Synthesis of Corrosion Inhibitors Based on (Thio)Urea, Orthophosphoric Acid and Formaldehyde and Their Inhibition Efficiency

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Abstract

In this article, the optimal conditions for the synthesis of two types of oligomeric corrosion inhibitors, polymethylene diamidophosphate (PDAF-1) and polymethylene thiodiamidophosphate (PTAF-2), based on compounds such as thiourea, urea, and orthophosphoric acid containing nitrogen and phosphorus, as well as their formulas, are determined. At first, (thio)diamidophosphate - PDAF-1 brand corrosion inhibitor was synthesized using urea and orthophosphoric acid in a 2:1 mol ratio at a temperature of 135-140 ℃. The second type of polymethylene thiodiamidophosphate (PTAF-2) corrosion inhibitor was synthesized based on the process of condensation in an aqueous environment at a temperature of 60 ℃, by adding formaldehyde to this obtained compound in a stoichiometric 1:1 mol ratio. The resulting substance is a white solid, non-volatile, the composition of the main component is 98.7%, and other substances - 1.3%. IR-spectra investigated the structure of these two types of corrosion inhibitors. Also, the inhibition efficiency of these corrosion inhibitors was studied by gravimetric and electrochemical methods in corrosive media such as HCl, H_2SO_4 and NaCl=3%. In addition, the factors affecting the inhibition efficiency, such as the pH of the solution, the duration of time, and the concentration of the inhibitor, were also studied. According to the obtained results, the inhibition efficiency of these corrosion inhibitors was between 95.3 and 97.8%. Also, electron microscopy studied and analysed the protection mechanism of corrosion inhibitors on the steel surface.

Keywords: Corrosion inhibitor, Dithioamidophosphates, Formaldehyde, Orthophosphoric acid, Polymethylene thiodiamidophosphate.

Introduction

Protection of metals against corrosion in various corrosive environments[1–3]. A corrosion inhibitor is a compound that is added in low concentrations to a corrosive solution to reduce or minimize the corrosion rate [4–6]. When it comes to the economic damage of this corrosion process, as an example, we can cite the following figures, for example: according to the results of international research conducted by NACE (IMPACT 2016), the annual economic damage of the corrosion process worldwide is 2.5 trillion US. It is concluded that, this figure in each country section, it is about 3.4% of the average gross domestic product (GDP) of each country[7-9]. The results of many years of scientific

research carried out by world scientists show that the environment should be taken into account when choosing corrosion inhibitors, and that the use of compounds containing nitrogen and sulfur and substances based on them is more effective for acidic environments[10]. In addition, such as aldehydes, thioaldehydes, including various alkaloids, such as papaverine, strychnine, quinine, and nicotine, have been proven to be highly effective corrosion inhibitors and meet the requirements for corrosion inhibitors. Many researchers showed that using corrosion inhibitors based on benzoates, nitrites, and inhibitors based on them, as well as chromates and phosphates, have a high inhibition efficiency for alkaline and acidic solutions[11,12]. An anti-corrosion additive is proposed, which is a mixture of orthophosphoric acid, water and a tertiary amine. It has been shown that the synthesized new anti-corrosion composition based on nitrogen- and phosphorus-containing organic compounds, which provides a high protective effect under conditions of sulfide corrosion of steel, amounting to $Z = 53.0-80$ at low dosages, 9% [13].

The main goal of this work is to study the optimal conditions for the first time synthesis of oligomeric corrosion inhibitors based on urea, thiourea, formaldehyde and orthophosphoric acid, and also to study their inhibition efficiency by gravimetric and electrochemical methods.

Materials

The experiments were carried out with samples of carbon steel grade St30 and steel samples of this brand were purchased from "Uzbekistan Metallurgical Combinat" JSC. Water (cooling water in the cooling system of "Mubarak gas processing" and "Shurtan gas processing" plants) was used as a corrosion medium (water composition and properties are as follows: total hardness 6.3 mg-eq/l, total alkalinity 2.08 mg-eq/l, 6.3 mg-eq/l, total alkalinity 2.08 mg-eq/l, Ca^{2+}-4.2 mg-eq/l, Mg^{2+}- mg-eq/l, HCO_3^--2.00 mg-eq/l, CO_3^{2-}-0.08 mg-eq/l). Other chemical reagents: hydrochloric acid, sulfuric acid, thiourea, orthophosphoric acid, and formaldehyde were purchased "chemically pure" from "Merit Chemicals" company.

Methods

Polarization curves analysis
The corrosion-inhibiting properties of an aqueous dispersion of the studied corrosion inhibitor (PDAF-1 and PTAF-2), both with and without additives, were studied by the potentiostatic method on a PI-50-1.1 tool with a PR-8 program, by recording polarization curves on steel electrodes in different corrosion media aqueous, acidic and saline media.

IR analysis
The composition of the inhibitors was investigated using IR-spectra and elemental analysis with Shimadzu IR Tracer-100.

Preparation of polymethylenedi(thio)amidophosphates (PDAF-1 and PTAF-2).
The influence of reaction parameters on the condensation of the interaction of urea and thiourea with orthophosphoric acid and the course of their oligomerization in the mass were studied. It is known that the interaction of urea compounds in a mass depends on their structure, concentration and other factors, consideration of concentration effects in reactions and the influence of reagents on their reactivity. Synthesizing nitrogen- and phosphorus-containing oligomeric corrosion inhibitors without water environment, a reaction first occurs with the formation of (thio)diamidophosphate according to the following scheme.1:
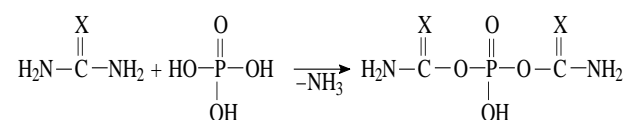
Scheme 1. Synthesis of (thio)diamidophosphate-PDAF-1

Where X–O and S
The ratio of orthophosphoric acid and urea is 1:2. Condensation is carried out in a urea melt at a temperature of 408-413 K.
Next, the calculated amount of formaldehyde was added to the resulting product, and the process of condensation of formaldehyde with di(thio)amidophosphates was carried out at a temperature of 333 K in an aqueous environment. The reaction between formaldehyde and

di(thio)amidophosphates can be represented according to the following Scheme 2.

$$H_2N-\overset{\overset{X}{\|}}{C}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{X}{\|}}{C}-NH_2 + CH_2O \xrightarrow[-H_2O]{}$$

$$\longrightarrow H_2N-\overset{\overset{X}{\|}}{C}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{X}{\|}}{C}-NH\left[-CH_2-HN-\overset{\overset{X}{\|}}{C}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{X}{\|}}{C}-NH\right]_n-H$$
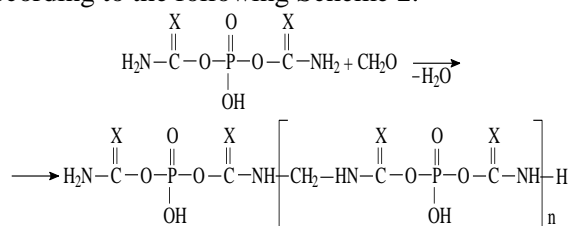
Scheme 2. Synthesis of polymethylenedi(thio)amidophosphates PTAF-2.

