according to the GOST 9.506-87 (Russian Federation standards). In all gravimetric tests, the volumetric dilution of the fluid was 1:1000. The feeder shear blades are often made of high-speed steel, so the grade R6M5 high-speed steel was chosen as a test material. The corrosion test was carried out in distilled water for 24 h. The temperature of the corrosive medium was 70°C.

Corrosion rate was calculated by the formula:

$$K = \frac{\Delta m}{S \times t}$$

where K – corrosion rate (g/m^2·h); Δm – sample mass difference before and after testing, g; S – sample surface area, m^2; t – exposure time in a corrosive medium, h.

The anti-corrosion effect Z of the cutting fluid was calculated by the formula:

$$Z = \frac{K_1 - K_2}{K_1} \times 100\%$$

where K_1 – corrosion rate in water, K_2 – corrosion rate in a cutting fluid emulsion, g/m^2·h.

The most efficient sample in terms of corrosion protection in distilled water was chosen according to gravimetric tests and recommended for further testing. The following physicochemical characteristics were determined both for the sample and G-425 cutting fluid:

– anti-corrosion effect in the emulsion flow;
– the mechanism of anti-corrosion action by the method of polarization curves;
– adsorption on the steel surface in a range of dilutions.

For the gravimetric experiment in a flow, a GE-UEK-07 cell was used. To maintain constant circulation of the emulsion, the cell is equipped with a stirrer. Thus, a continuous spraying of blades with cutting fluid emulsion is simulated. The new cutting fluid should be as efficient as the G-425 in hard water, so in this experiment tap water was chosen as a corrosive medium. During the experiment, the temperature of 70°C was maintained using a laboratory stove. After the corrosion products were removed, the image of the sample surface was taken using an Olympus BX51 optical microscope at ×500 magnification.

The corrosion inhibition mechanism for the cutting fluids was studied by the method of polarization curves. The curves were recorded using an P-8 potentiostat-galvanostat. The surface area of the working electrode, made of the R6M5 steel, was 1 cm^2. The potential sweep rate was 1 mV/s. A silver chloride electrode was used as a reference electrode, and a platinum electrode was used as an auxiliary electrode. The cutting fluid dilution was 1:1000. The emulsions were thermostatted at 70°C.

The inhibition coefficients of the partial reactions were determined by the formula:

$$\gamma_{a,c} = \frac{i_{blank}}{i_{fluid\,(a,c)}}$$

where i_{blank} – the corrosion current density in water without cutting fluid, $i_{fluid\,(a,c)}$ – the corrosion current density in the cutting fluid emulsions for the anode and cathode reactions, respectively.

The stationary potential and corrosion current values were determined by extrapolation of the linear sections of polarization curves. The electrochemical protective effect was calculated by the formula:

$$Z = (1 - \frac{i}{i_{blank}}) \times 100\%$$

where i – the corrosion current density in a cutting fluid emulsion, i_{blank} – the corrosion current density in water without cutting fluid.

To calculate the adsorption of the cutting fluids on steel surface, the surface tension and wetting isotherms of aqueous cutting fluid emulsions were built. Surface tension was determined by the hanging drop method using a Kruss DSA25 drop shape analyzer. The contact angle of wetting of R6M5 steel by the emulsion was determined by the sessile drop method, for which a Kruss DSA25 device was also used.

Adsorption value was calculated by the formula [13]:

$$\Gamma_{S-L} = \frac{1}{RT} \frac{d(\sigma_{L-V} \cos\theta)}{d(\ln C)}$$

where C – the volume concentration of the cutting fluid (dimensionless), σ_{L-V} – the surface tension of the aqueous fluid emulsion at the liquid-air interface, θ – the contact angle of steel with water-cutting fluid emulsions.

To define the dilution range for the novel cutting fluid, its adsorption isotherm was compared with the one of the G-425. The working dilution range of a cutting fluid was assumed to be dependent on its ability to adsorb on the metal surface. The higher is the fluid adsorption in the working dilutions range, the more diluted fluid can be used.

Results and Discussion

Fatty amines, phosphonates, carboxylates, phosphate esters, and sarcosinates can be used as efficient corrosion inhibitors in a neutral environment [14–16]. However, when developing a cutting fluid composition, only the inhibitors soluble in its lipophilic component should be selected. For the test cutting fluid compositions, a number of corrosion inhibitors were used: phosphonate compounds, sodium salts of ethoxylated fatty alcohol carboxylates. However, these compounds were immiscible with the main component of the cutting fluid, so the fluid concentrate was opaque and heterogeneous. Thus, for the inhibitor in the novel composition, the following requirements were taken into account:

- the inhibitor must be soluble in the cutting fluid concentrate;
- the inhibitor must be available in Russia;
- the protective action of the novel cutting fluid, containing the inhibitor, must be equal to or greater than that of the G-425 cutting fluid.

