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The nature of the formation of adsorption layers on aluminum surfaces under the inhibitory protection by plant extracts

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The paper studies how a corrosion inhibitor made of vegetable waste from food production - pomegranate peel - is adsorbed on the surface of aluminum. The mechanism of inhibitor action is largely driven by the fact that the active substances are chemisorbed on the metal surface and form a film that isolates this surface from the aggressive influence of the environment.

Keywords: plant material, pomegranate peel extract, inhibitor, adsorption.

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Introduction

A number of works study the adsorption of organic substances on metal surfaces to protect against the effects of aggressive environments. For example, the authors of [1-4] established the basic kinetic regularities of forming protective metal-organic films in acidic environments in the presence of complex-forming corrosion inhibitors. Studies of the phase layers' growth dynamics using polarization resistance and mathematical modeling methods have shown that the thickness and protective properties of the film increase in time according to a parabolic law and obey the laws of diffusion kinetics [4]. In [5], the polarization resistance method was used to prove that the formation of protective layers during the inhibition of steel by sulfanilamide in aqueous solutions of hydrochloric acid with different pH has peculiarities, caused by the predominance of protonated or nonprotonated molecule forms. It was found that only protective films formed from protonated molecules can provide high and stable inhibition efficiency.

In light of modern sanitary and hygienic requirements to increase the level of environmental friendliness of production, compositions based on plant products (black pepper extract, fennel essential oil, caffeic acid, Rosmarinus ficinalis oil, perianth of Garcinia mangosteen fruit) active in protecting the steel surface from corrosion damage in acidic environments were developed, and their adsorption properties were studied [6-11].

Research teams proposed powder rust converters and volatile atmospheric corrosion inhibitors based on the pitted waste of fruit and berry crops [12], developed and investigated the mechanism of adsorption of corrosion inhibitors on the steel surface based on modified mustard oil and the water-soluble fraction of processing waste products of fatty oil production [13, 14]. It was established that both chemisorption and physical adsorption occur during inhibition.

A promising direction is obtaining inhibitors from extracts of rapeseed [15], basil, cinnamon, sage, cloves, spirulina, pomegranate peel [16] to protect the equipment of industrial enterprises. In tap water, the degree of steel protection is 91.3-94.7%, in a solution of 0.1M hydrochloric acid it is 93.4%. Pomegranate peel extract showed the best protective properties.

A review of the existing works showed that plant inhibitors were mostly studied on steel samples, while aluminum and its alloys are widely used in the food and chemical industries, construction, and the manufacture of ships and aircraft. In the food and chemical industry, aluminum is used as a material for equipment, storage, and transportation of food, water, nitric and acetic acids, etc. As a structural material, not aluminum itself is used, but rather its alloys, which have significantly higher mechanical properties. For example, Al-Mg alloys are characterized by a number of competitive physical and mechanical properties and have high corrosion resistance. However, it is known that the protective oxide film on the alloy surface is unstable in the presence of chlorides and local depassivation of the alloy occurs [17, 18].

Therefore, it is important to study the surface of aluminum alloys in chloride salt environments to determine the effect of plant extracts as corrosion inhibitors on the equipment for food and chemical production.

I. Statement of the research problem

The paper aims to study the active substances in the composition of the water-alcohol extract of pomegranate peel as a promising raw material for creating an inhibitor, and the nature of its adsorption on the surface of aluminum alloys in a saline solution.

II. Experimental part

The inhibitor was obtained from food waste – pomegranate peel (PP), by extraction with a water-alcoholic solution. Before extraction, the raw material was dried to a constant weight at 308 K and grounded. The component composition of the volatile substances of the plant extract was studied by chromatography-mass spectrometry on a gas chromatograph "FINIGAN FOCUS" with a mass-selective detector (Termo Electronics). The carrier gas was helium, the flow rate of the carrier gas in the column was 1.2 ml/min. Ionization was by electron impact with the electron energy of 70 eV.