Where X – O and S

Corrosion inhibitor obtained on the basis of formaldehyde and diamidophosphates has the following physicochemical properties: white color, solid aggregate, non-volatile, purity 98.7%, and other impurities - 1.3%. However, studies have shown that the temperature regime of synthesis significantly affects their ratio in the final product. In addition to the constant ratio of initial reagents to this synthesis process, the effect of temperature on the process was also studied, where the increase of the reaction temperature from 60 ºC to 100 ºC leads to an increase in the percentage of polymer from 11 to 33%. Also, the continued increase in temperature causes the polymer to achieve homogeneity. In addition, the viscosity of polyamide phosphate increased from 0.06 to 0.13 dl/g[14]. It follows that in order to obtain a high molecular weight polyamide phosphate, the starting reactants should be taken in an equimolar ratio, as shown in Table 1.

Table 1. The effect of the ratio of initial reagents on the composition of the resulting product. (T=100 ^{0}C, τ= six hours).

Ratio Form.+Aduct. urine	Output, %	$\eta_{пр}$ 0.5 aq. solution. dl/g	Elemental analysis			
			nitrogen		phosphorus	
			Computed	Found	Computed	Found
1:3	67,8	0,075		18,1		18,8
1:2	74,5	0,07		17,9		18,3
1:1	88,3	0,06	18,4	17,4	19,1	19,2
2:1	80,6	0,05		16,9		18,5
3:1	76,4	0,04		17,2		18,4

Among different mole ratios, the highest yield was observed when the mole ratio of the starting materials was 1:1 in Fig. 1. The kinetics of formaldehyde consumption and inhibitor formation compared to the initial substances was studied and the decrease of the slope was observed in Fig. 2.
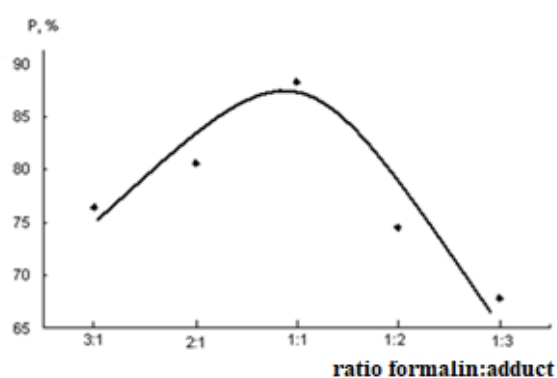
1—1:3;   2—1:2;   3—3:1;   4—2:1;   5—1:1

Figure 1. Dependence of polymer yield on the ratio of starting substances. T=373 K, time 6 hours.
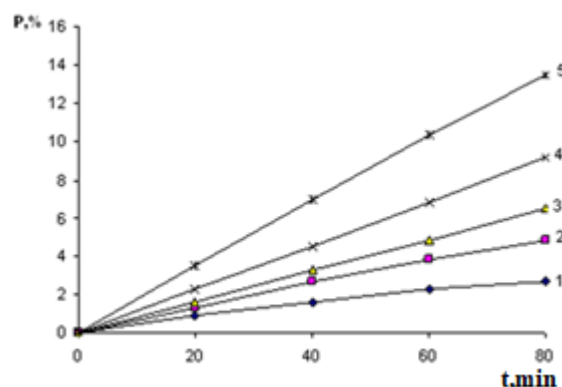
Figure 2. Kinetic dependence of polycondensation in the Form system: Adduct.urine. in an aquatic environment. (T=373K).