Table 1 shows the composition and anti-corrosion effect for the test samples of cutting fluids. The exact inhibitor content is not disclosed. Since the lubricating component is an ester, it can be hydrolyzed in a highly alkaline medium, so the preferable pH-range of the novel cutting fluid is below 9. It was taken into account when selecting inhibitors, and the pH-value of the aqueous emulsions of cutting fluids in a dilution of 1:1000 was in the range 8–9.

Table 1. Test samples of cutting fluids: composition, R6M5 steel corrosion rate, anti-corrosion effect in distilled water.

No.	Corrosion inhibitor (percentage)	K, g/(m^2·h)	Z, %
G-425	Nonionic surfactant, amine class (10–30%)	0.027	78
1	Anionic sulfur-containing surfactant (20–25%)	0.061	50
2	Nonionic surfactant, amine class (1–3%), anionic surfactant, sulfonic acid class (2–5%), nonionic surfactant, alkoxylated fatty alcohol class (15–20%)	0.082	32
3	Nonionic surfactant, amide class (15–20%)	0.077	36
4	Nonionic surfactant, amide class (15–20%), bioactive cationic surfactant (BA-FAP) (2–5%)	0.073	45

No.	Corrosion inhibitor (percentage)	K, g/(m²·h)	Z, %
5	Nonionic surfactant, amide class (35–40%)	0.058	52
6	Nonionic surfactant, amide class (20–30%), anionic sulfur-containing surfactant	0.038	69
7	Anionic surfactant, amine class (20–30%)	0.006	95
8	Anionic surfactant, amine class (20–30%), nonionic surfactant, imidazoline class (2–5%)	0.019	84
9	Anionic surfactant, amine class (20–30%), anionic phosphorus-containing surfactant (2–5%)	0.010	92
10	Nonionic surfactant – fatty acid ester of alkanolamine (15–20%)	0.074	39
	Corrosive medium without cutting fluid	0.121	

The sample 7 demonstrates the highest anti-corrosion effect, in this case an anionic surfactant of the amine class effectively inhibits corrosion. In presence of the samples 1, 3–6, a continuous dark coating (patina) is formed on the steel surface due to corrosion process (Figure 1). The corrosion product layer could not be removed mechanically, and the corroded surface was cleared of it only by grinding. The formation of patina can lead to the failure of the shear blades, so it should be avoided.
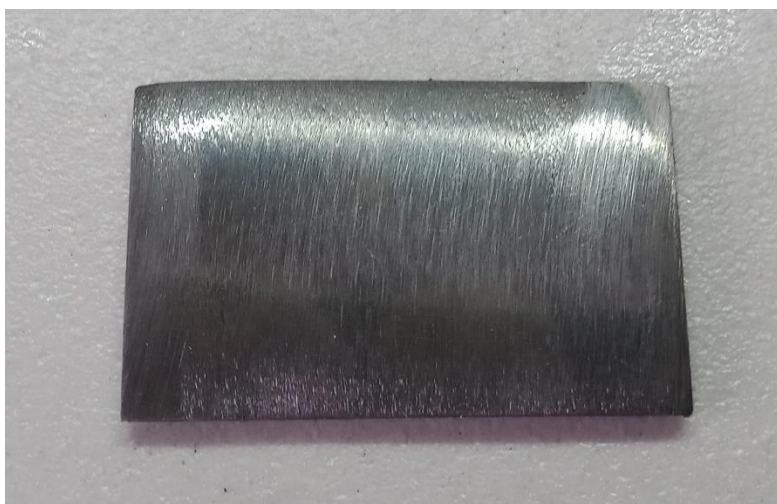

Figure 1. Patina on the steel surface after corrosion in the sample 3 emulsion.

A weak protection effect and formation of patina on the steel surface may be due to the fact that most of the corrosion inhibitors studied are efficient primarily in acidic media. For example, in numerous papers bioactive benzalkonium [17], imidazolium tris(pentafluoroethyl)trifluorophosphate (FAP) [18], imidazolines [19] and fatty acid amides

[20–24] are reported as acid corrosion inhibitors, however, there are fewer studies on anti-corrosion properties of these compounds in neutral media [25, 26]. According to [16], as a rule, the anti-corrosion effect of fatty acid amides is lower compared to fatty acid salts with the carbon chain of the same length. In addition, a relatively low corrosion resistance of high-speed steels should be taken into account [27].

