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IN CORROSIVE ENVIRONMENTS, CORROSION INHIBITORS CONTAINING NITROGEN, SULFUR AND PHOSPHORUS BASED ON RECYCLED MATERIALS IMPACT ON METAL ST 20

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Annotation. In the world, corrosion of metals, including carbon steel, is a serious problem in many industries, especially during processes such as pickling and acid washing of steel. Therefore, the development of inhibitory compositions is of great theoretical and practical importance. One of the ways to protect metals from corrosion is the use of organic inhibitors, which are heterocyclic compounds containing phosphorus, sulfur, nitrogen and having π bonds.

Keywords: inhibitory compositions, alcanolamin, Incorgaz T 21, adsorption free energies, gravimetric detection.

Purpose of work. Development of a technology for the production of phosphorus, nitrogen, metal-containing new oligomers based on compounds containing inhibitory compositions and their use to obtain polymer composite materials.

Methods. Studies were carried out by methods of chromium-mass spectroscopy, NMR, NMR, electron microscopy, elemental analysis, spectroscopy of electrochemical impedance. Data on the mechanism of the corrosion process in the studied media were obtained depending on the duration of the experiment and the concentration of inhibitory compositions and their adsorption characteristics were determined.

Obtaining a corrosion inhibitor is that they carry out the reaction of alcanolamin with an adduct (a mixture of phosphoric acid and urea) in a certain ratio of the components taken and in the presence of vegetable oil.

In a three-necked flask equipped with a stirrer, reflux condenser and thermometer, 20 g of adduct was charged. The resulting mixture was heated to a temperature of 120 °C until a homogeneous liquid mixture was formed and 10 g of alcanolamin was added with stirring. The mixture was then heated until completely homogeneous (1 hour, 120 °C). Then the temperature of the reaction mixture was cooled to 90 °C and 5.5 g of vegetable oil was added. The reaction mixture with continuous stirring at a temperature of 110 °C was kept for 2 hours. Then the product was cooled to room temperature.

Scientific novelty. Effective and cost-effective metal corrosion inhibitors based on organic compounds have been synthesized. The effectiveness of inhibitors in various aqueous media has been investigated. Corrosion current and corrosion rate, degree of protection, temperature dependence of the braking coefficient, concentration and conditions necessary for optimal protection are determined.

Practical value. The results of the study expand the protective mechanism of organic inhibitors and help establish a new direction for the effective protection of inhibitor metals. The inhibitors studied have good prospects for use in water supply, recycled water, as well as in the oil, petrochemical and gas chemical industries due to their low toxicity and high efficiency.

Introduction. The modern protection of metals from corrosion is the introduction into the hostile environment of specially selected inhibitor compounds. Corrosion inhibitors are organic and inorganic substances, the presence of which in small quantities dramatically reduces the dissolution rate of the metal and reduces its possible harmful effects. Inhibitor corrosion protection is widely used in many sectors of modern industrial production and agriculture: when transporting gas and oil through pipelines, to preserve metal products in the inter-operational period, to protect against corrosion by fuels and lubricants, as well as in water-salt, acid, alkaline, water-organic and organic environments, in fresh, sea water, and corrosion in atmospheric conditions and soil.

Based on the foregoing, we synthesized oligomeric corrosion inhibitors based on local raw materials, which protect metals from corrosion in the heat supply system and ensure reliable operation of all elements of the system by preventing the formation of any type of deposits on the internal surfaces of boilers (heaters) and pipelines of heating networks, and all types of corrosion damage to internal surfaces[1].

Corrosion of equipment is one of the main causes of premature failure of chemical equipment, due to exposure to corrosive substances. The most effective method of protecting equipment from corrosion is the use of corrosion inhibitors. We propose the use of oligomeric corrosion inhibitors, which, due to the film-forming ability of the oligomer, can form thin film coatings on the internal surfaces of equipment, having the inhibitory ability to protect equipment from corrosion [2].

Experimental part. Oligomeric corrosion inhibitors were obtained on the basis of a nitrogen-containing adduct of melamine and urea, which interacted with various reagents to synthesize corrosion inhibitors. The effect of corrosion inhibitor on steel-20 samples (characteristic of steel-20 material: chemical composition of the material in % C-0,17-0,24, Si-0,17-0,37, Mn-0,35-0,65, Ni-0,25, S-0,04, P-0,04, Cr-0,25, Cu-0,25, As-0,08) in an acidic environment for 240 hours studied according to GOST - 9.506-87, GOST -9.505-86, GOST - 9.502-82.

