

# Protection of low-carbon steel in phosphoric acid solutions by mixtures of a substituted triazole with sulfur-containing compounds

Ya. G. Avdeev\*, M. V. Tyurina and Yu. I. Kuznetsov

*A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119071 Russian Federation*

*\*E-mail: avdeevavdeev@mail.ru*

## Abstract

Based on IFKhAN-92 inhibitor, which is a substituted triazole, and sulfur-containing additives, efficient mixtures have been developed that protect low-carbon steel in phosphoric acid solutions in a broad range of acid concentrations (2.0–8.0 M) and temperatures (0–95°C).

**Key words:** *acid corrosion, corrosion inhibitor, phosphoric acid, mild steel, triazole.*

Received: September 5, 2014.

doi: [10.17675/2305-6894-2014-3-4-246-253](https://doi.org/10.17675/2305-6894-2014-3-4-246-253)

Phosphoric acid solutions, along with hydrochloric acid and sulfuric acid solutions, are used in etching of low-carbon steel for scale removal [1–3]. The rate of scale removal in phosphoric acid is comparable with that in HCl solutions and is much higher than that in H<sub>2</sub>SO<sub>4</sub> solutions [4, 5]. Compounds of various classes are considered as steel corrosion inhibitors in H<sub>3</sub>PO<sub>4</sub> solutions: quaternary ammonium salts [6], barbiturates [7], a substituted thiosemicarbazide [8], imidazole and its derivatives [9], substituted triazoles [10], amino- and mercaptotriazoles [11], allylthiourea [12]. However, only some of them (triazoles and sulfur-containing compounds) provide a high protection degree,  $Z > 90\%$ . A promising method to prevent steel corrosion in phosphoric acid solutions involves mixed inhibitors. Various additives are used to enhance the effect of inhibitors: halide anions for quaternary ammonium salts and purine derivatives [13, 14], cerium (IV) cations for sodium oleate [15], and uracil for a substituted tetrazole [16]. Addition of sulfur-containing compounds makes it possible to use the “PKU” industrial inhibitor in these media [17].

Based on IFKhAN-92, a triazole derivative, we have developed efficient inhibitor blends for the protection of low-carbon steels in mineral acid solutions [18, 19]. It appeared expedient to develop a formulation for the protection of low-carbon steel in phosphoric acid solutions based on IFKhAN-92 inhibitor.

## Experimental procedure

The corrosion rate of St3 low-carbon steel in H<sub>3</sub>PO<sub>4</sub> solutions was determined from the mass loss of specimens (at least three specimens per experimental point) sized 50.0 mm × 20.0 mm × 1.5 mm, using 50 ml of the acid solution per specimen, in the temperature range

of  $t = 0\text{--}95^\circ\text{C}$ . Prior to the experiments, the specimens were cleaned on an abrasive disc (ISO 9001, 60 grit) and degreased with acetone. The test duration was 2 h.

The efficiency of inhibitors was estimated from the inhibition coefficient,  $\gamma = k_0/k_{\text{in}}$ , and the degree of protection  $Z = [(k_0 - k_{\text{in}})/k_0] \cdot 100\%$ , where  $k_0$  and  $k_{\text{in}}$  are the corrosion rates in the non-inhibited solution and in the solution with the additive being studied, respectively.

Solutions were prepared from  $\text{H}_3\text{PO}_4$  (“chemically pure” grade) and distilled water. The base concentration of IFKhAN-92, both alone and in mixtures, was  $C_{\text{in}} = 5.0$  mM, and that of additives was 0.5 mM. The following compounds were studied as additives to enhance the protective effect of IFKhAN-92: potassium iodide, potassium rhodanide, sodium diethyldithiocarbamate (DEDTC), 2-mercaptobenzothiazole, thiourea, phenylthiourea (PTh), tolylthiourea (TTh), and diphenylthiourea (DPTh). Due to the low solubility of IFKhAN-92 and some of the additives (DEDTC, 2-mercaptobenzothiazole, PTh, TTh, DPTh) in phosphoric acid solutions, they were added as solutions in ethanol. The resulting ethanol concentration in the etching solution did not exceed 1.2 mol/l.

