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INFLUENCE OF TECHNICAL GLYCERINE AND COMPOSITION ON HIS BASE ON 20 STEEL AND ALUMINIUM CORROSION DURABILITY IN 0,1% NACL

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Summary. *The sharp deterioration of the ecological state of the environment is associated not only with the activities of various plants, but also with the lack of high-quality recycling of industrial waste and reliable, safe anticorrosive protection of equipment. In this regard, over the past decade, increased attention has been paid to the search for eco-friendly corrosion protection agents, in particular, through the use of waste from the woodworking, food and other industries: extracts of wood chips, natural resins, and the breakdown products of vegetable fats (technical glycerin). Therefore, the creation of so-called «Green» inhibitors is an urgent and promising task.*

Gravimetric and electrochemical studies, we found that technical glycerin (TG) has an anticorrosive effect on steel and aluminium in a 0.1% NaCl solution. Its effectiveness in the concentration range of 1.0–2.5 g/l is practically unchanged, the degree of protection Z is 57–67%. The inhibitory properties of TG due to its adsorption on the surface of these metals with a predominance of the energy (double-layer) component of the protective effect. The inhibitor retard both electrode reactions on steel 20 and aluminium, while reducing corrosion currents by 2–4 times.

An increase in the anticorrosive properties of TG without an increase of its concentration is achieved through the use of synergistic reagents. Triethanolamine in the composition with TG did not exert an inhibitory effect, while the extract of oak chips (EO) with the ratio of TG: EO components = 3:l2 increased the degree of protection of steel 20 and aluminium to 80–82%.

The protective mechanism of the created composition is somewhat different from the mechanism of the main component. The compromise potential of both metals shifts to a more negative side, the nature of the cathode and anode curves changes, in particular, the portion of the limiting diffusion current disappears. Corrosion currents decrease by ~ 8 times.

Key words: *extract of oak chips, corrosion rate, compromise corrosion potential, corrosion current, limiting diffusion current, Tafel constants.*

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Problem statement. The catastrophic ecological state of the environment is the result not only of the production activities of the chemical, energy, oil and gas-producing and processing industries, but also of the lack of high-quality disposal of wastes from food, wood-harvesting and woodworking industries [1]. In addition, this problem is further complicated by the negative effects of metals fund corrosion products and the use of insufficiently safe anti-corrosion protection agents.

Recently, increased attention has been focused on the use of waste processing plant raw materials as corrosion inhibitors [2–5]. This particularly applies to products of plant fats (technical glycerine) [6], wood chips extracts [7], rapeseed shot pellents [8], natural resins, etc. [9].

Analysis of known research results. Inhibitors derived from natural materials can satisfactorily protect steel, aluminum, copper, etc., from corrosion in both neutral and acidic media [10–12]. However, their degree of protection even at sufficiently high concentrations

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does not exceed 60–70%. Enhancement of their effectiveness is achieved by creating synergistic compositions. Thus, the protective effect of oak chip extracts in the composition consisting of organic and inorganic synergists increases to 90–95% [13]. Therefore, the search and study of the anti-corrosion properties of inexpensive organic environmental safety substances will allow to create new so-called «Green» inhibitory synergistic compositions with a wide range of action.

The goal of the work. Evaluate anticorrosion properties and mechanism of action of technical glycerine and its compositions with triethanolamine and oak chips extract relative to steel 20 and aluminium in neutral environment.

Materials and research methods. Corrosion tests were carried out by gravimetric method on 20 steel in the state of supply (disc samples of 20 mm diameter) and on aluminium (rectangular samples of 20x30 mm). As the environment used 0.1% NaCl solution. Inhibitors – technical glycerine (TG), triethanolamine (TEA), oak chips extract (EO) [10] and synergetic compositions based on them were introduced into corrosive medium at concentrations of 1.0 and 2.0 g/l. Corrosion rate and protective effects of inhibitors were calculated according to known formulas [14]. Electrochemical studies were carried out by IPC-Pro potentiostat in a potentiodynamic mode with 1 mV/s potential scanning on 1 cm^2 samples with an isolated side surface. Reference electrode – saturated silver chloride. Corrosion currents and Tafel constants were determined by graphoanalytic method [15]. The adsorption potential shift was $\Delta\Psi_1$ calculated by the formula:

$$\Delta\Psi_1 = \Delta E \,/\, [1 - b_c\, b_a \,/\, (b_c + b_a)\, b_0],$$

Where ΔE – displacement of corrosion potential in the presence of inhibitor, b_c b_a – Tafel constants, $b_0 = 2.3\,R\,T/F = 0.059$.

