

## ВЛИЯНИЕ ВОДОСМЕШИВАЮЩЕЙСЯ СМАЗОЧНО-ОХЛАЖДАЮЩЕЙ ЖИДКОСТИ НА ОСНОВЕ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ НА КОРРОЗИЮ СТАЛИ Р6М5 В НЕЙТРАЛЬНОЙ СРЕДЕ

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*Целью данной работы является исследование физико-химических и антикоррозионных свойств Gelltex - 430 - водосмешиваемой смазочно-охлаждающей жидкости на основе поверхностно-активных веществ. Композиция предназначена для смазывания и охлаждения лезвий ножниц капельного питателя стеклоформирующих машин. Она содержит минеральные и растительные масла, эмульгаторы и ингибиторы коррозии. Смазочная композиция замедляет коррозию быстрорежущей стали Р6М5 в нейтральной среде с защитным эффектом до 88% и имеет анодный механизм ингибирования коррозии, т.е. замедляет анодную парциальную коррозионную реакцию (окисление металла) и стимулирует катодную парциальную реакцию (восстановление окислительных компонентов коррозионной среды - деполяризатора). Использование данной смазки в кислой среде является нежелательным, поскольку она может вызвать охрупчивание стали за счет наводороживания. Смазка способна к образованию разных типов мицелл, что объясняется наличием двух горизонтальных участков на изотерме поверхностного натяжения ее водного раствора. Изменение формы мицелл может повлиять на антикоррозионные свойства смазки, что подтверждается результатами гравиметрических испытаний. Оптимальное рабочее разбавление для данной смазки составляет 1:800, при этом меньшее разбавление может уменьшить ее антикоррозионный эффект. Желательно, чтобы диапазон рабочих разбавлений смазки находился в пределах горизонтального участка на изотерме поверхностного натяжения. Смазка способна к взаимодействию с ионами кальция (возможно, путем комплексообразования или образования осадков), что ограничивает ее применение в жесткой воде – слишком высокая концентрация ионов кальция в воде может изменить ее структуру и антикоррозионные свойства.*

**Ключевые слова:** поверхностно-активное вещество, смазочно-охлаждающая жидкость, эмульсия смазочно-охлаждающей жидкости, ингибитор коррозии, поверхностное натяжение, мицеллообразование

## INFLUENCE OF A WATER-MISCIBLE SURFACTANT-BASED CUTTING FLUID ON THE CORROSION OF R6M5 STEEL IN A NEUTRAL MEDIUM

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*The aim of the work is to research physico-chemical and anti-corrosion properties of surfactants-based water-miscible cutting fluid Gelltex G-430. This cutting fluid is designed for lubricating and cooling of drop feeder scissors of glass-forming machines. It contains mineral and vegetable oils, emulsifiers and corrosion inhibitors. The cutting fluid slows the corrosion of the high-speed steel P6M5 in a neutral medium with a protective effect up to 88%. The cutting fluid demonstrates anodic mechanism of corrosion inhibition. It slows anodic process (oxidation of the metal) and stimulates cathodic process (reduction of the corrosive medium). Therefore, use of this lubricant in acidic media is undesirable because it can cause hydrogen accumulation in the steel and embrittle it. In a water solution, the lubricant builds different types of micelles, which is explained by two horizontal sections on the surface tension isotherm. Change in form of the micelles can affect the anti-corrosion properties of the lubricant. It is confirmed by gravimetric tests. The optimum dilution for this cutting fluid is 1:800. A lower dilution can worsen its protective effect. The range of recommended dilutions of the lubricant should be within horizontal sections on the surface tension isotherm. The lubricant is able to interact with calcium ions (probably building complexes or forming precipitates) and it limits its use in a hard water – a too high concentration of calcium ions in the water can change the structure and anti-corrosion properties of the lubricant.*

**Key words:** surfactant, cutting fluid, cutting oil emulsion, corrosion inhibitor, surface tension, micelles formation

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## INTRODUCTION

Cutting fluids are designed to reduce wear and heating of steel tools in the processing zone. A lot of cutting fluids are used in the technology. Mineral, vegetable and synthetic oils [1] are, as a rule, the main component of oil-based cutting fluids. Cutting fluids reduce friction and wear, they inhibit corrosion, create a protective film, and prevent the growth of bacteria that can destroy the metal [2]. Water-miscible lubricants always contain emulsifiers contributing to the formation of oil-water emulsion. Various additives are used to improve the properties of the lubricant: emulsifiers, foaming agents, bactericides [1-4]. There are also some water-based lubricants which do not contain oils and contain only water and anti-friction additives [5-7].

