Protection of metals in phosphoric acid solutions by corrosion inhibitors. A review

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Abstract

The article summarizes the literature data and patents on the protection of steels and nonferrous metals in phosphoric acid solutions with various corrosion inhibitors. Some aspects of practical use of H_3PO_4 solutions, their properties and corrosivity toward various metals are reviewed. It is shown that the overwhelming majority of individual organic and inorganic compounds, as well as composite inhibitors offered for the protection of metals in this medium are of low efficiency due to weak adsorption on metal surfaces. A promising method for the protection of steels in phosphoric acid media involves the use of formulations containing triazole derivatives and sulfur-containing additives. The components of these mixtures form polymolecular protective layers on the metal surface that are highly efficient in slowing down corrosion processes even at temperatures up to 100°C. An important property of these protective layers is a strong chemical bond of the inhibitor molecules with the metal surface and with each other inside the layer. Inhibited H_3PO_4 solutions resistant to the accumulation of corrosion stimulators – Fe(III) salts – may become a new and promising field of use for this acid. The bibliographic list includes 170 sources.

Keywords: corrosion inhibitors, acid corrosion, phosphoric acid, orthophosphoric acid, steels, nonferrous metals, triazoles.

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Introduction

Solutions of orthophosphoric (hereinafter referred to as phosphoric) acid H_3PO_4 , along with other mineral acids, are in use in modern industries for removal of heat scale, rust, limescale, and other mineral deposits from steel surfaces. H_3PO_4 -based formulations are used for the treatment of petroleum and gas reservoirs from carbonate deposits [1].

Back in the beginning of the XX century, U.R. Evans [2], who discussed various aspects of acid etching of steels, considered H_3PO_4 solutions as an alternative to inhibited solutions of hydrochloric and sulfuric acids. He stated that H_3PO_4 excelled those acids since its traces remaining on the metal caused no corrosion due to weak solubility of iron phosphates that build up a protective film. It was stated as a drawback that at a normal temperature, etching in H_3PO_4 was slow and it was necessary to heat solutions to 85°C,

which sometimes was inconvenient. Nevertheless, the method was considered valuable, especially when a thorough rinsing after etching was difficult. According to Evans, this method was approved by the Dutch Corrosion Committee and recommended by Büttner <author's remark: G. Büttner, *Korr. Met.*, 1931, **7**, 251>, who found that the use of inhibitors could be avoided in H_3PO_4 and that iron phosphate remaining on the metal gave a very good primer for painting. After etching in H_2SO_4 and HCl solutions, steel parts are often submerged in dilute H_3PO_4 for a short time. Such samples behave better after painting than those treated in H_2SO_4 or HCl.

The nonvolatile phosphoric acid allows the process of steel etching to be intensified without special material costs through increasing the temperature. Analysis of literature data [3] shows that, all other things being equal, hydrogenation of steels is much weaker in H_3PO_4 solutions than in H_2SO_4 and HCl. The high speed of heat scale removal from the surface of low-carbon steel in H_3PO_4 solutions is comparable with that in HCl solutions and considerably exceeds sulfuric acid media [4, 5]. In 1 N acid solutions it exceeds HCl, H_2SO_4 , HNO₃ and HClO₄ in the rate of dissolving iron(III) oxide, being inferior only to HF [6].

Phosphoric acid demonstrates low reactivity toward various rocks built by calcium carbonate in comparison to HCl and HNO₃ [1]. For example, at 20°C the rate of the reaction of 5–50% H₃PO₄ with marble is 1–2 g/(m²·h). The maximum rate occurs in the acid concentration range of 20–45%, while the dissolution stops at a mass percent of the acid $\omega_{H3PO4} > 60\%$.