The sample 9 also contains not only the anionic amine surfactant, as the sample 7, but also an anionic phosphorus-containing surfactant. In [28], the corrosion protective action of an oil-containing cutting fluid was found to be significantly improved when using a combined additive – an anionic phosphorus-containing surfactant and amine corrosion inhibitor. However, the sample 9, containing both an amine and a phosphorus-containing anionic surfactants, appeared to be less efficient than the sample 7. A decreased protective effect may be due to the hydrophilicity of this phosphorus-containing surfactant. The hydrophilic-lipophilic balance (HLB) value for this surfactant is 14, indicating its high solubility in water [29]. This inhibitor cannot be strongly adsorbed on the metal surface because of its high hydrophilicity [16, 30].

At the same time, a high anti-corrosion effect of a phosphorus-containing surfactant in the case of oil-containing cutting fluids was discussed in [28]. After the oil is adsorbed on the metal surface, the consequent adsorption of the hydrophilic surfactant is facilitated due to the interaction of its lipophilic fragments with oil.

The sample 7 was selected for further testing and designated as experimental sample (ES). Figure 2 shows the polarization curves for the G-425 fluid and experimental sample.
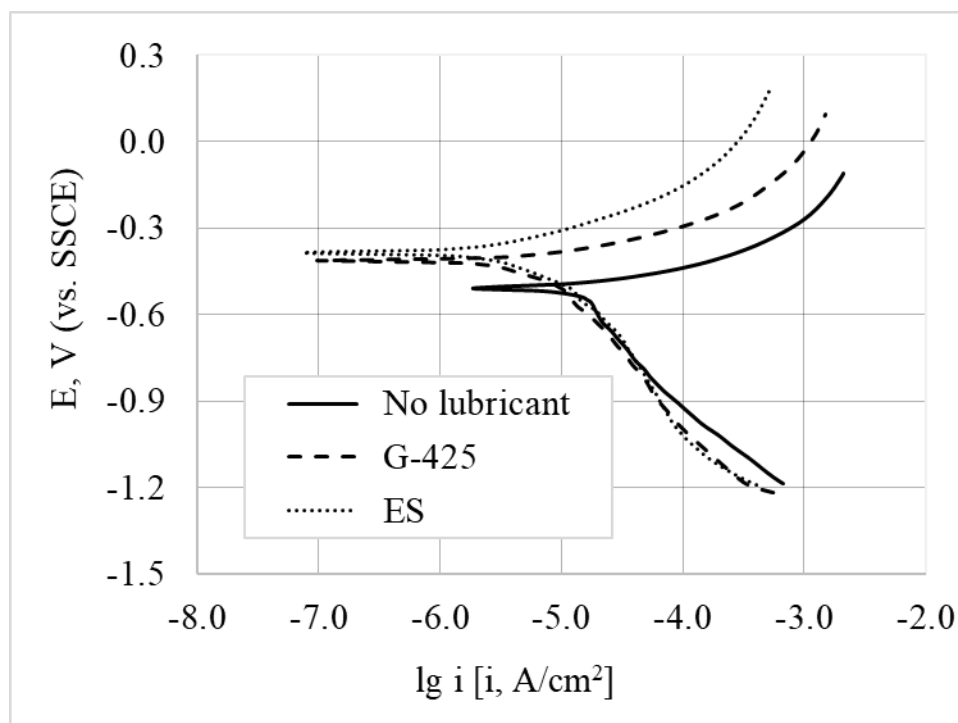

Figure 2. Polarization curves for the R6M5 steel at 70°C.

The curves indicate that the anodic partial reaction parameters change in presence of both cutting fluids. In contrary, all the cathodic branches are close, *i.e.* for the blank experiment and both cutting fluids.

In Table 2 the values of electrochemical corrosion characteristics are given for the R6M5 steel at elevated temperature.

Table 2. Electrochemical corrosion characteristics for the R6M5 steel in presence or absence of the cutting fluids.

Lubricant	E_0, V	b_a, V	b_c, V	i_0, μA/cm^2	z, %	γ_a ($E=-300$ mV)	γ_c ($E=-650$ mV)
No	−0.506	0.06	0.49	12	–	–	–
G-425	−0.401	0.08	0.42	6	50	8.8	1.1
ES	−0.360	0.12	0.38	4	67	66.5	0.9

The inhibition coefficients values of partial corrosion reactions indicate the corrosion inhibition mechanism to be anodic.