Cutting fluids reduce financial losses from metal wear, so elaboration of new cutting fluids is a promising task. The basic requirements for cutting fluids are efficiency, low consumption, easy disposal [8-10],

cheapness (it is desirable to use secondary raw materials for producing cutting fluids [11-14]). The toxicity of cutting fluids must be as low as possible. According to several studies, some lubricants can cause allergic reactions and lead to oncological diseases [1, 10].

Anti-corrosion properties of the lubricant are important [15]. They are crucial, for example, for mechanisms operating at high temperatures or in an aggressive medium. The anti-corrosion effect of the lubricant can be achieved by adding corrosion inhibitors to the composition [16]. As a rule, corrosion inhibitors are surfactants that change the electrochemical potential between the metal and the corrosive medium [17]. Emulsifiers the lubricant contains can simultaneously act as corrosion inhibitors.

They need to take into account that the corrosion mechanism may change during the operation of the tool. For example, scissors of feeders of glass-forming machines come into contact with glass mass, which can reach a temperature of 1250 °C [18]. The scissors are lubricated with an emulsion of a water-

miscible cutting fluid. Prior to the contact with molten glass, corrosion of wet scissors occurs by an electrochemical mechanism. When the scissors contact with the glass, their temperature rises sharply, the emulsion dries up, and a layer of lubricant remains on the scissors. Corrosion mechanism, thus, changes [19].

When designing a lubricant, it is important to consider the nature of the corrosive medium in which they are to be used. Often, tap water is used as a solvent for the cutting fluid. Tap water contains calcium, magnesium and other ions. Metal ions and the lubricant can interact with each other. The lubricant can build complexes with metal ions, form a precipitate or the structure of the micelles can change. These transformations can decrease the anti-corrosion effect of the lubricant. Manufacturers often note the maximum water hardness allowable for a cutting fluid [20, 21]. Catalytic activity of the metal surface must also be taken into consideration - chemical transformations are possible when the cutting fluid is applied to it [22]. It is a promising idea to use some additives which can bind metal ions into lasting complexes because precipitation of salts on the shears reduces their life time.

For water-miscible cutting fluids, it is important to accurately determine the operating concentration. If the concentration of the surfactant in the emulsion is too low or too high, the anti-corrosion effect can decrease. The surfactants the cutting fluid contains are characterized by the critical micelle concentration (CMC), at which the surfactant begins to build micelles. CMC can be changed by introducing various additives to the composition [23, 24]. Determination of the CMC is especially important if the lubricant contains only surfactants and does not contain oils. CMC of a mixture of  $n$  surfactants is determined by the additivity rule [25]:

$$CMC_{mixture} = CMC_1 \cdot N_1 + CMC_2 \cdot N_2 + \dots + CMC_n \cdot N_n \quad (1)$$

where  $CMC_1$ ,  $CMC_2$  and  $CMC_n$  are critical micelle concentrations of each surfactant;

$N_1$ ,  $N_2$ ,  $N_n$  – their mole fractions.

This work is devoted to the study of oil-based water-miscible cutting fluid Gelltex-430 [26]. This cutting fluid is used for lubrication and cooling of shears of drop feeders of glass-forming machines. It is based on mineral oils and also contains surfactants, corrosion inhibitors and bactericides. The effect of the cutting fluid on the corrosion of high-speed steel P6M5 in neutral medium was investigated in the work. The steel has the following composition (%) [27]: C – 0.82-0.9; Si – up to 0.5; Mn – up to 0.5; Ni – up to 0.4; Cr – 3.8-4.4; Mo – 4.8-5.3; W – 5.5-6.5; V – 1.7-2.1; Co – up to 0.5; S – up to 0.025; P – up to 0.03.

Here are listed the physical and chemical properties of the lubricant which we are studying in this research:

1. Surface tension of aqueous emulsion –  $\sigma$ .
2. Possibility of interactions between the lubricant and the corrosive medium.
3. Protective effect  $\gamma$  of the lubricant which is the ratio of corrosion rate without lubricant to the corrosion rate in presence of lubricant.
4. Effect of the lubricant on partial corrosion reactions (oxidation of the metal and reduction of the depolarizing agent – oxidizing component from the corrosive medium).