Phosphoric acid has the form of crystals with a density of 1870 kg/m³ (20°C). It mixes with water in any ratio with exponential variation of viscosity and density, is non-toxic and has no oxidizing properties [1]. H₃PO₄ is a strong acid in aqueous solutions^{*} ($pK_{aI} = 2.12$, $pK_{aII} = 7.20$, $pK_{aIII} = 12.32$). Dissociation by the first stage is exothermic but endothermic by the second and third stages [8]. It is considered that aqueous H₃PO₄ solutions (0.1–10 mol/kg) may involve the following ion-molecular equilibria with participation of both monomeric and dimeric molecular forms [9]:

$$\begin{split} H_{3}PO_{4} &= H^{+} + H_{2}PO_{4}^{-}, \\ H_{2}PO_{4}^{-} + H_{3}PO_{4} &= H_{5}P_{2}O_{8}^{-}, \\ H_{6}P_{2}O_{8} &= H^{+} + H_{5}P_{2}O_{8}^{-}. \end{split}$$

This is confirmed by the experimental data on vapor pressure, electric conductivity, pH and osmotic pressure measurements in aqueous acid solutions, as well as by the results of their studies by Raman spectroscopy.

Reference data on the corrosion resistance of various metals and alloys in H_3PO_4 and its solutions under diverse conditions are summarized in the reference book [10]. It should

^{*} Some authors [1] attribute H_3PO_4 to medium-strength or even weak acids [7].

be noted that under certain conditions, such media are rather corrosive to metallic materials. Solutions of H₃PO₄ itself, especially when heated, actively react with contacting steels, which is contrary to U.R. Evans' concept on the possibility of replacing inhibited inorganic acids with phosphorus acid [2]. For example, the corrosion rate (k) of St3 steel (content in mass percent, %: 0.14-0.22 C, 0.05-0.17 Si, 0.40-0.65 Mn, up to 0.30 Ni, up to 0.30 Cu, up to 0.30 Cr, up to 0.08 As, up to 0.05 P, up to 0.05 S, balance Fe) in 2 M H_3PO_4 (0–95°C) is from 2.4 to 520 g/(m²·h). A growth in acid concentration (C) in the solution (60°C) from 1 to 8 M accelerates corrosion from 29 to 190 g/($m^2 \cdot h$) [11]. Similar trends in the behavior of low-carbon steels were found elsewhere [12-15]. Alloyed nickel-chromium steels containing 17-23% Cr and 6-28% Ni are more resistant to H₃PO₄. In solutions with $\omega_{H3PO4} \le 20\%$, the k values of these acids at 150°C are ≤ 1 g/(m²·h) according to the data of 8-hour testing, and some steels maintain resistance to corrosion even at 200°C [15]. However, E.V. Filimonov et al. [16, 17] found that nickelchromium steel X18H10T (content in mass percent, %: 0.11 C, 9.66 Ni; 18.66 Cr, 0.57 Ti, remainder Fe) in H_3PO_4 (100–150°C) may be in an unstable passive state where several similar samples present in an absolutely the same corrosion medium are destroyed at rates differing by more than an order of magnitude. The maximum corrosion rate of the samples (k) reaches tens of $g/(m^2 \cdot h)$. Special issues of stability of steel structures in H₃PO₄ during its manufacturing are addressed in [18, 19].

The importance of phosphoric acid in modern industries, as well as the high corrosivity of its hot solutions to steels makes it necessary to critically analyze the literature on the methods of inhibitor protection of metals and alloys in this environment and find its physicochemical regularities. The presence of efficient inhibitors for phosphoric acid environments is important in practical terms, because it expands the application fields of H_3PO_4 by lowering its corrosivity towards various process equipment that it may contact.

General issues of inhibitor protection of metals and alloys in aqueous media, as well as the specifics of the mechanism of action of various groups of metal corrosion inhibitors (CI) in these media are addressed in the monograph [20] and reviews [21–27]. However, these studies provide no detailed examination of the specifics of using CI for the protection of metals in acid solutions.