Results and its discussion. Corrosion inhibitor IK-2 synthesized on the basis of secondary raw materials, 1 : 0.5 with alcanolamin with an adduct (a mixture of phosphoric acid and urea).

Recovered petroleum products contain mineral salts and mechanical impurities, such as sodium chloride, calcium chlorine, magnesium chlorine, gaseous carbon dioxide.

The effects of corrosion inhibition were studied when exposed to acid and alkaline fluids flowing through pipes (table 2).

Synthesized multicomponent corrosion inhibitors. The mechanism of protection against corrosion and the formation of self-regulating surface layers was revealed (Fig. 1).

Fig.1. The effect of IK-2 (a) and Incorgaz T 21 (b) on the metal St-20 at 30–60 °C

The results of the study show that the synthesized compositions of corrosion inhibition slow down the corrosion processes both on the surface of pure steel and on the surface of corrosive steel. Synthesized inhibitory corrosion, reducing the concentration of atomic hydrogen, also prevents the fragility of the metal [3].

The values of the free energy of adsorption indicate that the inhibitors function by physical adsorption on the surface of the metal. Typically, adsorption free energies of up to 20 KJ / mol correspond to the electrostatic interaction between charged molecules and a charged metal (indicating physical adsorption), while values more negative than 40 KJ / mol include charge separation or transfer from molecules inhibitor to the metal surface to form a coordination type bond (indicating chemisorption). The results presented in the table show that the values of the free energy of adsorption for all studied systems lie between –9.8 and –10.7 kJ / mol, which indicates spontaneous adsorption of additives by the mechanism of physical sorption.

The thermodynamic model is very useful for explaining the phenomenon of adsorption of an inhibitor molecule. Adsorption enthalpy can be calculated according to the Vant-Hoff equation:

$$\ln K_{ads} = \frac{-\Delta H^{\circ}_{ads}}{RT} + \text{constant}\,, \qquad (1)$$

where ΔH°_{ads} and K_{ads} are the adsorption enthalpy and the adsorption equilibrium constant, respectively (table 1).

Figure 2 shows a graph of the relationship between $\ln K_{ads}$ и 1/T for inhibitors IK-1, IK-2, IK-3, IK-4 and IK-5. Straight-line graphs were obtained, and the adsorption enthalpy was obtained from the slope of the linear graph [4; 5; 6].

Adsorption enthalpy (ΔH) can be roughly considered as the standard adsorption enthalpy ΔH ° ads under experimental conditions, and the obtained values were 22.5, 20.2, 18.6, 16.1 and 18.1 KJ / mol for IK-1 inhibitors, IK-2, IK-3, IK-4 and IK-5, respectively.

Table 1 – Freundlich adsorption parameters for inhibitors IK-1, IK-2, IK-3, IK-4 and IK-5 at various temperatures

Inhibitor	Temperature, °C	$\Delta H°_{ads}$, кЖ/моль$^{-1}$	K_{ads}, г·л$^{-1}$	n	R^2
IK-1	30	–10,7	1,21	0,62	0,98
	40	–10,3	0,98	0,67	0,98
	50	–9,8	0,86	0,69	0,97
	60	–10,6	0,92	0,86	0,98
IK-2	30	–10,2	1,24	1,02	0,97
	40	–10,2	0,99	1,04	0,98
	50	–10,4	0,87	1,03	0,99
	60	–10,5	0,91	1,05	0,99
IK-3	30	–10,3	1,25	0,97	0,98
	40	–10,2	1,03	0,93	0,99
	50	–10,4	0,96	1,01	0,99
	60	–10,3	0,86	1,02	0,97
IK-4	30	–10,5	1,24	1,01	0,98
	40	–10,2	1,02	1,03	0,98
	50	–10,4	0,93	0,98	0,99
	60	–10,3	0,87	1,02	0,99
IK-5	30	–10,7 /	1,21	0,62	0,98
	40	–10,2	0,99	1,04	0,98
	50	–10,4	0,96	1,01	0,99
	60	–10,3	0,87	1,02	0,99