The inhibitor adsorption on the surface of the aluminum alloy was studied using a polarization resistance indicator P5126. This is a two-electrode electrochemical converter, which includes two identical cylindrical metal electrodes: diameter – 6 mm, length – 30 mm, area of each electrode – 6 sm^2, distance between electrodes – 7 mm. In our study, the electrode material is D16t alloy according to GOST4784-97 of the following composition: aluminum (up to 94.7%), copper (up to 4.9%), magnesium (up to 1.8%), manganum (up to 0.9%), silicon (up to 0.5%), iron (up to 0.5%), and impurities of other metals (no more than 0.15%).

The electrolyte is a 3% NaCl solution, the temperature is 297±2 K.

The surface morphology of the aluminum alloy and local chemical analysis after exposure of the samples in a corrosive environment were studied with a ZEISS EVO 50 XVP scanning electron microscope with an INCA Energy 350 x-ray spectral microanalysis system (Oxford Instruments).

III. Results and discussion

Based on the results of chromatography-mass spectrometry, the PP components were identified by comparing the retention times of peaks on the chromatogram and full mass spectra of individual components with the corresponding results for pure compounds in the NIST-5 mass spectrum library and also using linear retention indices. The relative quantitative content of the chemical components of the extract was calculated by the method of internal normalization of peak areas without sensitivity correction factors.

It was determined that the composition of water-ethanol and water-isopropyl extracts of PP contains 36-37 individual substances (Fig. 1, Table 1). All of them are known organic compounds, namely: terpene alcohols, aldehydes, phenolic compounds, flavonoids, etc. The polyphenolic composition is represented by phenolic acids in the form of gallic and ellagic acids, flavonoids - by catechin, epicatechin, kaempferol, myricetin, quercetin, and its derivatives, as well as stilbenes (resveratrol). Terpenoids are represented by alcohols (linalool, geraniol, borneol, nerol), phenols (carvacrol) and aldehydes (E-citral). The research results showed that the peel of pomegranate fruit contains up to 28 % of high molecular polyphenols (Fig. 2).

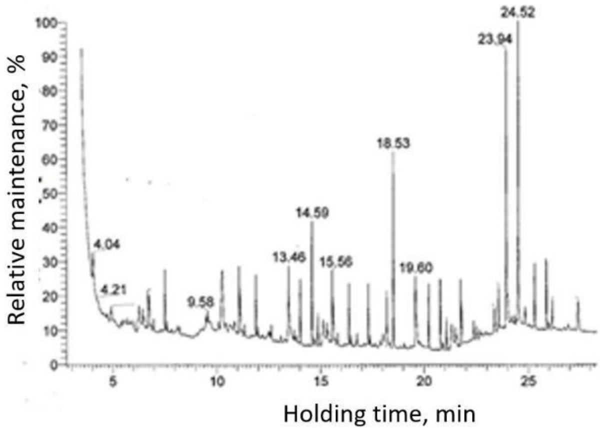


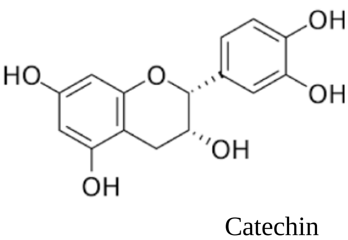
Fig.1. Chromatographic and mass spectra of water-alcohol extract of pomegranate peel.

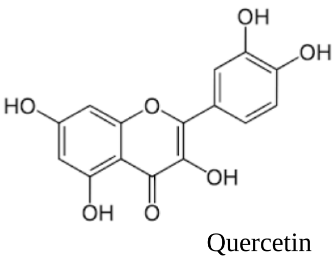
According to [9, 13, 14], tannins, as well as carbohydrates, phenols, amino acids, and aldehydes, are the components of plant extracts that can significantly affect the corrosion process. In polyphenols, hydroxyl groups account for 15-30% of the molecular weight [9], which is promising for the formation of sorption bonds with the metal surface by the donor-acceptor mechanism or ionic bonds with metal cations. Since the reactive groups are in an ortho-position to each other, the complexes formed in this way have a chelated structure. The protective effect depends on the molecules' orientation to the aluminum surface. When placed flat, stable chemical bonds can form between the hydroxyl groups of compounds and aluminum atoms. Whereas, with increasing concentration, the molecules locate perpendicularly to the sample surface and form easily mobile complex compounds with aluminum ions. That is

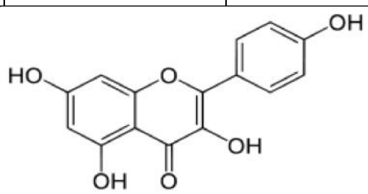
Table 1.