## Experimental results and discussion

The corrosion of St3 steel in  $\text{H}_3\text{PO}_4$  solutions grows systematically with an increase in  $t$  and  $\text{H}_3\text{PO}_4$  concentration,  $C_{\text{H}_3\text{PO}_4}$  (Tables 1, 2). An increase in  $t$  by  $95^\circ\text{C}$  in 2 M  $\text{H}_3\text{PO}_4$  increases the corrosion rate of steel,  $k_0$ , 216-fold. At  $60^\circ\text{C}$ , an increase in  $C_{\text{H}_3\text{PO}_4}$  from 1.0 M to 8.0 M increases  $k_0$  6.6-fold.

**Table 1.** Corrosion rates of St3 steel ( $\text{g}/(\text{m}^2 \cdot \text{h})$ ) in 2.0 M  $\text{H}_3\text{PO}_4$  and coefficients of corrosion inhibition by nitrogen-containing compounds and formulations based on IFKhAN-92 at various temperatures. The specimen exposure time was 2 h.

Inhibitor	$k, \gamma$	Temperature					
		$0^\circ\text{C}$	$25^\circ\text{C}$	$40^\circ\text{C}$	$60^\circ\text{C}$	$80^\circ\text{C}$	$95^\circ\text{C}$
–	$k$	2.4	5.8	20.2	37.9	141	518
5.0 mM IFKhAN-92	$k$	0.46	1.14	4.8	15.7	24.9	83.7
	$\gamma$	5.2	5.1	4.2	2.4	5.7	6.2
0.5 mM KCNS	$k$	2.7	6.6	16.2	31.2	78.0	315
	$\gamma$	0.89	0.88	1.2	1.2	1.8	1.6
5.0 mM IFKhAN-92 + 0.5 mM KCNS	$k$	0.08	0.14	0.20	0.35	0.89	1.23
	$\gamma$	30.0	41.4	101	108	158	421
0.5 mM 2-mercaptobenzothiazole	$k$	0.42	1.54	7.6	43.6	146	276
	$\gamma$	5.7	3.8	2.7	0.87	0.97	1.9
5.0 mM IFKhAN-92 + 0.5 mM 2-mercaptobenzothiazole	$k$	0.10	0.16	0.33	0.61	0.95	1.06
	$\gamma$	24.0	36.3	61.2	62.1	148	489

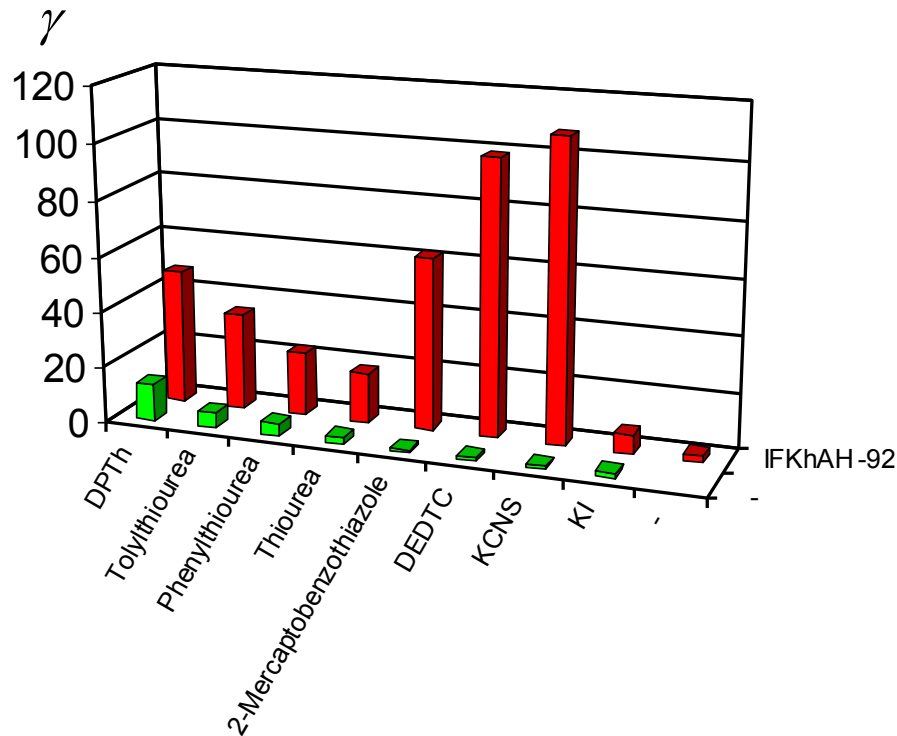
**Table 2.** Effect of H<sub>3</sub>PO<sub>4</sub> concentration on St3 corrosion rate (g/(m<sup>2</sup>·h)) and coefficients of corrosion inhibition by IFKhAN-92 and by formulations on its basis (60°C). The specimen exposure time was 2 h.