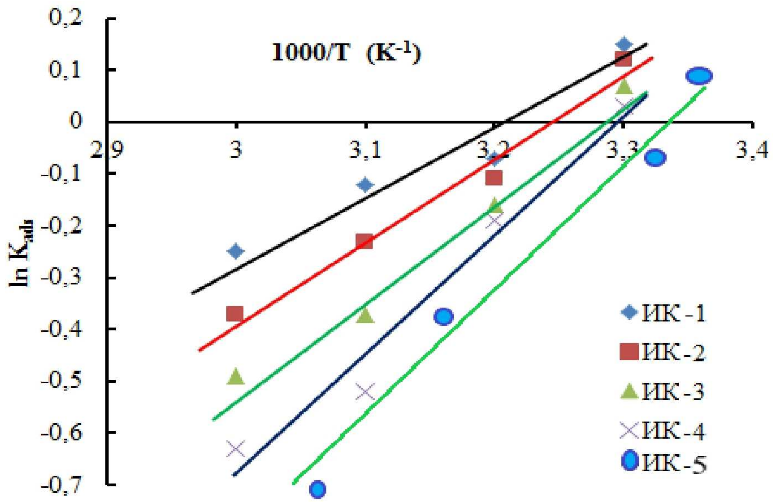


Fig. 2. The dependence of lnKads from 1 / T for inhibitors of IK-1, IK-2, IK-3, IK-4 and IK-5

IK-2 inhibits steel-20 corrosion with a maximum inhibition efficiency of 98.87 % at 30 °C and a maximum concentration of inhibitor. Inhibitor adsorption obeys the Langmuir adsorption isotherm by the formation of a monolayer on the metal surface; this result was confirmed by the use of a thermodynamic adsorption model. The heats of adsorption were low, which indicated physical adsorption on the metal surface [7–8].

The chemistry of this interaction and the structure of the reaction products were proved by ЯMR spectrometry on a Bruker Avance 400 spectrometer with an operating frequency of 400 МГц. The following signals were observed in ЯMP spectra of corrosion inhibiting compositions, IK-2: ^{1}H ЯMR 1,102 (т., 3H CH_3), 1,20 (м., 1H, CH2), 1,195 (м., 2H, CH = CH2), 2,60 (д., 2H, CH2-C), 3,55 (м., 4H, N-CH_2). 13C ЯMP 19.59 (CH_3), 44.31-44.81(CH-CH_2), 65.32 (H-CH_2), 40.51, 40.61 (N-CH2), 126.23, 133.44 (CH = CH) (Fig. 3).

This study clearly shows that the presence of the studied inhibitors protects a weak steel surface from corrosion (Fig. 4).

On the image 4 (B) separate and joint distribution of iron, carbon and oxygen on the surface can be observed steel-20.

Upon gravimetric detection, the inhibitor inhibition was studied at 30 ° C and 90 ° C for 24-2400 hours. As can be seen from the table, 0.05 % of the inhibitor significantly reduces the corrosion rate and increases the effectiveness of the inhibitor with increasing temperature [9]. Based on the results of a gravimetric study, experiments were carried out to study diagram curves in various media with a synthesized inhibitor (fig 5).