The electrochemical protective effect for ES is higher than that for G-425, which is consistent with the gravimetric data. The data on corrosion rate and anti-corrosion effect in the emulsion flow are summarized in Table 3. The sample surface images after removal of the corrosion products are shown in Figure 3.

Table 3. Corrosion rate and corrosion protective effect in the emulsion flow.

Cutting fluid	K, g/m^2·h	Z, %
–	0.617	–
G-425	1.512	–
ES	0.118	81

Figure 3. The R6M5 steel surface after removal of the corrosion products, from left to right: blank experiment, G-425, ES. Magnification ×500.

The corrosion rate in the G-425 emulsion was higher than that in a corrosive medium without any cutting fluid. For explanation of this phenomenon, gravimetric tests were carried out using the R6M5 steel subjected to the corrosive action of the cutting fluid components (lubricating base and corrosion inhibitor) taken separately. The experiment was performed for 24 h in tap water at 70°C. The volumetric concentration of the lubricating base and inhibitor correlated with their concentration in the cutting fluid emulsion at dilution of 1:1000, *i.e.* 0.7–0.9 ml/l for the base and 0.1–0.3 ml/l for the inhibitor. The corrosion rate was determined by the gravimetric method, and, in addition, the fraction of the corroded surface area (%) was calculated according to the GOST 9.311-87 (Russian Federation standard). The results are presented in Table 4.

Table 4. Corrosion weights and corroded surface fraction for the cutting fluid components.

Component	K, g/m²·h	Fraction of corroded surface area, %
–	0.001	98
Lubricating base	0.073	90
Corrosion inhibitor	0.075	10

According to the data obtained, the pattern of corrosion damages of the R6M5 steel changes in presence of cutting fluid components. In tap water without any additive, a continuous uniform coating of corrosion products is formed on the steel surface. The layer is tightly bound to the surface preventing further corrosion, the mass corrosion rate being very low. In presence of the lubricating base, the mass corrosion rate is significantly higher, so the corrosion is supposed to be stimulated by the lubricating base. However, in this case, the distribution of corrosion products over the steel surface becomes somewhat more local, and as a result, the fraction of the corroded surface decreases. In presence of the corrosion inhibitor the corrosion product distribution is also localized, and the corroded surface fraction is significantly reduced, although the corrosion rate value is close to that in the experiment described above. Thus, it can be concluded that the anti-corrosion action of the commercial cutting fluid is not pronounced, however, the corrosion products can be easily removed from the shear blades due to their local distribution. The difference in the corrosion products distribution in the blank experiment and the one with the G-425 emulsion can be evaluated by examining of the surface images (Figure 3).

In addition to the anti-corrosion effect, an important consumer property of a cutting fluid is lubricity. This property is assumed to be dependent on the fluid adsorption value on the blade surface. The surface tension, wetting and adsorption isotherms for the commercial cutting fluid and ES are shown in Figures 4–6.
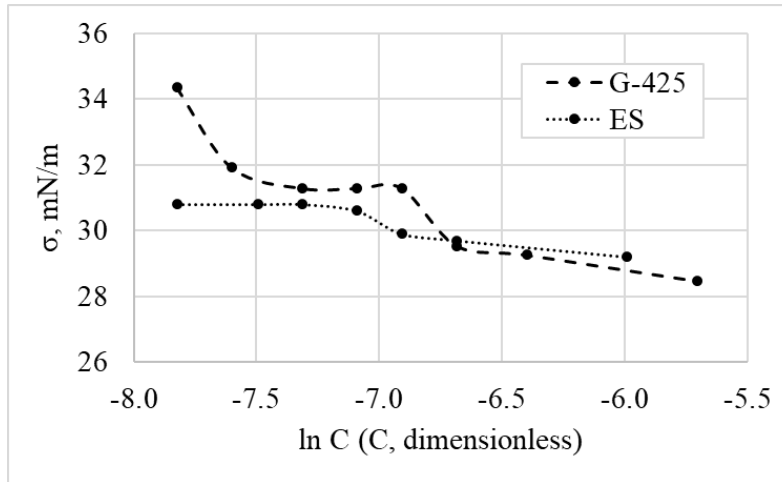
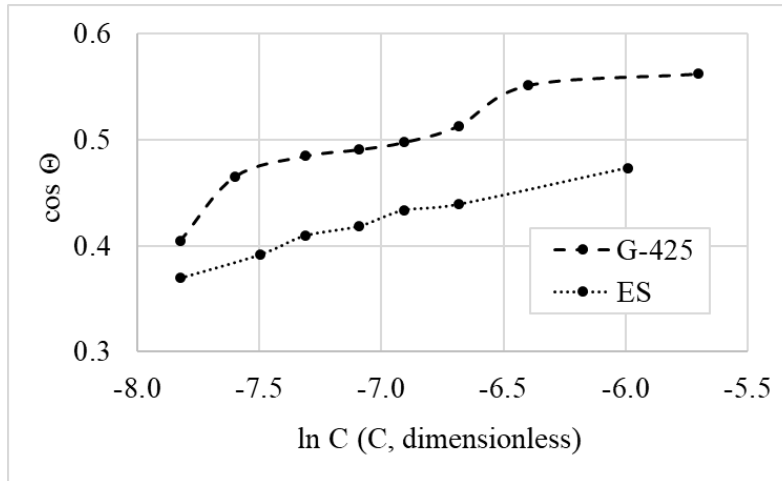**Figure 4.** Surface tension isotherms for the G-425 и ES water emulsions.