Component composition of volatile substances of pomegranate peel extract

Peak	Component name	Holding time, min	Quantitative ratio, %	
			water-ethanol	water-isopropyl
1	Hexan-2-ol	4.04	1.1	1.0
2	Benzyl alcohol	4.21	1.0	0.3
3	Ethyl butanoate	4.92	0.6	0.2
4	(Z)-2-Hexen-1-ol	5.91	0.9	0.1
5	Hexanal	9.58	0.4	0.3
6	Benzoic aldehyde	10.26	2.6	2.1
7	Phenylethyl alcohol	11.39	1.3	1.5
8	d-Mannose	13.00	1.1	1.5
9	Lilac aldehyde	13.46	2.9	3.1
10	Camphene	13.89	0.4	0.5
11	Cinnamic aldehyde	14.01	3.8	4.1
12	Carvacrol	14.59	2.9	3.1
13	E-citral	14.92	1.9	1.1
14	Nerol	15.56	5.8	5.0
15	Geraniol	16.06	9.9	8.5
16	Borneol	18.24	1.1	1.0
17	Linalool	18.32	2.3	2.0
18	1,2-benzenedicarboxylic acid	18.53	0.1	0.1
19	Gallic acid	18.69	-	3.1
20	Octadecanoic acid	19.60	4.6	4.0
21	Linoleic acid	18.09	4.2	4.1
22	Hexadecanoic acid	18.24	5.4	6.0
23	(9Z)-Octadecenoic acid	19.62	6.1	6.0
24	Resveratrol	19.21	-	1.1
25	Linolenic acid	16.74	0.3	0.2
26	Ellagic acid	18.81	-	2.0
27	α-caryophyllene	21.01	1.3	1.0
28	Quercetin	23.07	6.4	6.0
29	Quercetin-3-monoglucoside	23.15	7.9	7.7
30	Quercetin-3-monoglucuronoside	23.49	3.6	3.0
31	α –terpineol	23.94	1.5	1.0
32	Catechin	24.16	2.4	2.0
33	Epicatechin	24.46	2.5	2.0
34	Kaempferol	24.49	7.8	7.0
35	Myricetin	24.84	5.5	5.0
36	Lupeol	27.41	1.8	1.1
37	Betulin	27.54	2.4	2.1







Catechin Quercetin Kaempferol

Рис. 2. Formulas of active ingredients of the PP extract.

why the protective properties of the inhibitor significantly depend on the optimal choice of its concentration.

The polarization resistance is known to be inversely proportional to the corrosion rate and characterizes the thickness of the protective film formed on the surface of a metal sample [10, 13]. The change in polarization resistance during the formation of protective layers (during 2 weeks) with the inhibitor participation on the surface of the aluminum alloy D16t in 3 % NaCl is shown in Figure 3. Compared to the solution without the inhibitor (curve 1), we observe a gradual increase in polarization resistance (curves 2-4) with an increase in the inhibitor concentration from 1 to 4 g/l. Optimal stable parameters for the formation of protective layers are observed after exposure of metal samples for 24-48 hours in 3 % NaCl solution at an inhibitor concentration of 3-4 g/l. At lower concentrations of the inhibitor (after 48 hours of exposure), the adsorption of the active components of the inhibitor on the aluminum surface is accompanied by the processes of their desorption into solution and a decrease in the thickness and density of the protective layer, resulting in a significant decrease in polarization resistance (Fig. 3, curves 2, 3).