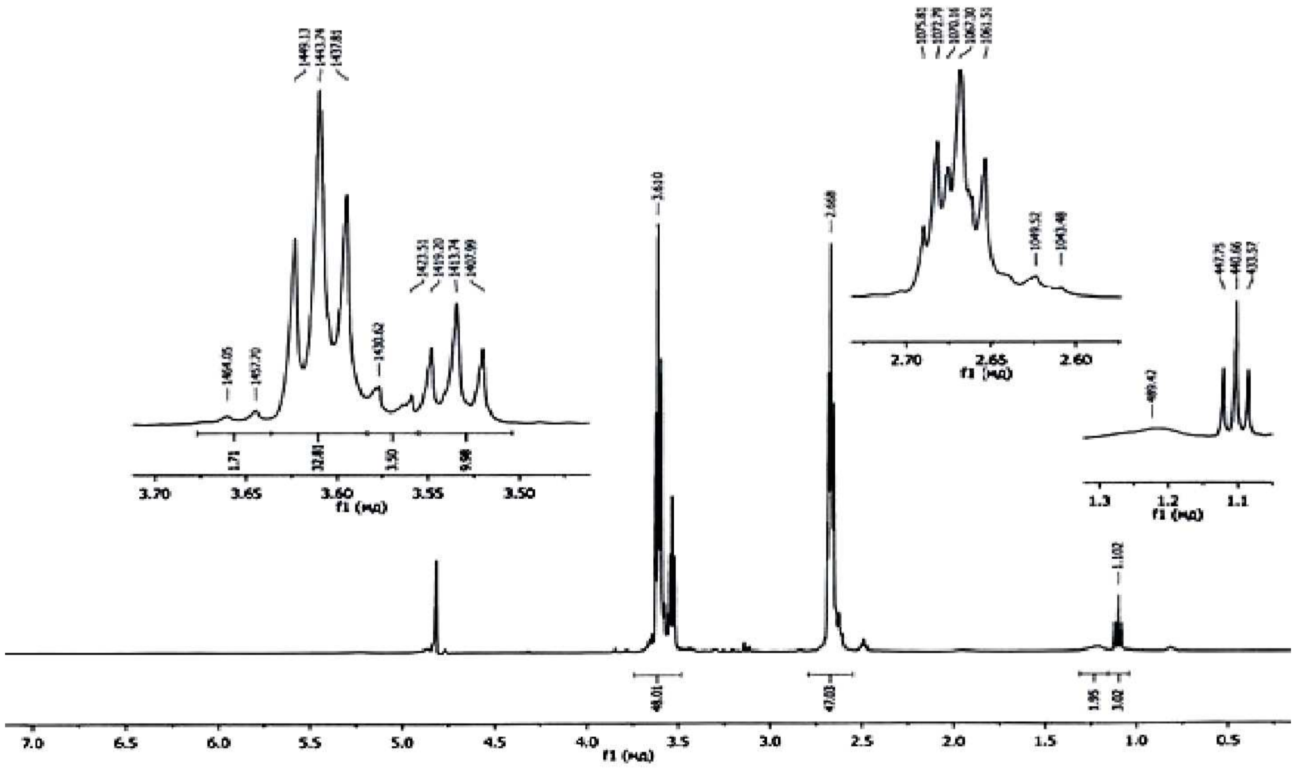


Fig. 3. [1]H-ЯMR – range of corrosion inhibiting compositions, IK–2

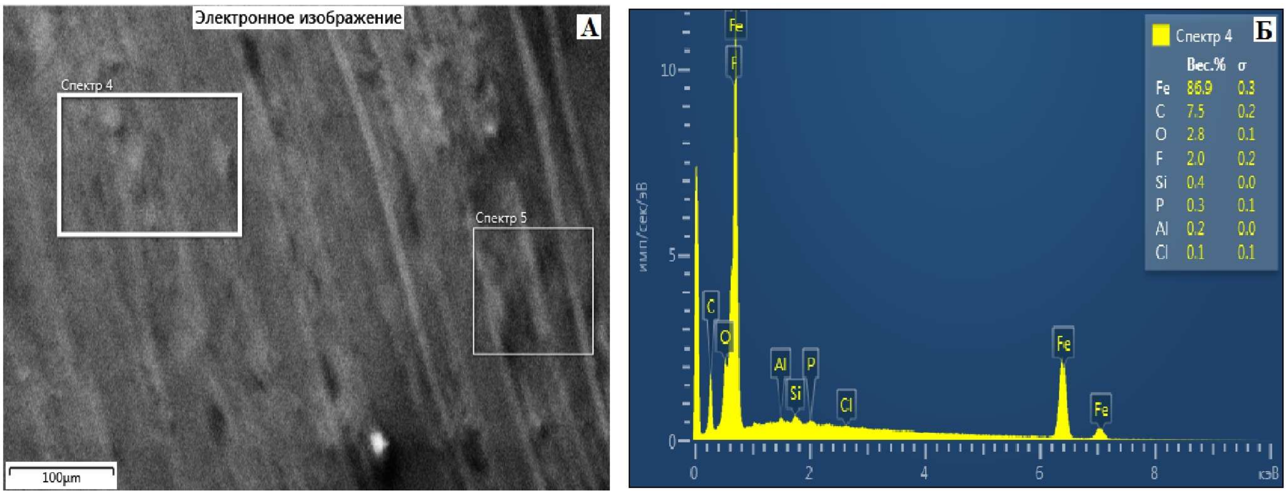


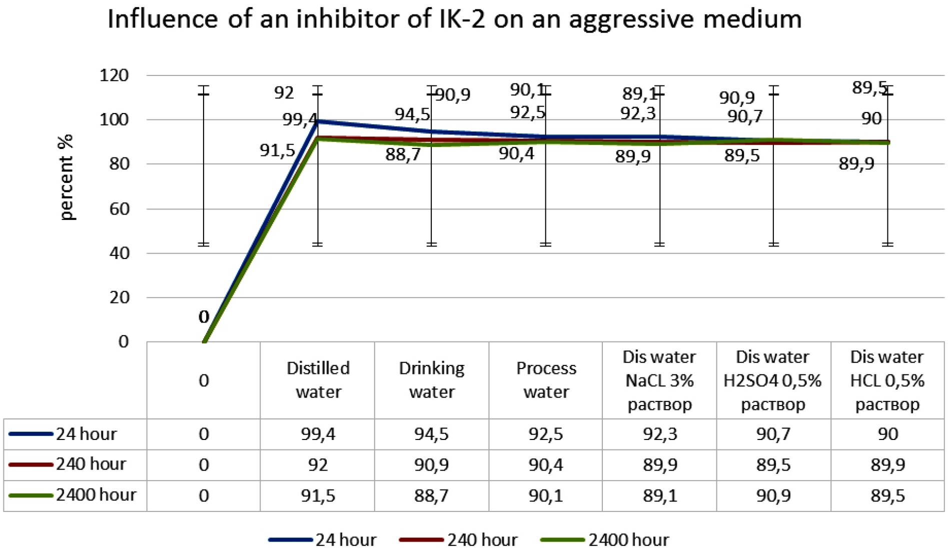
Fig. 4. Scanning Electron Microscopy (A) and elemental analysis (B) steel-20, treated with anticorrosive composites of the brand IK – 2

Table 2 – IK-2 metal inhibitors St-20 in various aggressive environments

№	Field	Sample Area S (m^2)	Exposure time (h)	Corrosion rate without inhibitor (mm/r)	Inhibitor Corrosion Rate (mm/r)	Degree of protection Z %
1	2	3	5	6	7	8
24 hour						
1	Distilled water	0,002033	24	0,2410	0,00157	99,4
2	Drinking water	0,002033	24	0,2980	0,0162	94,5
3	Process water	0,002033	24	0,4010	0,0298	92,5
4	Dis water NaCL 3 % раствор	0,002033	24	0,3410	0,0262	92,3
5	Dis water H_2SO_4 0,5 % раствор	0,002033	24	0,4980	0,0462	90,7
6	Dis water HCL 0,5 % раствор	0,002033	24	0,5010	0,0498	90,0

End of Table 2

1	2	3	5	6	7	8
240 hour						
7	Distilled water	0,002033	240	0,4582	0,0362	92,0
8	Drinking water	0,002033	240	0,5518	0,0499	90,9
9	Process water	0,002033	240	0,5698	0,0542	90,4
10	Dis water NaCL 3 % раствор	0,002033	240	0,5582	0,0562	89,9
11	Dis water H_2SO_4 0,5 % раствор	0,002033	240	0,6698	0,0698	89,5
12	Dis water HCL 0,5 % раствор	0,002033	240	0,6951	0,0698	89,9
2400 hour						
13	Distilled water	0,002033	2400	0,7511	0,0705	91,5
14	Drinking water	0,002033	2400	0,8582	0,0962	88,7
15	Process water	0,002033	2400	0,9918	0,0980	90,1
16	Dis water NaCL 3 % раствор	0,002033	2400	1,0211	0,0805	89,1
17	Dis water H_2SO_4 0,5 % раствор	0,002033	2400	1,0582	0,0962	90,9
18	Dis water HCL 0,5 % раствор	0,002033	2400	1,0991	0,0998	89,5