Inhibitor	$k, \gamma$	$C_{\text{H}_3\text{PO}_4}, \text{M}$			
		1.0	4.0	6.0	8.0
–	$k$	29.0	68.2	126	192
5.0 mM IFKhAN-92	$k$	13.9	16.8	13.4	3.4
	$\gamma$	2.1	4.1	9.4	56.5
5.0 mM IFKhAN-92 + 0.5 mM KCNS	$k$	0.33	0.47	0.75	1.0
	$\gamma$	87.9	145	168	192
5.0 mM IFKhAN-92 + 0.5 mM 2-mercaptobenzothiazole	$k$	0.34	0.77	1.2	1.5
	$\gamma$	85.3	88.6	105	128

In 2 M H<sub>3</sub>PO<sub>4</sub> ( $t = 0\text{--}95^\circ\text{C}$ ), addition of 5 mM IFKhAN-92 slows down steel corrosion only slightly:  $Z = 58.3\text{--}83.9\%$ . As  $C_{\text{H}_3\text{PO}_4}$  is increased from 1.0 to 6.0 M ( $t = 60^\circ\text{C}$ ), the  $k$  value of steel in the acid inhibited with IFKhAN-92 does not change considerably, so  $Z$  grows from 52.4 to 89.4%. Transition to 8.0 M H<sub>3</sub>PO<sub>4</sub> results in a considerable decrease in  $k$  and a growth of  $Z$  to 98.2%.

One of the methods to enhance the protective effect of triazoles in mineral acid solutions is by addition of hydrophobic compounds [20]. Anion-active (KI, KCNS, DEDTC) and molecular additives (2-mercaptobenzothiazole, thiourea, PTh, TTh, DPTh) were studied in this context (Fig. 1). DEDTC and 2-mercaptobenzothiazole do not behave as steel corrosion inhibitors at the concentration studied ( $\gamma = 0.98$  and  $0.87$ , respectively). Weak corrosion inhibition is observed in the presence of KCNS, KI, thiourea, PTh, or TTh ( $\gamma = 1.22, 1.74, 2.4, 4.5$  or  $5.8$ , respectively). Steel dissolution is inhibited considerably only by DPTh ( $\gamma = 13.3$ ).

Combined application of IFKhAN-92 and sulfur-containing anionic additives (KCNS and DEDTC) makes it possible to protect steel in 2.0 M H<sub>3</sub>PO<sub>4</sub> ( $t = 60^\circ\text{C}$ ), providing  $Z \geq 99.0\%$ . The maximum protection is given by the mixture containing KCNS. The  $\gamma_{\text{mix}}$  value for the IFKhAN-92 + KCNS mixture is 1.7 times larger than that for the most efficient mixture containing a molecular additive, *i.e.*, IFKhAN-92 + 2-mercaptobenzothiazole (Fig. 1). Somewhat unexpected was the weak corrosion inhibition by the 5.0 mM IFKhAN-92 + 0.5 mM KI mixture, though in sulfuric acid solutions the addition of KI enhanced the protective effects of triazoles most efficiently [18]. It is likely that iodide anions are poorly adsorbed on steel surface in phosphoric acid solutions due to competition with phosphate anions. Because of that, they do not enhance corrosion inhibition with IFKhAN-92.



**Figure 1.** Inhibition of St3 steel corrosion in 2.0 M  $\text{H}_3\text{PO}_4$  ( $t = 60^\circ\text{C}$ ) by hydrophobic additives (0.5 mM) and their mixtures with IFKhAN-92 (5.0 mM).