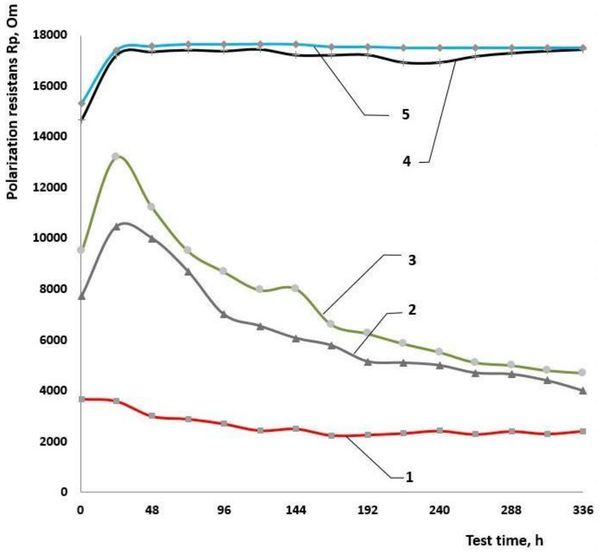


Fig. 3. Changes in polarization resistance during the formation of protective layers on the surface of D16t aluminum alloy in a 3 % NaCl solution: 1 – without inhibitor; 2-5 – with the inhibitor, g/l: 2 – 1; 3 – 2; 4 – 3; 5 – 4.

Samples that were kept in a 3% NaCl solution for 48 hours (Fig. 4) in the presence of an inhibitor have smooth, clean surfaces, while without inhibitors, the formation of corrosion products is observed, which are clearly visible on the electrode surface.

The corrosion inhibition coefficient (γ) and the degree of protection of the electrode (Z) immersed in the solution containing the inhibitor were determined, following [18], from the ratio of the polarization resistance of the electrode in the background solution and in the presence of the inhibitor (Table 2) after 48 hours of exposure.

The results of the study by scanning electron microscopy confirm the formation of a protective layer on the aluminum surface in the presence of the inhibitor (Figs. 5-7). The elemental composition of the surface, evaluated by EDX analysis, indicates a decrease in the percentage of Al (from 92.98% in air, 84.99% in solution without the inhibitor to 54.61% in the presence of PP extract) and an increase in the content of Carbon (from 11.20% to 33.06%) and Oxygen (from 3.81% to 12.32%), which are part of the active substances of the inhibitor. The decrease in Aluminum content and increa-se in Carbon and Oxygen content indicates the formation of a protective film on the surface of the aluminum alloy containing the active ingredients of the extract.

Table 2.

Results of determining the anticorrosive effectiveness of the PP inhibitor by the method of polarization resistance (48 hours in 3% NaCl solution)

Inhibitor concentration, g/l	R_p, Ом	γ	Z, %
0	3000	–	–
1	10000	3.33	70.00
2	11220	3.74	73.26
3	17360	5.78	82.72
4	17560	5.85	82.92

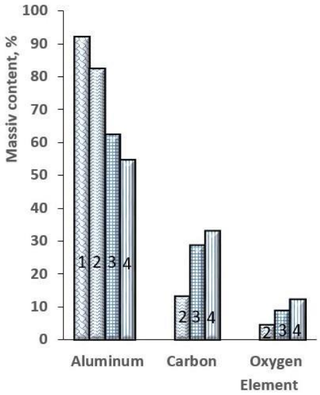
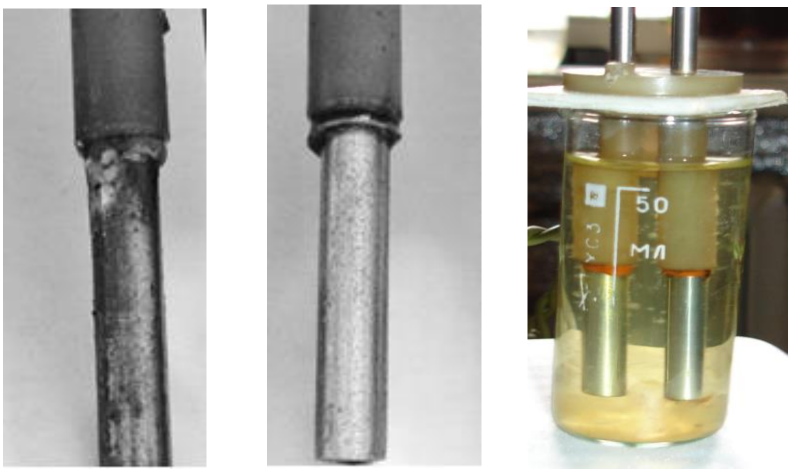