IR spectrum analysis

The structure of the synthesized corrosion inhibitors was studied and analyzed by IR spectrum analysis of its components and results are presented in Fig. 3.
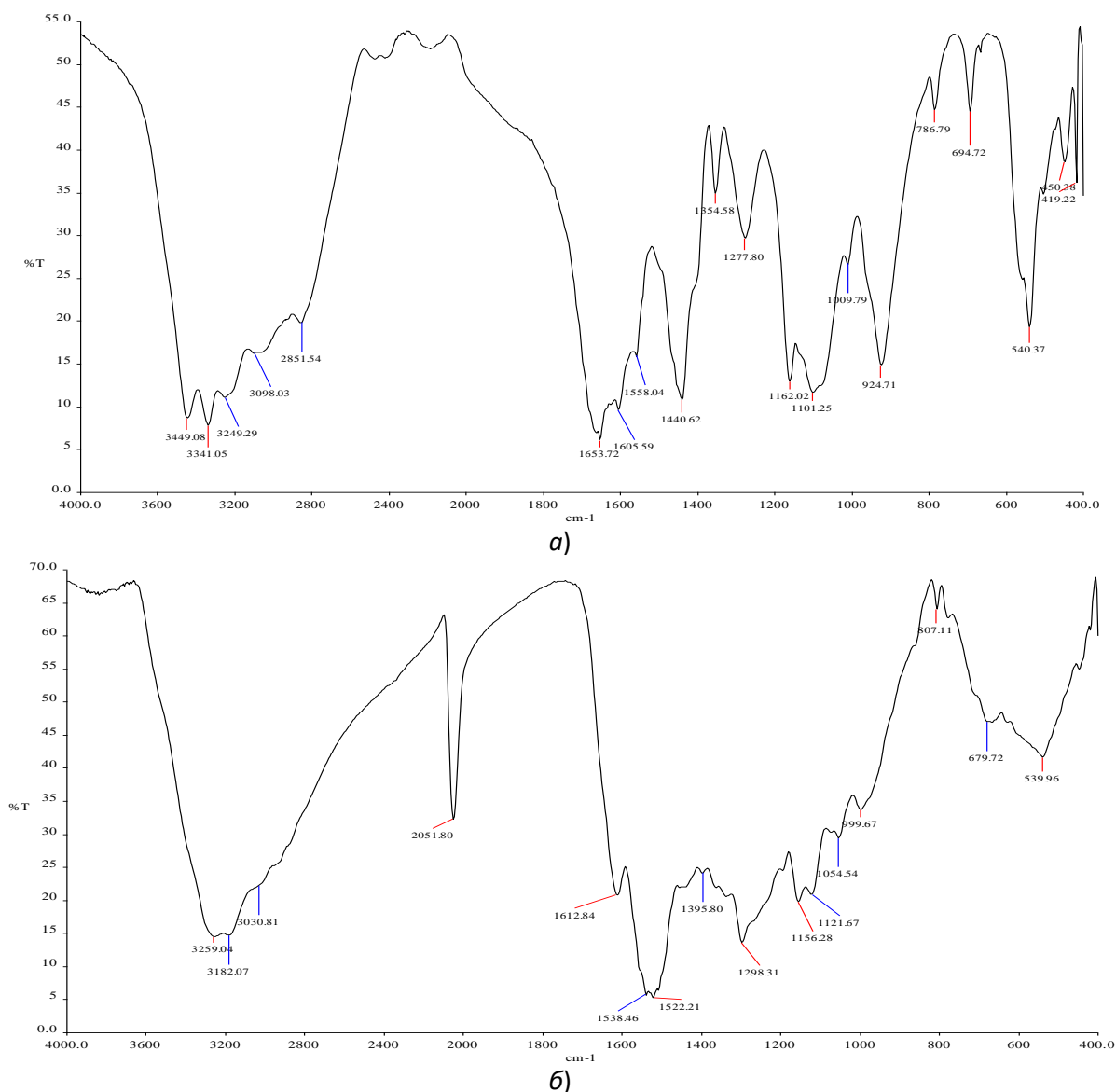
Figure 3. IR spectrum of (a) polymethylene diamidophosphate and (b) polymethylene thiodiamidophosphate

The IR spectra from Figs. 3 a & 3b of the starting reagents and the resulting compound contain bands in the region of 3449, 3341 and 3182 cm^{-1}, corresponding to free hydroxyl groups. The structure of primary and secondary amides and thioamide compounds is characterized by the occurrence of valence vibrations in the IR spectrum regions at 1395, 1522, 1605 and 3449, 3259, 3249, 3098 cm^{-1}, respectively. In this case, the valence bands of C=S and C=O groups appear in the region of 1612, 1653 and 1680 cm^{-1}, and in the regions of 2851 and 1440 cm^{-1} . We observed the allowed resonances of CH- and CH$_2$- groups. Unbonded and bonded P=O phosphorus-oxygen bonds were observed to appear in the regions of 1277, 1298, and 924 cm^{-1}.

Results and Discussion

Studying physicochemical and inhibitory properties of synthesized oligomeric corrosion inhibitors

The corrosion-inhibiting properties of an aqueous dispersion of the corrosion inhibitor under study (PTAF-2), both with and without additives, were studied by the potentiostatic method on a PI-50-1.1 device with a PR-8 program, by recording

polarization curves on steel electrodes in aqueous water, acidic and saline environments. The initial aqueous dispersion of the test oligomer was purified by dialysis[15,16]. One of the accurate and at the same time fast methods for studying the anti-corrosion properties of inhibitors is the experimental study of polarization curves and polarization resistance of a steel electrode or probe in aqueous, saline and acidic environments. Figs. 4-6 show the results of measuring the polarization resistance of a steel probe in various environments, as well as in the presence of inhibitors.
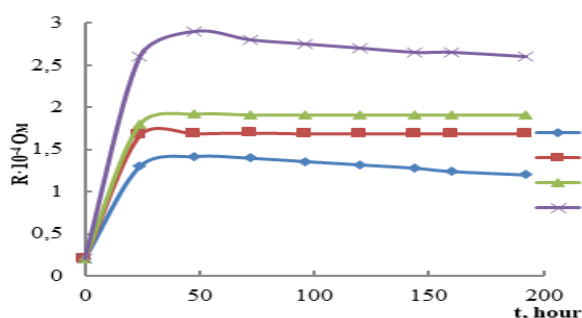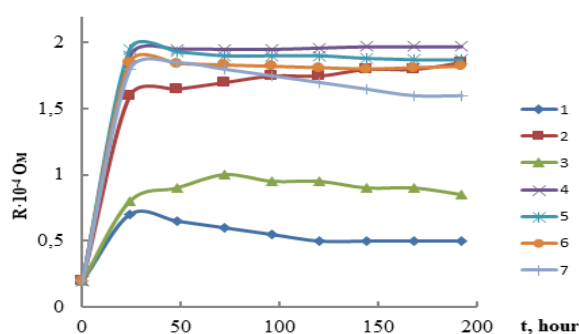

1– H_2O; 2–C=0,001%; 3– C=0,01%; 4–C=0,1%

Figure 4. Change in the polarization resistance of a steel electrode in an aqueous environment in the presence of an inhibitor PTAF-2.
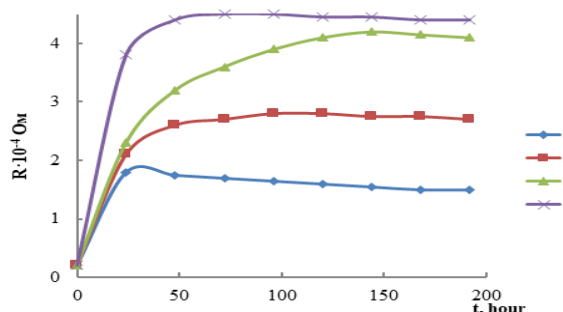
l. NaCl-C=3%; 2-C=0,001%; 3-C=0,01%; 4- C=0,1%

Figure 5. Change in polarization resistance in a salt environment in the presence of the PTAF-2 inhibitor

1-HCl, C=5%; 2- H_3PO_4 (extraction) and PTAF-2 C = 0.001%; 3- H_3PO_4 (term), PTAF-2 C=0.001%; 4- HCl, C=5% with PTAF-2

C=0.001%; 5- HC1, C = 5% with PTAF-2 C = 0.001%; 6- HC1, C=5% with PTAF-2 C=0.1%; 7- HC1, C=5% with PTAF-2 C=1%.