At  $t = 60^\circ\text{C}$ , combinations of IFKhAN-92 with molecular additives also slow down steel corrosion in 2.0 M  $\text{H}_3\text{PO}_4$  considerably:  $Z = 94.4\text{--}98.4\%$ . In the solution containing a mixture of IFKhAN-92 and 2-mercaptobenzothiazole, the  $k$  value of steel is 1.3–3.5 times smaller than in solutions containing combinations of thiourea and its substituted derivatives. One can observe that steel corrosion inhibition by mixtures containing substituted thioureas decreases in the series: DPTH > TTh > PTh > thiourea. It can be explained by a decrease in hydrophobicity of sulfur-containing compounds in this series. Apparently, hydrophobization of steel surface with compounds of this kind facilitates the adsorption of hydrophobic IFKhAN-92 inhibitor on the surface and hence enhances corrosion inhibition. The more hydrophobic a thiourea derivative is, the more strongly it modifies the metal surface and enhances the adsorption of IFKhAN-92.

Subsequent study was carried out with a mixture of 5.0 mM IFKhAN-92 with 0.5 mM of the most efficient anionic (KCNS) and molecular additive (2-mercaptobenzothiazole). In 2.0 M  $\text{H}_3\text{PO}_4$  at  $t = 0\text{--}95^\circ\text{C}$ , these mixtures with IFKhAN-92 provide  $Z = 96.7\text{--}99.8$  and  $95.8\text{--}99.8\%$ , respectively, though the additives themselves have low efficiency under these conditions:  $Z_{\text{KCNS}} \leq 44.4\%$  and  $Z_{\text{2-MBT}} \leq 82.5\%$ . In the range of  $t = 0\text{--}80^\circ\text{C}$ , the  $k$  on steel for the inhibitor formulation containing KCNS is 1.1–1.7 times smaller than that for the mixture containing 2-mercaptobenzothiazole. It is only at  $t = 95^\circ\text{C}$  that the  $k$  on steel in the solution containing a mixture of IFKhAN-92 and KCNS is 1.2 times higher than that in a

similar solution containing 2-mercaptobenzothiazole. The inhibition coefficient of both mixtures increases with temperature. The  $\gamma_{\text{mix}}$  value of the IFKhAN-92 + KCNS mixture increases 14.0-fold as  $t$  increases by 95°C, whereas that for the IFKhAN-92 + 2-mercaptobenzothiazole mixture increases 20.4-fold.

The mixtures studied protect steel in a broad range of acid concentrations ( $C = 1.0$ – $8.0$  M):  $Z$  is up to 98.9–99.5% for the formulation of IFKhAN-92 with KCNS and 98.8–99.2% for the formulation with 2-mercaptobenzothiazole. An increase in  $C_{\text{H}_3\text{PO}_4}$  from 1.0 M to 8.0 M increases  $\gamma_{\text{mix}}$  2.2-fold (IFKhAN-92 + KCNS) and 1.5-fold for the IFKhAN-92 + 2-mercaptobenzothiazole mixture. The IFKhAN-92 + KCNS formulation is most efficient at all  $C_{\text{H}_3\text{PO}_4}$  values.