Technical glycerine (propane-1, 2, 3 triol) – the product of hydrolytic splitting of carbohydrates (starch, wood flour, sugar) is formed in the production of biodiesel and is a colorless, hygroscopic liquid, well mixed with water and aqueous solutions of salts.

Results and discussion. Gravimetric tests of the protective effect of technical glycerine showed that this reagent has moderate protective properties in 0.1% solution NaCl: steel 20 protects by 58%, aluminium by 67%, slowing the corrosion rate of steel by 2.4 times, and aluminium – by 3 times. Increasing the concentration of TG from 1 to 2.5 g/l has practically no effect on its anti-corrosion activity on either steel 20 or aluminium (Table 1).

Table 1

Influence of technical glycerine (TG) and composition on his base on 20 steel and aluminium corrosion durability in 0,1% NaCl

Material	Medium	Concent. inhib., g/l	$K_m \cdot 10^6$, g/cm²h	*П*, mm/year	*γ*, time	*Z*, %
1	2	3	4	5	6	7
20 Steel	0,1% NaCl	-	7,3	0,08	-	-
	0,1% NaCl+ТГ	1,0	3,1	0,03	2,4	58
		2,5	3,1	0,03	2,4	58
Aluminum	0,1% NaCl	-	0,3	0,009	-	-
	0,1% NaCl+ТГ	1,0	0,1	0,003	3,0	67
		2,5	0,1	0,003	3,0	67
20 Steel	0,1% NaCl+ ТГ+TEA (3:1)	1,0	4,6	0,05	1,6	37
Aluminum	0,1% NaCl+ ТГ+TEA (3:1)	1,0	0,1	0,003	3,0	67

(to be continued)

1	2	3	4	5	6	7
20 Steel	0,1% NaCl+ ТГ+ЕД (3:2)	1,0	1,3	0,014	5,6	82
Aluminum	0,1% NaCl+ ТГ+ЕД (3:2)	1,0	0,06	0,067	5,0	80

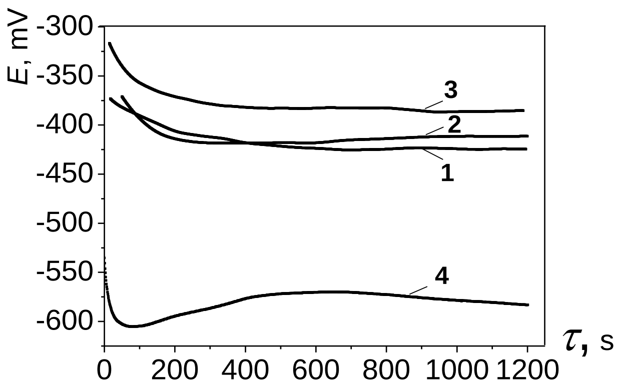

Figure 1. Compromise potential determining on 20 steel in 0,1% NaCl (1) and with additions: 2–1 g/l TG; 3–2,5 g/l TG; 4–1 g/l TG+ EO

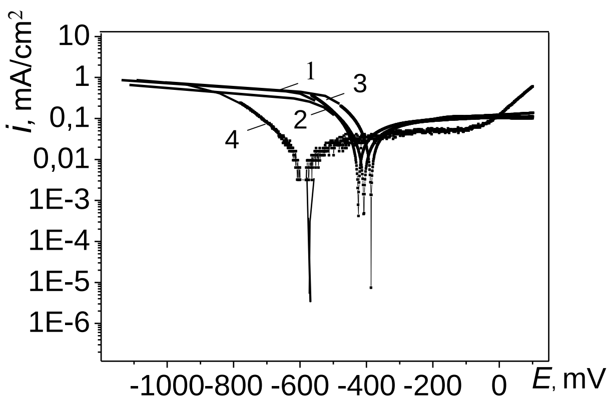

Figure 2. Polarization curves of 20 steel in 0,1% NaCl (1) and with additions: 2–1 g/l TG; 3–2,5 g/l TG; 4–1 g/l TG+ EO

It is known that triethanolamine (TEA), as part of the inhibitory compositions based on SFA (synthetic fatty acids), intensify their protective properties against medium carbon steels in 3% NaCl solution [16]. However, in our case (TEA) in the TG composition (at a 1:3 ratio), in contrast, reduces the protective properties of TG (the antagonist) relating to 20 steel and does not alter its efficiency relating to aluminum. Perhaps by partially adsorbing on steel, TEA reduces the surface area with adsorbed TG, which is manifested in the reduction of the inhibitory action of the composition. On the aluminum oxidic film, the adsorption of TEA is negligible or absent, thereby maintaining the efficiency of TG protection.