Figure 6. Change in polarization resistance in an acidic environment in the presence of the PTAF-2 inhibitor.

The results of calculating the braking coefficient (g) and protection level (Z) values are presented in Tables 2-3, from which it can be seen that the most significant results were obtained in the presence of 0.1 and 0.01% solutions of the corrosion inhibitor obtained by ammonium dihydrogen phosphate with formaldehyde (IR- 5).

The work uses the method of alternative research of graphical processing of corrosion curves. For these purposes, polyamides, phenol-formaldehyde resins, and other polymers are quite acceptable. The traditional way of graphically processing polymerization curves to determine the corrosion rate is to extrapolate in semilogarithmic coordinates the rectilinear sections of the cathode and anodic branches until their mutual intersection. However, despite the obvious simplicity of the method, its practical use is often associated with a number of complications. The construction of tangents itself is quite subjective, and for a more reliable extrapolation an additional accurate determination of the corrosion potential is necessary.

The inhibitory properties of the composition of the oligomeric corrosion inhibitor (PTAF-2) synthesized by us are presented in Table 2.

Table 2. Protective properties of the composition (PTAF-2) in relation to steel in an aqueous environment.

With inhibitor mg/l	Protective effect, %, at temperature K		
	293	313	333
100	94,6	91,3	89,2
200	95,1	93,0	90,4
300	96,6	94,1	92,0
400	97,8	96,4	95,3

The research results indicated that at a composition concentration (PTAF-2) of 100 mg and a temperature of 293-333 K; the protective effect is 89.2-94.6%, depending on the composition ratio. With an increase in the inhibitor concentration (PTAF-2) from 100 to 400 mghl-1, the protective effect against corrosion increases and reaches 95.3-97.8% at 293-333 K. An important property of inhibitors is the preservation of the protective effect at elevated temperatures. From the data in Table 2, it can be seen that the protective

effect decreases with increasing temperature (from 293 to 333 K), but still remains significant. The results obtained confirm the possibility of using the proposed composition (PTAF-2) as a metal corrosion inhibitor in relation to aqueous and saline environments. Table 3,2 shows data on the effectiveness of the corrosion inhibitor in aqueous and saline environments. To identify the process of concentration-dependent corrosion inhibition, steel plates were immersed in a potential measuring cell containing aqueous solutions of the test oligomer. Experimental data on studying the corrosion rate of steel plates in aqueous dispersions (PTAF-2) both with and without additives showed that when the concentration changes, the stationary potential of the electrode shifts to the positive region, due to the formation of a barrier type of corrosion protection. This effect increases significantly with increasing concentration of the oligomeric inhibitor in the aqueous dispersion[17].

Polarization measurements give reason to believe that the aqueous dispersion of the oligomer under study, as a surfactant, is initially adsorbed on the surface of the steel electrode with the subsequent formation of a film that prevents further corrosive destruction of the metal.

As a result, both the hydrogen ion discharge reactions (increased hydrogen evolution overvoltage) and the ionization reactions (anodic dissolution) of iron slow down. In this case, it is necessary to assume that the dipoles of the surfactant are located with negative ends towards the solution, which contributes to a shift of the potential of zero charge and, consequently, the stationary potential in the positive direction. The shift of the points of zero charge in the positive direction is accompanied by a simultaneous increase in the overvoltage of hydrogen evolution and a slowdown in the corrosion destruction reaction. Along with this, it should be noted that the nature of the adsorption of the inhibitor on the surface of the steel electrode, the effectiveness of its action, as well as whether the inhibitors belong to the cathodic and anodic types depend not only on its nature, but also to a large extent on the potential of the medium. Judging by the steady-state potential, with the addition of an oligomeric inhibitor based on (PTAF-2), the degree of protection increases significantly. Moreover, more effective protection against corrosion occurs in the presence of a 0.1% solution of PTAF-2, the protective coefficient of which passes through a maximum[18].

Table 3. Protective properties of corrosion inhibitor oligomer in aqueous and salt media at 293 K

Sample name	C, conc.. %	Environment	Braking coefficient,γ	Degree of protection, Z
PTAF-2	0,1	Water	26,7	98,2
PTAF-2	0,01	Water	19,6	94,6
PTAF-2	0,001	Water	14,3	91,5
PTAF-2	0,1	NaCl=3%	19,5	96,7
PTAF-2	0,01	NaCl=3%	15,8	93,3
PTAF-2	0,001	NaCl=3%	10,4	89,9

The mechanism of action of this oligomeric corrosion inhibitor is determined mainly by the transition of the surface-protected metal to a stable surface film state with the participation of particles of fine additives. However, the action of inhibitors in this case is more complex than in film formation, and is also associated with the nature of adsorption of surfactant ions. For example, with a positive surface charge of the electron relative to the solution, an oligomeric inhibitor, which is anions, will be adsorbed on it, while with a negative surface charge, the inhibitor, which is undissociated molecules[19].

Gravimetric method

The inhibition efficiency of corrosion inhibitors was determined using the gravimetric method, and all experiments were carried out at temperatures of 20 ± 3 ^{0}C. The rate of general corrosion was determined from metal samples in the form of plates made of steel grade St3 measuring $40\times12\times2$ mm with a surface. Each value of samples the corrosion rate was calculated based on the following the Eq. 1:

$$\rho = \frac{\Delta A}{S \cdot T}, \text{г} / (\text{м}^2 \cdot \text{ч}), \qquad 1$$

Where ρ - corrosion rate, g/(m^2·h);
A - weight loss of the metal, g;
S - sample surface area, m^2;
T - test duration, hours.

The protective effect of inhibitors is using below the Eq. 2:

$$z = \frac{\rho_o - \rho}{\rho_o} \cdot 100\% \qquad 2$$

Where-Z is the protective effect, %;

ρ_o - without inhibitor, g/(m^2 h);

ρ- with inhibitor, g/(m^2 h).

All the test results are given in Tables 4 and 5.