## EXPERIMENTAL PART

To plot surface tension isotherm, we prepared aqueous solutions of the cutting fluid with dilution ranging from 1:200 to 1:1500 and with a step of 1:100. The surface tension  $\sigma$  of these solutions was determined by the hanging-drop method using the Kruss DSA25E device. We plotted a  $\sigma$  - C graph where C is the volume concentration (dimensionless) of the lubricant and  $\sigma$  is the surface tension. The experiment was repeated after 24 h. Consumers of the lubricant do not always use the emulsion immediately after preparation, so it's important to study its state some time later after preparation.

To detect interactions between water hardness ions and the lubricant, we measured the dependence of electrical conductivity on the concentration for calcium chloride and the cutting fluid. Conductivity was measured using "Anion-4100" conductometer. The time required for reaching an equilibrium state was 3 min. Solutions were prepared on bidistilled water using "chemically pure" grade reagents. Initially, we measured electric conductivity for each of the substances separately. Then, we mixed the solutions of these substances in certain proportions and measured electric conductivity for obtained mixtures. We plotted graphs for the dependence of  $\Delta\kappa$  on the composition of the mixture ( $\Delta\kappa = \kappa\Sigma - \kappa_{mixture}$ , where  $\kappa\Sigma$  is the sum of the electrical conductivity of the complementary solutions,  $\kappa_{mixture}$  is the electrical conductivity of their mixture). If there is a peak on the plot, it means that the lubricant can interact with calcium chloride building a complex or forming a precipitate.

The inhibiting effect of the cutting fluid was determined by gravimetry method, according to GOST 9.506-87 [28]. For gravimetry tests, we used flat samples with dimensions of 30×20×2 mm, made of steel P6M5. Before testing, the samples were treated with sandpaper, degreased with acetone, rinsed with distilled water, dried and weighed on analytical scales

with a precision of 0.0001 g. Further, the samples were put into solutions imitating the corrosive medium - tap water. The composition of the corrosive medium is presented in Table 1. The lubricant was added to the corrosion medium, in volume proportions of 1:1000, 1:800, 1:600. The solutions were thermostated, the temperature of the experiment was 40 °C. After a certain period of time, the samples were removed from the solutions, rinsed with distilled water, cleaned from corrosion products, degreased with acetone, dried and weighed again. The corrosion rate was calculated by the formula:

$$K = \frac{\Delta m}{S \cdot t}, \quad (2)$$

where K is the corrosion rate (g/m<sup>2</sup>·h); Δm – mass difference of the samples before and after the test, g; S – surface of the samples, m<sup>2</sup>; t – time of experiment, h.

Protective effect and inhibition coefficient were calculated by formula:

$$Z = \frac{K_1 - K_2}{K_1} \cdot 100\%, \quad (3)$$

where K<sub>1</sub> is the corrosion rate in an uninhibited medium, g/m<sup>2</sup>·h; K<sub>2</sub> – corrosion rate in an inhibited medium, g/m<sup>2</sup>·h.

Table 1

Composition of the corrosive medium (based on distilled water)

Таблица 1. Состав коррозионной среды (основа – дистиллированная вода)

Component	Contain, mg/l
NaCl	37
Ca(OH) <sub>2</sub>	9.25
H <sub>2</sub> SO <sub>4</sub>	14.5
FeSO <sub>4</sub> ·7H <sub>2</sub> O	7
NaHCO <sub>3</sub>	361

To estimate the influence of lubricant on the cathodic and anodic partial reactions, we used the polarization curves method. Potentiodynamic curves were obtained using an IPC-pro potentiostat with potential change rate of 0.02 mV/s. We used silver chloride electrode as reference electrode and platinum electrode as auxiliary electrode. All the potentials in this article are referred to the silver chloride electrode. The temperature of the solutions was 313 K. The composition of the corrosive medium was the same as for gravimetry tests.

The electrochemical inhibitory effect of the lubricant was determined as the ratio of polarization resistances for the "idle" experiment (without lubricant) and for the experiment with lubricant:

$$\gamma = \frac{R_p}{R_{p(idle)}}, \quad (4)$$

where R<sub>p</sub> is the polarization resistance of the corrosion process in presence of lubricant, R<sub>p</sub> (idle) is the polarization resistance of the "idle" experiment.

The inhibition factors of partial reactions γ<sub>a</sub>, γ<sub>c</sub> (anodic and cathodic reactions, respectively) were determined as the ratio of current densities in uninhibited and in inhibited solutions:

$$\gamma_{a,c} = \frac{i_{(idle)}}{i}, \quad (5)$$

where i<sub>(idle)</sub> is the current density for "idle" experiment, i is the current density for the experiment with lubricant. For the anodic reaction, we selected current density at -0.35 V, for the cathodic reaction – current density at -0.55 V.