The extract of oak chips, in contrast, enhances the protective properties of TG, showing a synergistic effect on both steel and aluminum in a medium of 0.1% NaCl. The degree of protection increases to 82% (steel) and 80% (aluminum), and the corrosion inhibition index γ is 5.6…5.0 times against 2.4…3.0 (Table 1). The mutual amplification of the protective action may be the result of both the additional adsorption of the EO and the possible interaction of the extract components with the TG.

The mechanisms of influence of TG and its composition with EO on partial electrode reactions on 20 steels and aluminum were evaluated on the basis of polarization studies. It was found that the compromise potential on 20 steel in 0.1% NaCl solution under the influence of TG shifts towards less negative values: at a concentration of 1 g/l at 14 mV, and at 2.5 g/l – 40 mV (Fig. 1). A 0.8 g/l EO composition, on the contrary, shifts the compromise potential toward more negative values by up at 168 mV. Corrosion currents of 20 steel in the presence of TG are reduced by 2–4 times, and under the influence of the composition – by 8 times. TG almost does not change the nature of the cathodic curve, it only slightly reduces the limit diffusion currents, while the composition practically levels the area of the limit diffusion current (Fig. 2, Table 2). Such a change in the cathode curve may be result from the participation of the EO in the depolarization process. An increase in Tafel constants indicates the cathodic and anodic electrode reactions being impeded and confirms mixed character of protective action of both TG and its composition with EO.

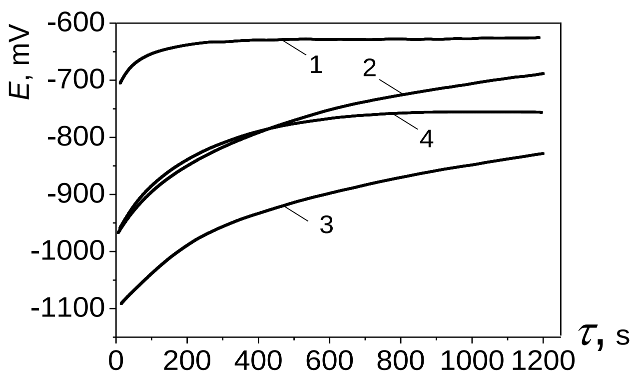

Figure 3. Compromise potential determining on aluminium in 0,1% NaCl (1) and with additions: 2–1 g/l TG; 3–2,5 g/l TG; 4–1 g/l TG+ EO

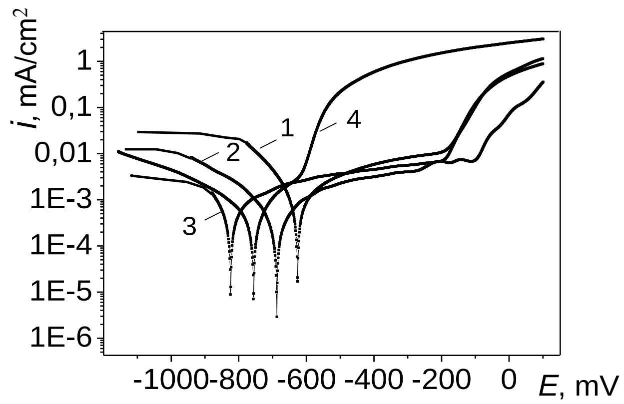

Figure 4. Polarization curves of aluminium in 0,1% NaCl (1) and with additions: 2–1 g/l TG; 3–2,5 g/l TG; 4–1 g/l TG+ EO

Calculated values of the adsorption potential shift on 20 steel under the influence of TG indicate the prevalence of the energy effect over the blocking effect, which is significantly enhanced by the addition of EO.