Table 4. Comparative assessments of the protective properties of oligomeric corrosion inhibitors at pH=6

Inhibitor	Concentration, mg/l	Protective effectiveness against general corrosion, %, with mineralization, mg/l		
		30	100	270
1	2	3	4	5
	250	98	98	98
PDAF-1	150	98	98	95
	50	95	95	90
	250	98	98	98
PTAF-2	150	98	98	98
	50	95	95	95

Table 5. Comparative assessments of the protective properties of oligomeric corrosion inhibitors at pH=3

Inhibitor	Concentration, mg/l	Protective effectiveness against general corrosion, %, with mineralization, mg/l		
		30	100	270
	250	95	95	95
PDAF-1	150	95	95	94
	50	92	92	90
	250	95	95	95
PTAF-2	150	94	94	93
	50	92	92	91

The difference in protection between the inhibitors in Tables 4 and 5 above and the inhibitors in Table 6 is explained by the following conditions:

-in the first case, the inhibitor coating is formed under the influence of an aggressive environment;

-in the second case - mechanically, and this protection slightly increases corrosion resistance.

From the data presented in Table 6, it is known that the inhibition efficiency is 5% for PDAF-1, and the maximum protective effect is observed for PTAF-2 at 10-20%. This effect can be explained by the formation of a protective film on the surface of the samples with better diffusion of inhibitors in electrolytes and easier diffusion[20].

Table 6. Comparative assessments of the protective properties of corrosion inhibitors in aggressive environments

Inhibitor	Protective effectiveness against general corrosion, %, with mineralization, mg/l				
	6	24	96	120	240
1	2	3	4	5	6
pH=6					
PDAF-1	98	94	90	84	80
PTAF-2	98	95	91	83	79
pH=3					
PDAF-1	97	94	90	82	80
PTAF-2	96	93	89	81	76

Both oligomers slow down not only the anodic, but also the cathodic reaction, i.e. are mixed type corrosion inhibitors. Their influence on the cathodic process is almost the same, but the inhibition of the anodic reaction is more noticeable in the case of PDAF-1. The protective ability of oligomeric corrosion inhibitors was assessed by comparing the

densities of corrosion currents obtained by polarizing the electrode under study. The lower the corrosion current density at the same polarization, the lower the corrosion rate and the higher the protective ability of coatings.

The level of corrosion protection of these corrosion inhibitors was studied by comparing the current

density at the electrodes in the media with and without the inhibitor. In this case, it was found that the lower the current density, the slower the corrosion rate, that is, the higher the level of protection of the inhibitors.

Tables 7-8 below clearly show the levels of protection of two types of oligomeric corrosion inhibitors in two types of (3% NaCl and H$_2$SO$_4$) corrosion environments. In this case, the current density in the electrodes was 893 mA in the saline medium, and 1584 mA in the acidic medium.

However, with the addition of an inhibitor to the corrosion medium, for PDAF-1 it was 12.14 mA in saline medium and 58.76 mA in acidic medium, for PTAF-2 it was 44.20 mA in saline medium and 19.80 mA in acidic medium tables 9-11. From the given data, it is known that the slowing down of the cathodic process occurs due to the difficulty of diffusion of dissolved oxygen to the cathodes, through a layer of corrosion products or an insulating film[21].

Table 7. The degree of protection and braking coefficient of different oligomeric corrosion inhibitors in a saline environment (NaCl 3%)

№	Composition	E$_{см}$ B Stationary potential	I$_c$, мA (standard) mA Corrosion rate	γ Braking coefficient	Z %, Degree of protection
1	NaCl 3%	0,780	893	-	-
5	PDAF-1	0,460	12,14	73,56	98,64
6	PTAF-2	0,490	44,20	20,20	95,08

It can be seen that both PDAF-1 and PTAF-2 types corrosion inhibitors have a corrosion protection rate of 98-99% in salty and acidic environments.

Table 8. The degree of protection and braking coefficient of different oligomeric corrosion inhibitors in acidic environments (3%H$_2$SO$_4$)

№	Composition	E$_{см}$ B Stationary potential	I$_c$, мA Corrosion rate	γ Braking coefficient	Z %, Degree of protection
1.	H$_2$SO$_4$ 3%	0,280	1584	-	-
2.	PDAF-1	0,360	58,76	26,95	96,29
3.	PTAF-2	0,360	19,80	80,00	98,75

Table 9. Dependence of polarization resistance on time in a solution of 3% NaCl

№ Sample	Time in day				
	1 day	5 day	10 day	15 day	20 day
Electrolyte	157	125	125	120	120
PDAF-1	157	145	145	140	138
PTAF-2	158	166	166	169	169

Table 10. Dependence of polarization resistance from time in aquatic environment

№	№ Sample	Time in day				
		1 day	5 day	10 day	15 day	20 day
1	Electrolyte	1310	710	130	69	68
5	PDAF-1	1420	1360	200	185	184
6	PTAF-2	1340	1280	230	1230	225

Table 11. Dependence of polarization resistance from time to time in 3%H$_2$SO$_4$

№	№ Sample	Time in day				
		1 day	5 day	10 day	15 day	20 day
1	Electrolyte	110	45	40	30	30
5	PDAF-1	180	197	196	195	195
6	PTAF-2	145	51	44	38	38

Tables 12 and 13 below show the inhibition efficiency of these two types of corrosion inhibitors in aqueous media and the dependence of inhibition efficiency on concentration and time.

Table 12. Inhibitory properties of PTAF-2 in an aqueous environment (T=298-303 K)

Inhibitor concentration, g/l	Experiment time, h	Corrosion rate, g/m² day	Braking coefficient	Degree of protection, %
Without inhibitor	12	3,6	—	—
0,1	12	1,104	24,2	96,06
0,3	12	0,312	88,4	98,7
0,5	12	0,288	76,6	98,1
Without inhibitor	24	14,4	—	—
0,1	24	0,984	14,3	96,2
0,5	24	0,456	33,4	97,3
Without inhibitor	48	6,2	—	—
0,1	48	0,312	18,4	96,01
0,3	48	0,216	31,1	98,3
0,5	48	0,288	16,5	94,5

Table 13. Inhibitory properties of the tested inhibitors in an aqueous environment (T=298-303 K)

Type of inhibitor	Concentration, g/l	Time of experiment, days	Corrosion rate, g/m² day.	Degree of protection, %
Without inhibitor	—	10	3,7	—
PDAF-1	0,2	10	0,089	99,2
PTAF-2	0,32	10	0,076	99,1
Without inhibitor	—	20	3,8	—
PDAF-1	0,2	20	0,088	99,0
PTAF-2	0,2	20	0,086	98,9
Without inhibitor	—	30	3,5	—
PDAF-1	0,2	30	0,104	99,5,
PTAF-2	0,32	30	0,109	99,1
Without inhibitor	—	40	3,4	—
PDAF-1	0,2	40	0,128	98,9
PTAF-2	0,2	40	0,132	98,6

The reason these oligomeric corrosion inhibitors protect steel is that the inhibitors form complexes with metal cations. The stability of these complexes is the most stable in a pH 5 - 8 environment, increasing the temperature of the corrosive environment decreases the stability of the complexes.