## RESULTS AND DISCUSSION

### 1. Lubricant aggregation into micelles.

Fig. 1 shows plots of the "surface tension – concentration" dependence. The surface tension isotherms have horizontal sections. Within limits of these horizontal sections, micelles of specific kind are formed.

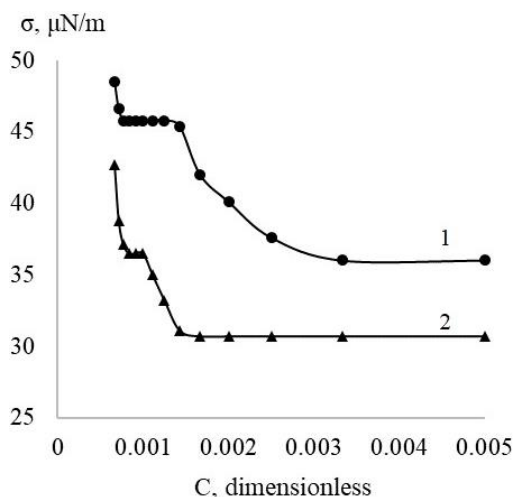


Fig. 1. Dependence of the surface tension on the volume concentration of the solution (exposure time is 1 h and 24 h after preparation); 1 – exposure 1h, 2 – exposure 24 h

Рис. 1. Зависимость поверхностного натяжения от объемной концентрации раствора (время выдержки 1 ч и 24 ч после приготовления); 1 – выдержка 1 ч, 2 – выдержка 24 ч

Dilution ranges in which the surface tension of the lubricant emulsion remains constant are:

- 1:1300 - 1:700 for exposure time of 1 h;
- 1:1200 - 1:900, 1:600 - 1:200 for exposure time of 24 h.

It is possible to assume the existence of two types of micelles because surface tension isotherms have two horizontal sections. In 24 h after preparation, the cutting fluid reduces the surface tension of water to a greater extent than in 1 h after preparation. Perhaps a lower surface tension means a better lubricity [29].

The operating concentration of the lubricant should be within a horizontal section on the surface tension isotherm. In this case, some errors made while preparing the emulsion will not significantly affect the protective effect of the lubricant because the form of micelles and their way of adsorption on the metal surface will not change significantly if the concentration is changed.

2. Study of interactions between lubricant and metal ions.

Fig. 2 shows plots of dependence of change in specific conductivity  $\Delta\kappa$  on the volume of salt solution. The total volume of salt solution and of distilled water added to it is 25 ml. There is a peak on the plot we obtained. Presence of this peak means that the lubricant can interact with calcium ions.

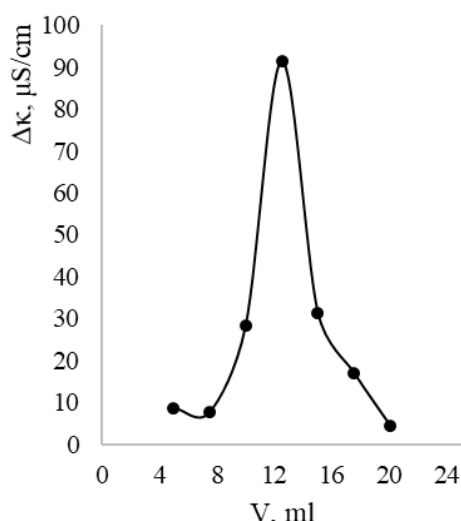


Fig. 2. Dependence of change in conductivity  $\Delta\kappa$  on the volume of added salt

Рис. 2. Зависимость изменения электропроводности  $\Delta\kappa$  от объема добавленной соли

3. Gravimetric tests.

Results of gravimetric tests are presented in Table 2.

Table 2

Results of gravimetric tests

Таблица 2. Результаты гравиметрических испытаний

Dilution	Protective effect Z, % after exposure time, h			
	3	7	12	18
1:1000	32.43	60.94	65.16	63.50
1:800	57.08	71.59	68.19	84.40
1:600	65.03	88.45	72.22	72.68

The highest protective effect of this cutting fluid is obtained after 18 h with a dilution of 1:800. At a higher dilution, the concentration of micelles in the solution decreases and the protective effect decreases.