Fig. 5. Diagram comparing the content of Aluminum, Oxygen and Carbon on the surface of D16t alloy samples: 1 – in the air; 2 – in a 3% NaCl solution; 3, 4 – in a 3% NaCl solution with added PP inhibitor.



a *b* *c*

Fig. 4. Photos of samples during the study of polarization resistance in a 3% NaCl solution after 96 hours of exposure: *a* - without inhibitor; *b, c* - with PP inhibitor**.**

Element	Mass %	Atom %
Mg	1.44	1.64
Al	92.98	95.75
Si	0.25	0.25
Mn	0.45	0.23
Cu	4.88	2.13
Total	100.00	

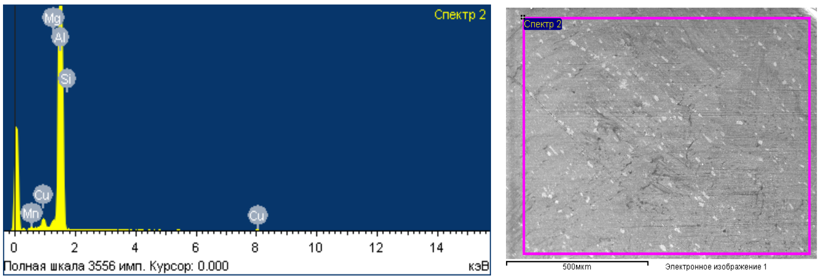
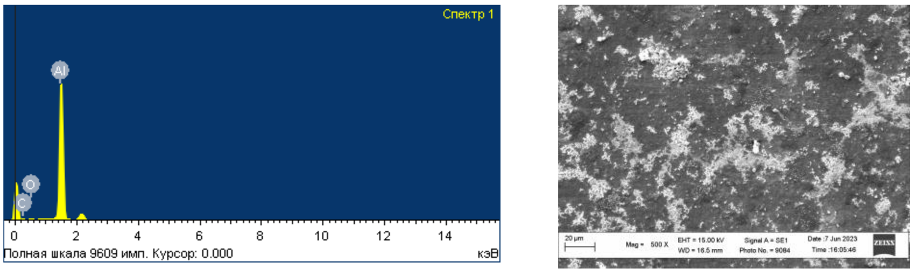


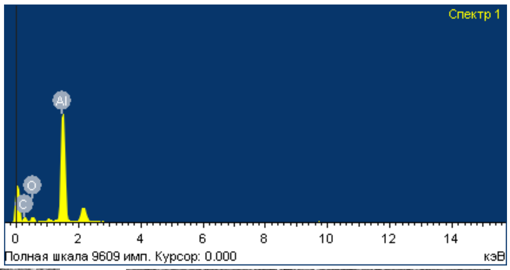
Fig. 6. Spectra of elemental composition and electron microscopic images of the surface of aluminum alloy D16t in the air.