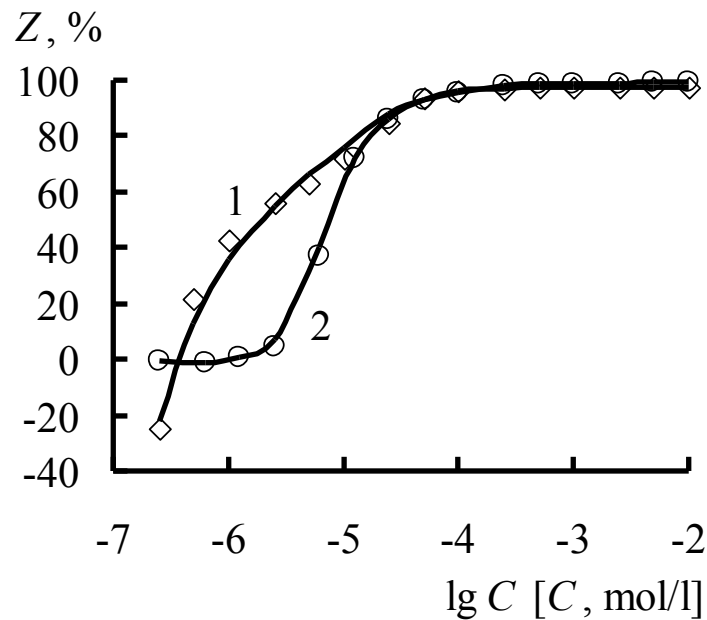
The corrosion of steel in 2.0 M  $\text{H}_3\text{PO}_4$  ( $t = 60^\circ\text{C}$ ) decreases with time during the first 2 h and then increases (Tables 2, 3). In a solution containing the mixtures studied, the mean  $k$  of steel decreases with time during the corrosion test. As a result,  $Z = 99.6\%$  (IFKhAN-92 + KCNS) and  $Z = 99.5\%$  (IFKhAN-92 + 2-mercaptobenzothiazole) in 6-hour tests, compared to  $Z = 98.3$  and  $97.6\%$ , respectively, in 0.5 h tests.

**Table 3.** Corrosion rates of St3 steel and coefficients of corrosion inhibition in 2.0 M  $\text{H}_3\text{PO}_4$  by formulations of IFKhAN-92 with KCNS and 2-mercaptobenzothiazole at various exposure times.  $t = 60^\circ\text{C}$ .

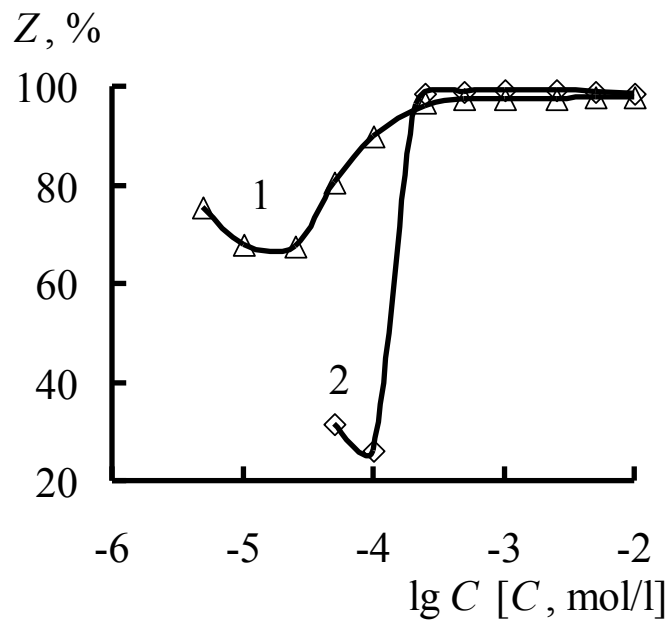
Inhibitor	Specimen exposure times							
	0.5 h		1.0 h		4.0 h		6.0 h	
	$k$ , g/(m <sup>2</sup> ·h)	$\gamma$	$k$ , g/(m <sup>2</sup> ·h)	$\gamma$	$k$ , g/(m <sup>2</sup> ·h)	$\gamma$	$k$ , g/(m <sup>2</sup> ·h)	$\gamma$
–	82.3	–	52.5	–	45.6	–	51.3	–
5.0 mM IFKhAN-92 + 0.5 mM KCNS	1.40	58.8	0.70	75.0	0.23	198	0.22	233
5.0 mM IFKhAN-92 + 0.5 mM 2-mercaptobenzothiazole	2.00	41.2	1.00	52.5	0.36	127	0.25	205

The IFKhAN-92 + KCNS mixture with fixed  $C_{\text{KCNS}} = 0.5$  mM demonstrates an S-shaped plot of  $Z_{\text{mix}}$  versus IFKhAN-92 concentration (Fig. 2). Values of  $Z \geq 90\%$  are reached at  $C_{\text{IFKhAN-92}} \geq 0.05$  mM (25 and 60°C), which, based on the shape of experimental  $Z_{\text{mix}} - C_{\text{IFKhAN-92}}$  plots, corresponds to the maximum coverage of the metal surface with the inhibitor. The same mixture with  $C_{\text{IFKhAN-92}} = 5.0$  mM also manifests an S-plot of  $Z_{\text{mix}}$  versus  $C_{\text{KCNS}}$  (Fig. 3). This formulation loses efficiency at  $C_{\text{KCNS}} < 0.25$  mM. At  $t = 60^\circ\text{C}$ , the maximum protective effect of the 5.0 mM IFKhAN-92 + KCNS mixture is observed at