At a lower dilution, other types of micelles are formed (see Fig. 1) and the protective effect also reduces. Thus, a too high concentration of the lubricant is harmful, it can worsen the anti-corrosion properties of the lubricant. The optimum dilution for this lubricant is 1:800.

4. Electrochemical tests.

Polarization curves are shown on Figs. 3, 4.

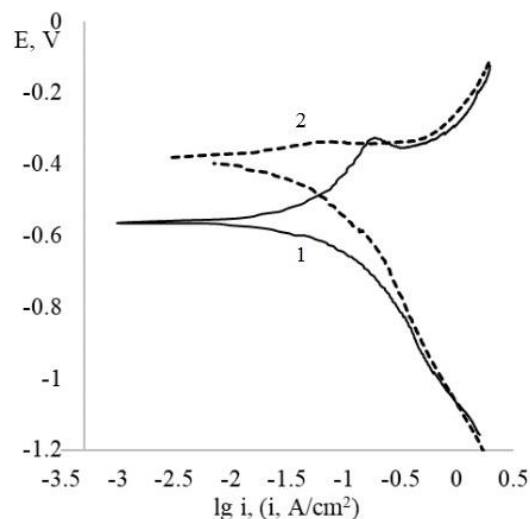


Fig. 3. Polarization curves for P6M5 steel in the corrosive medium: 1 – no lubricant, 2 – 1:1000 dilution

Рис.3. Поляризационные кривые для стали P6M5 в коррозионной среде: 1 – без смазки, 2 – объемное разбавление смазки 1:1000

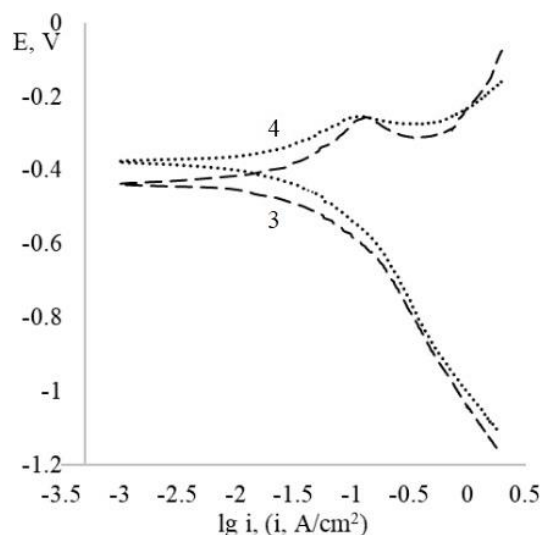


Fig. 4. Polarization curves for P6M5 steel in the corrosive medium: 3 – 1:800 dilution, 4 – 1:600 dilution

Рис. 4. Поляризационные кривые для стали P6M5 в коррозионной среде: 3 – разбавление смазки 1:800, 4 – разбавление 1:600

We calculated inhibition factors for anodic and cathodic reaction at potential values  $E = -0.35$  V and  $E = -0.55$  V, respectively. These values are presented

in Table 3. Inhibition factor of the cathodic reaction is lower than 1, it means that if the potential value is shifted to the cathodic domain of the polarization curve, the rate of the cathodic process increases.

**Table 3**

**Inhibition factors for partial corrosion reactions**  
**Таблица 3. Коэффициенты торможения парциальных коррозионных реакций**

Dilution	Inhibition factor $\gamma$	Inhibition factor for anodic reaction by $E = -0.35V$	Inhibition factor for cathodic reaction by $E = -0.55V$
1:1000	1.61	9.3	0.13
1:800	1.70	5.81	0.21
1:600	1.65	15.5	0.13

Thus, this lubricant has an anodic mechanism of corrosion inhibition. Use of anodic inhibitors in acidic media is undesirable because it can lead to the embrittlement of metal due to hydrogen accumulation in it. Moreover, anodic inhibitors can increase the corrosion rate by certain concentrations [30].

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#### CONCLUSIONS

Cutting fluid Gelltex G-430 is an efficient corrosion inhibitor for high-speed steel in neutral media. However, consumers of this lubricant should use it strictly following the manufacturer's instructions. This lubricant has an anodic mechanism of corrosion inhibition, so use of this lubricant in acidic media or at a too high concentration can reduce its anti-corrosion effect. The optimum dilution for this cutting fluid is 1:800. Consumers should also control the hardness of the water which is used for preparing lubricant emulsion because the lubricant can interact with calcium ions and a too high concentration of these ions is undesirable.

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