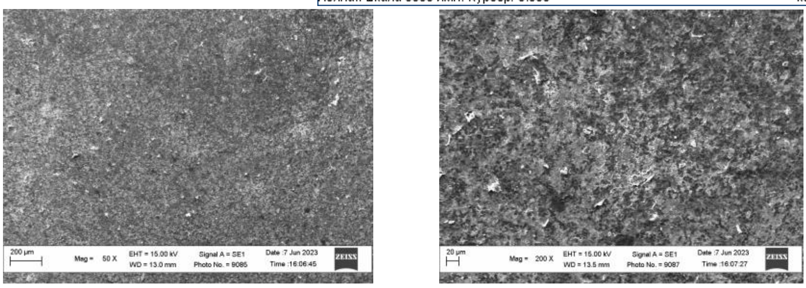
Element	Mass %
C	11.20
O	3.81
Al	84.99
Total	100.00



a

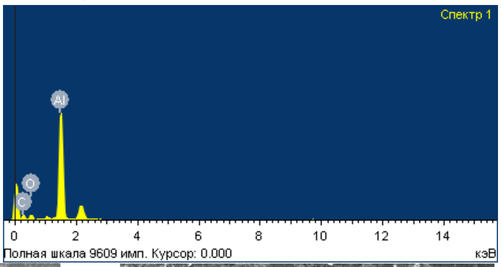
Element	Mass %
C	27.82
O	7.79
Al	64.39
Total	100.00

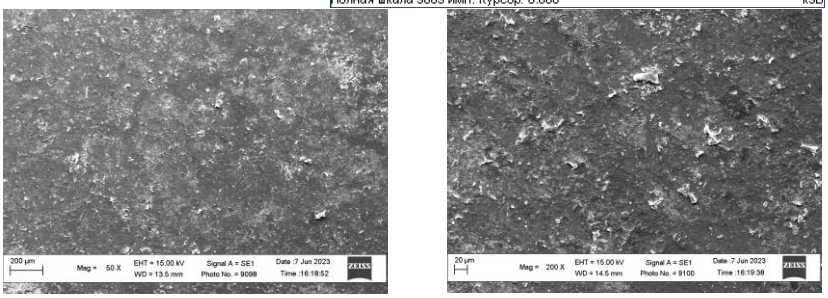




b

Element	Mass %
C	33.06
O	12.32
Al	54.61
Total	100.00





c

Fig. 7. Spectra of elemental composition and electron microscopic images of the surface of aluminum alloy D16t: after exposure in 3% NaCl solution (*a*) and with added PP inhibitor (*b*– 1 g/l; *c* – 4 g/l).

Subsequently, we compared the ratio of Aluminum content on the surface of the samples to Oxygen and Carbon, which are part of the inhibitor's active ingredients (Fig. 7). The content of other components was disregarded.

The electron microscopic images of the aluminum alloy D16t surface in the air differ significantly from the metal surface after exposure to a 3 % NaCl solution for 48 h, as a loose layer of corrosion products is observed on the later. When the inhibitor is introduced, an adsorption layer of extract organic compounds is formed on the surface of the aluminum alloy, the density of which increases with an increase in the inhibitor content from 1 g/l to 4 g/l. The weight percentage of Al decreased as a result of the formation of a protective layer.

Conclusions

Corrosion tests in a 3% NaCl solution confirmed the effectiveness of protecting the surface of D16t aluminum alloy with an inhibitor based on food waste - pomegranate peel extract. With the introduction of 4 g/l of the inhibitor, corrosion is inhibited by 82.9%.

The inhibitory effect results from the presence of functional molecule groups of the active substances that form adsorption bonds with local centers of the alloy surface. Based on the results of scanning electron microscopy, the active substances in the water-alcohol extract of pomegranate peel contribute to a significant restoration of the protective film in the vicinity of aluminum alloy intermetallics in a corrosive environment.

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Характер утворення адсорбційних шарів на алюмінієвих поверхнях при інгібіторному захисті рослинними екстрактами

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Досліджено характер адсорбції на поверхні алюмінію інгібітора корозії, виготовленого на основі рослинних відходів харчових виробництв – шкірки гранату. Механізм дії інгібітора значною мірою обумовлений тим, що активні речовини хемосорбуються на поверхні металу і утворюють плівку, що ізолює цю поверхню від агресивного впливу середовища.

Ключові слова: рослинна сировина, екстракт шкірки гранату, інгібітор, адсорбція.