$C_{\text{KCNS}} = 1.0 \text{ mM}$  ( $\gamma = 128$ ). A further increase in  $C_{\text{KCNS}}$  decreases  $\gamma$ . For example,  $\gamma_{\text{mix}}$  for the mixture of 5.0 mM IFKhAN-92 + 10.0 mM KCNS is 1.7 times smaller.

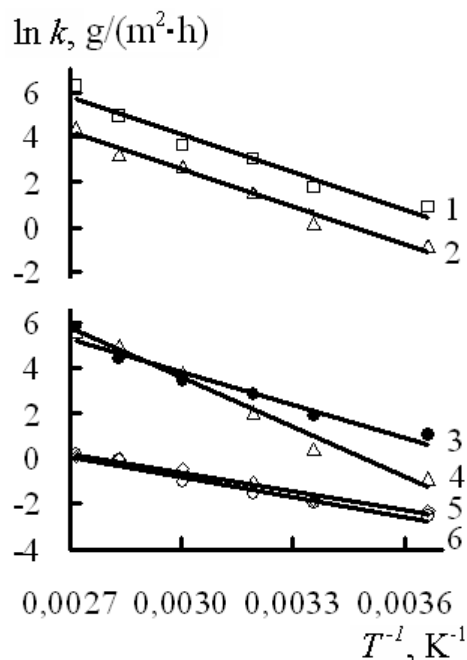


**Figure 2.** Dependence of the degree of protection by IFKhAN-92 + KCNS (0.5 mM) formulations on IFKhAN-92 concentration for St3 steel corrosion in 2.0 M  $\text{H}_3\text{PO}_4$  at temperatures: 1 – 25 °C, 2 – 60 °C.



**Figure 3.** Dependence of the degree of protection by IFKhAN-92 (5.0 mM) + KCNS formulations on KCNS concentration for St3 steel corrosion in 2.0 M  $\text{H}_3\text{PO}_4$  at temperatures: 1 – 25 °C, 2 – 60 °C.

Using the Arrhenius equation, let us estimate the effective activation energies ( $E_a$ ) of steel corrosion in  $H_3PO_4$ . The calculation was based on the analysis of the  $\ln k - T^{-1}$  plot (Fig. 4). In 2.0 M  $H_3PO_4$ , the effective activation energy of the corrosion process,  $E_a$ , amounts to  $46 \pm 1$  kJ/mol, which indicates that the reaction occurs in a mixed kinetics zone. It does not change in the presence of IFKhAN-92 inhibitor in solution. Addition of KCNS decreases  $E_a$  to  $39 \pm 1$  kJ/mol, whereas addition of 2-mercaptobenzothiazole increases it to  $60 \pm 1$  kJ/mol. The fraction of the diffusion component of the process increases considerably when both IFKhAN-92 and sulfur-containing additives are simultaneously present in a solution ( $E_a = 28 \pm 2$  kJ/mol).



**Figure 4.** Dependence of  $\ln k$  on  $T^{-1}$  for St3 steel corrosion in 2.0 M  $H_3PO_4$  (1) containing 5.0 mM IFKhAN-92 (2), 0.5 mM KCNS (3), 0.5 mM 2-mercaptobenzothiazole (4), 5.0 mM IFKhAN-92 + 0.5 mM 2-mercaptobenzothiazole (5), 5.0 mM IFKhAN-92 + 0.5 mM KCNS (6).

Our study has shown that IFKhAN-92 manifests a protective effect in phosphoric acid solutions only in the presence of small amounts of hydrophobic sulfur-containing compounds. Apparently, compounds of this kind are adsorbed on steel surface and hence make it more hydrophobic, thus facilitating the subsequent adsorption of the relatively hydrophobic particles of IFKhAN-92 inhibitor.