	0	Distilled water	Drinking water	Process water	Dis water NaCL 3% раствор	Dis water H2SO4 0,5% раствор	Dis water HCL 0,5% раствор
24 hour	0	99,4	94,5	92,5	92,3	90,7	90
240 hour	0	92	90,9	90,4	89,9	89,5	89,9
2400 hour	0	91,5	88,7	90,1	89,1	90,9	89,5

Fig. 5. Chart of St-20 metal inhibitors in various aggressive environments

The environmental safety of the use of the developed inhibitors in water supply systems and circulating circulating waters, as well as in the oil and gas chemical industries, is shown, their effectiveness is determined, which constitutes 98,25 %.

The research results show that the effectiveness of the applied oligomeric corrosion inhibitor can be observed in the presence of aromatic rings in them, the composition of thermostable and stable structures.

Conclusion. Synthesized new inhibitors of IK-2. The corrosion protection mechanisms of CT-20 steel materials have been studied using modern methods. The results showed that the inhibitors were effective at optimal concentration in aggressive environments HCl, H_2SO_4, NaCl.

It has been established that the protective properties of an inhibitor of the IK-2 brand depend on the composition, temperature and nature of the oligomer.

New effective composites of metal corrosion inhibitors in aggressive environments have been developed. A putative corrosion inhibitor based on alcanolamin and an adduct (a mixture of phosphoric acid and urea) was found. The effectiveness of synthesized new substances in gravimetric methods was studied. Corrosion rates, braking factors, and protection levels were studied.

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