Table 2

Influence of technical glycerine (TG) with EO composition
on 20 steel and aluminium electrochemical characteristics in 0,1% NaCl

Metal	Medium	$-E_{cor}$, mV	$i_{cor}\cdot 10^5$, mA/cm^2	i_d, mA/cm^2	Tafel constants		$\Delta\Psi$, mV
					b_c, mV	b_a, mV	
20 Steel	0,1% NaCl	425	40	0,5	43	45	–
	0,1% NaCl+ТГ*	411	20	0,3	50	52	24
	0,1% NaCl+ТГ**	385	10	0,4	50	52	93
Al	0,1% NaCl	625	10	0,03	43	29	–
	0,1% NaCl+ТГ*	688	3	0,01	61	57	126
	0,1% NaCl+ТГ**	825	3	0,003	58	59	392
20 Steel	0,1% NaC1+ТГ*+ЕД	583	2	–	63	75	376
Al	0,1% NaCl+ТГ*+ЕД	756	2	0,002	72	60	294

Note: TG concentration* – 1 g/l; TG** – 2 g/l TG**.

On aluminium the compromise potential under the influence of TG and its composition with EO is significantly shifted towards more negative values (Fig. 3, Table 2): by 63 mV for the inhibitor concentration 1 g/l and 200 mV – for 2.5 g/l. In contrast to steel, the EO in the TG composition reduces the amount of compromise potential shift on aluminum to the negative side (131 mV). Under the influence of TG for both concentrations corrosion currents decrease by 3.3 times, and limit diffusion – by 3–10 times. The composition reduces the corrosion current to $2\cdot 10^{-5}$ mA/cm^2. As with steel, the composition changes the characteristics of the cathode and anode curves (Fig. 4). The Tafel constants, compared to the non-inhibiting medium are growing, particularly noticeable in the presence of the TG+EO composition. The value of shift of the aluminium adsorption potential is significantly greater than steel, indicate on amplification of the energy component of the inhibitory effect.

Conclusions. It is shown that technical glycerine (TG) exhibit anticorrosion properties relating to 20 steel and aluminium in 0.1% NaCl. The protective effect is due to its adsorption on the surfaces of these metals with the double layer effect prevailing and consists in braking both electrode reactions. The effectiveness of TG as a corrosion inhibitor has been found to be higher on aluminium than on steel and enhanced in combination with oak chip extract. Triethanolamine in the TG composition does not affect its protective properties against aluminium and impairs their ratio of 20 steel.

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ВПЛИВ ТЕХНІЧНОГО ГЛІЦЕРИНУ ТА ЙОГО КОМПОЗИЦІЙ НА КОРОЗІЙНУ ТРИВКІСТЬ СТАЛІ 20 І АЛЮМІНІЮ У 0,1% РОЗЧИНІ NaCl

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Резюме. *Різке погіршення екологічного стану навколишнього середовища пов'язано не тільки з діяльністю різних підприємств, але й з відсутністю якісної утилізації виробничих відходів, надійного, безпечного протикорозійного захисту обладнання. У зв'язку з цим в останнє десятиліття посилена увага приділяється пошуку екобезпечних засобів захисту від корозії, зокрема шляхом використання відходів деревообробної, харчової та інших галузей промисловості: екстрактів стружки деревини, природних смол, продуктів розщеплення рослинних жирів (технічний гліцерин). Тому створення на основі отриманих речовин т. зв. «зелених» інгібіторів є актуальним і перспективним завданням. Гравіметричними й електрохімічними дослідженнями встановлено, що технічний гліцерин (ТГ) виявляє протикорозійну дію на сталь та алюміній в 0,1% розчині NaCl. Його ефективність у діапазоні концентрацій 1,0–2,5 g/l практично не змінюється, ступінь захисту Z становить 57–67%. Інгібуючі властивості ТГ зумовлені його адсорбцією на поверхні цих металів із переважанням енергетичної (подвійно-шарової) складової захисного ефекту. Інгібітор гальмує обидві електродні реакції на сталі 20 та алюмінії, знижуючи при цьому струми корозії у 2–4 рази. Підвищення протикорозійних властивостей ТГ без збільшення при цьому його концентрації досягається шляхом використання реагентів-синергістів. Триетаноламін у композиції з ТГ не виявив посилення інгібувальної дії, в той час, коли екстракт дубової стружки (ЕД) за співвідношення компонентів ТГ:ЕД = 3:2 збільшив ступінь захисту сталі 20 та алюмінію до 80–82%. Механізм захисної дії створеної композиції дещо відрізняється від механізму основного компонента. Компромісний потенціал на обох металах зміщується в негативний бік, характер катодної та анодної кривих зазнає змін, зокрема зникає ділянка граничного дифузійного струму. Струми корозії при цьому зменшуються ~ у 8 разів.*

Ключові слова: *екстракт дубової стружки, швидкість корозії, компромісний потенціал корозії, струм корозії, граничний дифузійний струм, константи Тафеля.*

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