## Conclusions

1. IFKhAN-92, an inhibitor of acid corrosion of metals, can be successfully used to protect low-carbon steel in  $H_3PO_4$  solutions when combined with sulfur-containing additives of anionic and molecular nature. Of the inhibitor formulations studied, the maximum corrosion inhibition is provided by mixtures of IFKhAN-92 with anionic sulfur-containing additives.

2. Using mixtures of IFKhAN-92 with KCNS and 2-mercaptobenzothiazole as examples, it has been shown that it is possible to protect low-carbon steel in phosphoric acid solutions in a broad range of acid concentrations (2.0–8.0 M) and temperatures (0–95°C).

## References

1. A. M. Yampolskii, *Travlenie metallov (Pickling of metals)*, Metallurgiya, Moscow, 1980, pp. 23–24 (in Russian).
2. N. S. Smirnov, M. E. Prostakov and Ya. N. Lipkin, *Ochistka poverkhnosti metallov (Cleaning of metals surfaces)*, Metallurgiya, Moscow, 1978, pp. 133–134 (in Russian).
3. Ya. G. Avdeev, I. G. Gorichev and A. Yu. Luchkin, *Int. J. Corros. Scale Inhib.*, 2012, **1**, no. 1, 26. doi: [10.17675/2305-6894-2012-1-1-026-037](https://doi.org/10.17675/2305-6894-2012-1-1-026-037)
4. A. S. Afanas'ev and T. B. Malysheva, in *Travlenie i obezzhirivanie trub iz stalei i splavov (Pickling and degreasing of pipes made of steels and alloys)*, Metallurgiya, Moscow, 1967, 59 (in Russian).
5. V. F. Gorsheneva, I. G. Gorichev and N. G. Klyuchnikov, in *Ingibitory korrozii (Corrosion Inhibitors)*, MGPI im V. I. Lenina, Moscow, 1980, 21 (in Russian).
6. X. Li, S. Deng and H. Fu, *Corros. Sci.*, 2011, **53**, 664.
7. M. Ozcan, R. Solmaz, G. Kardas and I. Dehri, *Colloids Surf. A: Physicochem. Eng. Aspects*, 2008, **325**, 57.
8. T. Poornima, Ja. Nayak and A. Nityananda Shetty, *Corros. Sci.*, 2011, **53**, 3688.
9. A. Ghanbari, M. M. Attar and M. Mahdavian, *Mater. Chem. Phys.*, 2010, **124**, 1205.
10. L. Wang, *Corros. Sci.*, 2006, **48**, 608.
11. A. Doner, R. Solmaz, M. Ozcan and G. Kardas, *Corros. Sci.*, 2011, **53**, 2902.
12. X. Li, S. Deng and H. Fu, *Corros. Sci.*, 2012, **54**, 280.
13. X. Li, L. Tang, H. Liu and G. Mu, G. Liu, *Mater. Lett.*, 2008, **62**, 2321.
14. X. Li, S. Deng and H. Fu, *Corros. Sci.*, 2011, **53**, 3704.
15. X. Li, S. Deng, H. Fu and G. Mu, *Corros. Sci.*, 2010, **52**, 1167.
16. X. Li, S. Deng and H. Fu, *Mater. Chem. Phys.*, 2009, **115**, 815.
17. E. S. Ivanov, *Ingibitory korrozii metallov v kislykh sredakh (Metal Corrosion Inhibitors in Acidic Media)*, Metallurgiya, Moscow, 1986, pp. 152–153 (in Russian).
18. Ya. G. Avdeev and A. Yu. Luchkin, *Int. J. Corros. Scale Inhib.*, 2013, **2**, no. 1, 53. doi: [10.17675/2305-6894-2013-2-1-053-066](https://doi.org/10.17675/2305-6894-2013-2-1-053-066)
19. Ya. G. Avdeev, P.A. Belinskii, Yu. I. Kuznetsov and O.O. Zel', *Protection of Metals and Physical Chemistry of Surfaces*, 2010, **46**, no. 7, 782.
20. Ya. G. Avdeev and Yu. I. Kuznetsov, *Russ. Chem. Rev.*, 2012, **81**, no. 12, 1133.