In the following Table 14, the dependence of the inhibition efficiency of these corrosion inhibitors in the hydrochloric acid environment on concentration and time is studied and the results are presented.

Table 14. Results of testing the inhibitor PDAF-1 in hydrochloric acid environment

Concentration HCl, %	Experiment time, h	Additive concentration, %	Average weight loss, g	Braking coefficient	Protective effect, %
25	24	1,0	0,1052	5,7	96,3
Without inhibitor	24	—	—	—	—
36	6	1,0	41,8	41,8	97,8
Without inhibitor	6	—	—	—	—
15	12	0,5	0,0233	0,53	98,1
15	30	1,0	0,0063	80,1	96,7
18	5	1,0	0,040	21,65	98,8
25	6	2,0	0,066	58,9	98,3
25	6	—	0,3811	—	—
20	3	1,0	0,0047	24,3	98,4
20	3	—	0,1562	—	—

In general, the inhibition mechanism of corrosion inhibitors is characterized by several factors: the composition of metals, the structure of the inhibitor, the aggressive corrosion environment, and the

composition and structure of the corrosion inhibitors. The NH groups in the inhibitor protect metals from corrosion by forming bonds with the metal surface. for this reason, attention is now being paid to the synthesis of compounds containing several NH groups in the molecule structure. In particular, since the PTAF-2 brand corrosion inhibitor also contains NH group, it has been determined that process adsorption as a result of electrostatic attraction on the metal surface has a physical nature.

Based on the results of the research, it can be said that the molecular structure of corrosion inhibitors containing nitrogen and oxygen heteroatoms is one of the important factors determining the ability to protect metals from corrosion. In these heteroatomic molecules, the unshared pair of electrons can be considered as an interaction with the empty d-orbitals of the iron atom. The presence of electron-donating substituents in corrosion inhibitor molecules increases the inhibition efficiency of corrosion inhibitors.

Electrochemical research

Electrochemical studies were also carried out to determine the inhibitory efficiency of the synthesized corrosion inhibitors, and according to the obtained results, the formation of a protective layer (film) of the inhibitors on the steel surface causes the inhibition of the anodic and cathodic process of iron ionization due to adsorption. Our proposed corrosion inhibitors not only slow down the anodic corrosion, but also slow down the corrosion in the cathodic process[22,23].
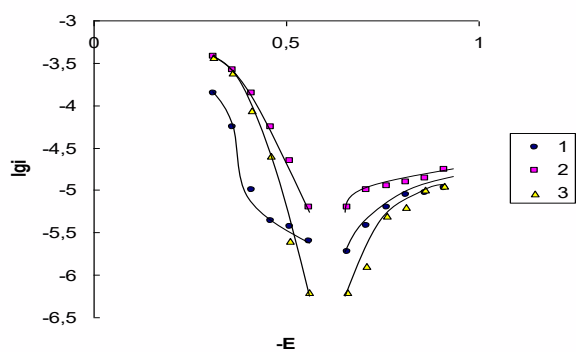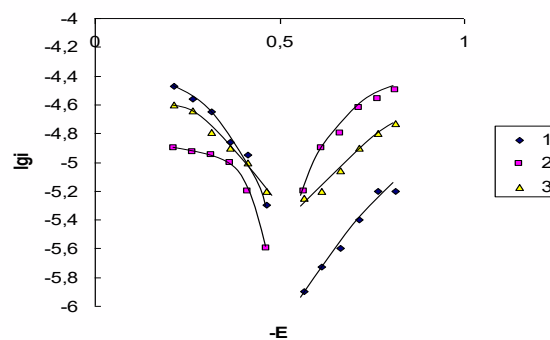

C %, 1-0.001; 2-0.01; 3-0.1

Figure 7. Polarization curves of the oligomeric corrosion inhibitor PDAF-1 in 3% sodium chloride saline solution.
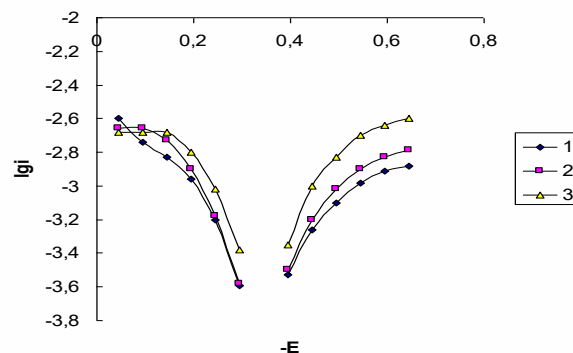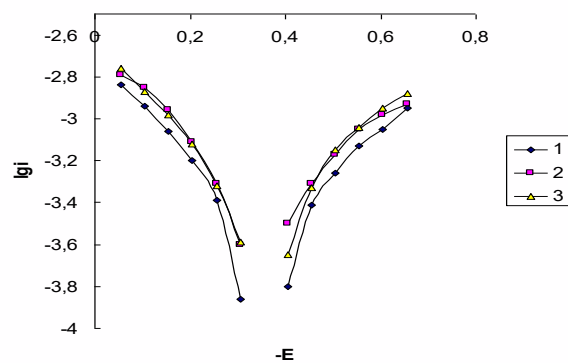

C %, 1-0.001; 2-0.01; 3-0.1

Figure 8. Polarization curves of the oligomeric corrosion inhibitor PDAF-1 in a 3% Sulfuric acid solution.

C %, 1-0.001; 2-0.01; 3-0.1

Figure 9. Polarization curves of the oligomeric corrosion inhibitor PDAF-1 in aqueous solution.

C %, 1-0.001; 2-0.01; 3-0.1

Figure 10. Polarization curves of the oligomeric corrosion inhibitor PTAF-2 in a Sulfuric acid solution.

It can be seen from the above Figs. 7 -10 that the test results were conducted for 7 days and the inhibition efficiency of the inhibitor was studied at different concentrations and in different corrosion environments. It can be seen that the shift of the potential to the positive side leads to an increase in the protection levels of the inhibitors[24].