Figure 5. Wetting isotherms of steel surface with the cutting fluid emulsions.
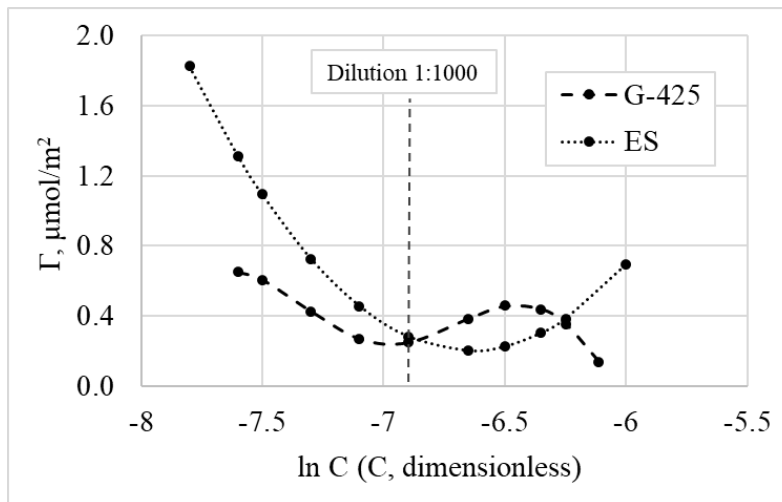
Figure 6. Adsorption isotherms for the cutting fluids studied on the steel surface.

At high dilutions an aqueous ES emulsion has a lower surface tension if compared to the G-425 emulsion. The appearance of wetting isotherms is similar, although the commercial cutting fluid wets the steel surface somewhat better if compared to the experimental sample. The lower is the contact angle, the more uniform is the cutting fluid film on the shear blades.

The appearance of adsorption isotherms for the two cutting fluids is different. In the case of the experimental sample, the adsorption isotherm goes through a minimum at a dilution of 1:800, while the adsorption isotherm of the commercial fluid has two extremes – at dilutions of 1:1200 and 1:700. The presence of extremes on the adsorption isotherm is typical for solutions of micelle-forming surfactants. The decrease in adsorption value with increasing concentration can be explained by the fact that at certain concentrations the interaction between the solute particles is stronger than their interaction with the substrate, and the surfactant is partially desorbed from the surface [29].

At a dilution of 1:1000, the adsorption values for both cutting fluids are close, and at higher dilutions the adsorption of the experimental sample is higher. Thus, at glass factories where the G-425 is used at a dilution of 1:1000 or higher, the use of experimental cutting fluid instead of the G-425 can be suggested, the lubricity being the same.

According to the tests carried out at a glass container plant in the Volga Federal District, the experimental cutting fluid was used in a dilution of 1:1000, and the G-425 is used at this plant in the same dilution. Thus, according to both the experiment and adsorption calculations, the novel cutting fluid is not inferior to the prototype in terms of lubricity.

Conclusions

1. A novel synthetic cutting fluid for shear blades of glass forming machines has been developed. The fluid is based on the G-425 serial product, and all the components are produced in Russian Federation.
2. The novel cutting fluid is characterized by a significantly higher anti-corrosion effect in hard water if compared to the prototype.
3. In presence of the G-425 corrosion products distribution on the R6M5 steel surface differs from that in an uninhibited environment.
4. The mechanism of corrosion inhibition was found to be anodic for both cutting fluids.
5. The experimental cutting fluid was shown to be not inferior to the serial product in terms of lubricity, which correlates with the data on adsorption on the steel surface.

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