Electron microscopic analysis

By studying the surface morphology of inhibited steel samples, it was possible to conclude the inhibition mechanism. Tests were mainly conducted with PTAF-2 brand corrosion inhibitor, the maximum protective concentration of the inhibitor (C = 0.1) was obtained, and the obtained results are depicted in Figs. 11 a, b and c. The results obtained by the method of electron microscopy correspond to the results obtained on the basis of gravimetric and electrochemical measurements carried out in the laboratory to study the inhibition efficiency.
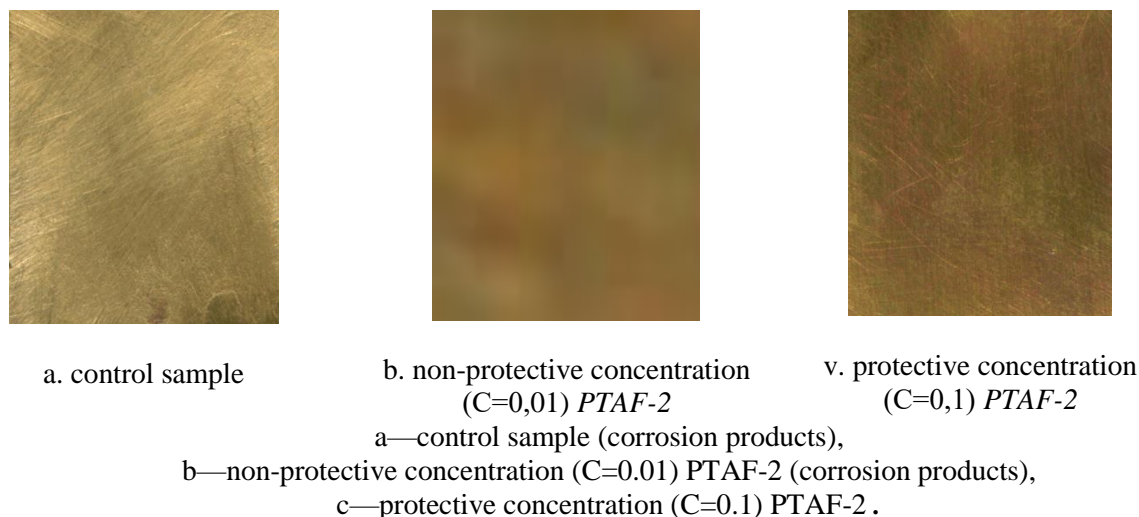

a. control sample

b. non-protective concentration (C=0,01) *PTAF-2*

v. protective concentration (C=0,1) *PTAF-2*

a—control sample (corrosion products),
b—non-protective concentration (C=0.01) PTAF-2 (corrosion products),
c—protective concentration (C=0.1) PTAF-2 .

Figure 11. Structure of the surface layer of steel samples kept in inhibitor environments

Based on local raw materials, we have created new high-temperature corrosion inhibitors in hydrochloric acid environments. For this purpose, new types of oligomeric corrosion inhibitors for water treatment have been synthesized and modified.

Protection of steel against corrosion with oligomeric inhibitors

In general, two main factors influencing the anticorrosion properties of oligomers can be distinguished: the ability to form complexes and molecular weight. Due to the fact that anionic polymers with a lower molecular weight have the best protective ability in relation to low-carbon steel, various oligomers deserve attention, which are often not only more accessible for practical use, but also safe for the environment. However, even at C < 500 mg/l, oligomers have the ability to prevent the precipitation of iron hydroxide, although to a much lesser extent. At C > 500 mg/l of oligomer, this ability increases with increasing pH: at pH 5, the solution contains 30 mg/l Fe^{3+} ions, and at pH 8 - already 45 mg/l, with 71.5 mg/l Fe^{3+} introduced. In addition, a purer oligomer synthesized in the laboratory is capable of retaining more iron ions in such solutions at relatively low concentrations (C = 0.5 g/l) (at pH 6 ÷ 6.5, C(Fe^{3+}) = 35 mg/l) than the industrial oligomer. It can be seen that the PDAF-1 oligomer is more strongly adsorbed on iron. This may be partly due to the presence of nitrogen atoms in its molecule, which, thanks to their unshared pairs of electrons, are capable of forming donor-acceptor bonds with the surface of iron. The high protective properties of the inhibitors PDAF-1 and PTAF-2 were studied. The mechanism of inhibition of steel corrosion by this composition is similar to the mechanism of protection by phosphonate complexes. It has been established that iron cations that go into solution during steel corrosion are displaced from metal-oligomeric soluble structures, which are deposited on the surface of the samples in the form of a sparingly soluble metal that partially blocks the surface of the metal and slow down the cathodic reaction of oxygen reduction. Particles of the oligomer itself and its complexes with iron cations are adsorbed on the metal surface and slow down the anodic dissolution of the metal. The tendency to complex formation in solution has been studied and the high dispersing ability of oligomers, on the contrary, can negatively affect the corrosion resistance of iron in their solutions, since this facilitates the removal of metal corrosion products from its surface. This feature of the compounds considered allows them to be used as detergents and

anti-scale compounds, and their combined use gives them anti-corrosion properties.

The comparison with other corrosion inhibitors
The protective effect of the corrosion inhibitor does not exceed 15-25% over the entire range of varied test parameters. From Table 15, it follows that the addition of a corrosion inhibitor increases the effectiveness of inhibitory compounds. Moreover, this effect begins already with 5% PDAF-1 content,

the maximum protective effect is observed in the corrosion inhibitor PTAF-2 with 10-20%, which can be explained by improved dispersion of inhibitors in the aggressive electrolyte and easier formation of a protective film of the inhibitor on the surface of the samples. Corrosion inhibitors, along with dispersing properties, already exhibit solvent properties - leading to a decrease in the concentration of the active component.

Table 15. Comparative assessments of the protective properties of oligomeric corrosion inhibitors in aggressive environments

Inhibitors	Efficiency of the aftereffect of inhibitors,%, during exposure to an aggressive environment, hour.				
	6	24	96	120	240
1	2	3	4	5	6
pH=6					
PDAF-1	98	94	90	84	80
PTAF-2	98	95	91	83	79
NALCO	97	92	88	80	72
pH=3					
PDAF-1	97	94	90	82	80
PTAF-2	96	93	89	81	76
NALCO	96	92	83	71	63

From Table 15, we can see that the inhibition efficiency of our proposed corrosion inhibitors was compared with the inhibition efficiency of NALCO corrosion inhibitor. In terms of protective properties, corrosion inhibitors PDAF-1 and PTAF-2 are not inferior to low mineralization of the electrolyte and surpass it in protective action in highly mineralized environments. The difference in the protective effect of inhibitors of the same exposure duration is explained by different conditions for the formation of protective films: in the first case, the film is formed from an aggressive environment, and in the second - mechanically, which gives a slight increase in the protective effect. This is clearly seen in the examples of samples PDAF-1, PTAF-2 and the NALCO inhibitor. Oligomeric corrosion inhibitors at concentrations <20 mg/l somewhat stimulate corrosion in H_2SO_4 solutions at room temperature. However, with increasing concentration they become inhibitors, and PTAF-2, which has a lower molecular weight, provides a higher degree of protection of steel from corrosion than other two

inhibitors. At elevated t = 80°C, the differences in the anti-corrosion properties of oligomers are more pronounced. PTAF-2 provides Z ≈ 90% at C > 10 mg/l. Both of oligomer corrosion inhibitors slow down not only the anodic, but also the cathodic reaction, i.e. are mixed type corrosion inhibitors. Their influence on the cathodic process is almost the same, but the inhibition of the anodic reaction is more noticeable in the case of PDAF-1. Oligomeric corrosion inhibitors are substances that protect metal surfaces from corrosion. The mechanism of the anti-corrosion effect of oligomeric corrosion inhibitors on metals, primarily steel, is to create a very thin film on the metal surface that protects the metal from corrosion. The protective ability of oligomeric corrosion inhibitors was assessed by comparing the densities of corrosion currents obtained by polarizing the electrode under study. The lower the corrosion current density at the same polarization, the lower the corrosion rate and the higher the protective ability of coatings.

Conclusion

In present research, synthesis of the new oligomer-type of corrosion inhibitor containing nitrogen and phosphorus based on (thio)urea and orthophosphoric acid, and formaldehyde also its various properties

were studied. The new oligomer-type of corrosion inhibitors were synthesized and its structure was confirmed by the IR spectroscopy. According to the obtained results, the valence vibration of amides and

thioamides appeared at 1395, 1522, 1605 and 3449, 3259 3249, 3098 cm^{-1}, the appearance of bands in the regions of 1612, 1653, and bands in the region of 1680 cm^{-1} indicates related groups C=S and C=O, and in the regions of 2851 and 1440 cm^{-1}, observed the CH– and CH$_2$– groups. Free and bound P=O groups appear in the valence vibration of 1277, 1298, and 924 cm^{-1}. The surface morphology of this modification was studied by the electron microscopy. In addition, optimum conditions for the synthesis of corrosion inhibitors, molar ratios of starting materials: (thio)urea and orthophosphoric acid 1:2, formaldehyde and di(thio)amidophosphates in a 1:1 molar ratio, and reaction temperatures of 408-413 K and 333 K were determined. The structure of both synthesized corrosion inhibitors was determined using IR spectra. The inhibition efficiency of both obtained corrosion inhibitors was studied by gravimetric and electrochemical methods in various aggressive environments. These corrosion inhibitors have been found to perform best in environments with a pH between 5 and 8.

Acknowledgment

Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- No potentially identified images or data are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at Termez Institute of Engineering and Technology, Termez, Uzbekistan, 190111.

Authors' Contribution Statement

A. N. K: Writing – Original draft. K. B.S: Reviewing and editing paper. Z. M. K: Reviewing and editing paper. S.K.Z: Software, validation. A. N. K and S. Y. G: Writing the original draft, conceptualization, investigation and visualization.

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تصنيع مثبطات التآكل المعتمدة على اليوريا (الثيو) وحمض الأرثوفوسفوريك والفورمالدهيد وكفاءتها التثبيطية

أبرور نوموزوف[1]، خاسان بيكنازاروف[2]، ساخوميدين خوجامكولوف[1]، ظفر ميسيروف[1]، سارفينوز يولداشوفا[1،3]

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الخلاصة

في هذا البحث، يتم تحديد الظروف المثالية لتصنيع نوعين من مثبطات التآكل قليلة القسيمات، بولي ميثيلين ديام يدوفوسفات (PDAF- 1)وبولي ميثيلين ثيوديام يدوفوسفات (PTAF-2)، استنادًا إلى مركبات مثل الثيوريا واليوريا وحمض الأرثوفوسفوريك المحتوي على النيتروجين والفوسفور. ، وكذلك يتم تحديد صيغها. في البداية، تم تصنيع (ثيو) ثنائي أميدوفوسفات ـ مثبط التآكل ذو العلامة التجارية PDAF-1 باستخدام اليوريا وحمض الأرثوفوسفوريك بنسبة 1:2 مول عند درجة حرارة 140-135 درجة مئوية. تم تصنيع النوع الثاني من مثبط التآكل بولي ميثيلين ثيوديام يدوفوسفات (PTAF-2)بناءً على عملية التكثيف في بيئة مائية عند درجة حرارة 60 درجة مئوية، وذلك عن طريق إضافة الفورمالديهايد إلى هذا المركب الناتج بنسبة متكافئة 1:1 مول. المادة الناتجة هي مادة صلبة بيضاء، غير متطايرة، تكوين المكون الرئيسي هو 98.7٪، والمواد الأخرى ـ 1.3٪. قامت أطياف الأشعة تحت الحمراء بدراسة بنية هذين النوعين من مثبطات التآكل. كما تمت دراسة كفاءة تثبيط مثبطات التآكل هذه بالطرق الوزنية والكهروكيميائية في الوسائط المسببة للتآكل مثل حمض الهيدروكلوريك، H_2SO_4 وكلوريد الصوديوم = 3%. بالإضافة إلى ذلك، تم أيضًا دراسة العوامل المؤثرة على كفاءة التثبيط، مثل الرقم الهيدروجيني للمحلول، والمدة الزمنية، وتركيز المثبط. ووفقا للنتائج التي تم الحصول عليها، فإن كفاءة التثبيط لهذه مثبطات التآكل تتراوح بين 95.3 و 97.8٪. كما قام المجهر الإلكتروني بدراسة وتحليل آلية حماية مثبطات التآكل على سطح الفولاذ..

الكلمات المفتاحية: مثبط التآكل، ثنائي ثيوأميدوفوسفات، الفورمالديهايد، حمض الأرثوفوسفوريك، بولي ميثيلين ثيودياميدوفوسفات.