The protection of metals by corrosion inhibitors in acid solutions was considered most thoroughly in monographs [28, 29] and review [30], but more than 30 years have passed since they were published. A number of reviews dedicated to some special groups of CIs in acids, such as unsaturated organic compounds [31], acetylenic compounds [32], unsaturated carbonyl compounds [33], azomethines [33, 34], N-containing six-membered organic heterocycles [35, 36], as well as the specifics of their mechanism of protective action, have been published in the recent 15 years.

Reviews [37, 38] describe the protective properties of CIs recommended for oil and gas industry. Reference data are contained in articles stated to be reviews, which are

dedicated to the effect of organic CIs on the electrochemical behavior of steels in acid solutions [39] or to reviewing separate CI groups: formulations of organic compounds with halide anions [40], derivatives of thiocarbamide and thiadiazole [41], polymer compounds [42], pharmaceuticals [43], amino acids [44], ecologically pure products [45], vegetal extracts [46]. Data on the protection of aluminum alloys in HCl and H_2SO_4 solutions are collected and summarized in [47]. Only two special reviews [48, 49] study the issues of inhibitor protection of metals in phosphoric acid.

In spite of the big number of reviews dedicated to CIs of metals for acid media, the emphasis in these studies is put on considering the issues concerning the protection of metals in HCl and H_2SO_4 solutions as the most important ones in practical terms. The problem of inhibitor protection of metals in phosphoric acid media lacked proper attention, though its solution is a complex practical task. Many CIs that efficiently protect metals in HCl and H_2SO_4 solutions are unfit for protection of metals in H_3PO_4 . In spite of the fact that reviews [48, 49] were published just recently, today they incompletely in cover the actual state of inhibitor protection of metals in H_3PO_4 solutions in many respects. From our point of view, some new, principally important results have been obtained in this field of CI science in recent years. A new theoretically founded trend discussed in the article includes the issues of creating inhibited H_3PO_4 -based solutions resistant to the accumulation of strong corrosion stimulators, Fe(III) salts, in these solutions.

Therefore, groups of compounds promising as CIs for phosphoric acid media that comply with process and environmental requirements of present-day industries should be determined. Understanding the specifics in mechanism of action of such compounds that determine the high quality of metal protection in H_3PO_4 solutions is very important.

1. Assortment of corrosion inhibitors for phosphoric acid solutions

The most complete information on successful use of CIs for protection of metals in phosphoric acid media under modern industrial conditions may be obtained by analyzing the assortment of CIs used at various industrial plants. We will carry out the analysis of the assortment of industrial CIs for phosphoric acid media by the example of industrial plants of the Russian Federation. In the USSR, a wide variety of acid corrosion inhibitors represented by more than 30 marketable product titles [28, 29, 50, 51] were developed and produced. The vast majority of them are toxic derivatives of pyridine and quinoline and do not comply with tough process and sanitary requirements of the modern industries. In addition, owing to economic reasons the production of many of these products was stopped or considerably reduced to date. Analysis of the list of corrosion inhibitors used in the USSR shows that only some of them, viz., PKU-3, PKU-3R, OB-1, OR-2, KhOD-4, KhOSP-10 and S-5U, are suitable for inhibiting the corrosion of steels in H₃PO₄ solutions (Table 1). The composition of PKU-3R and OR-2 inhibitors includes ammonium rhodanide as a synergistic additive [29, 52]. To improve the protective action of PKU-M inhibitor that is inefficient on steel 10 in 4 N H₃PO₄, addition of sodium dithiocarbamate

[53] is recommended. For example, adding 0.3 g/l sodium dithiocarbamate at t = 60-80 °C to the solution increases the inhibition coefficient (γ) of 3 g/l PKU-M 8.6–14.4 fold.

Inhibitor name	Chemical composition	Application medium	Protected metal	
DKII 3	Urotropine and benzyl chloride	4 N H ₃ PO ₄	Steel 10,	
PKU-3	condensation products	$(t = 80^{\circ}\mathrm{C})$	$\gamma = 90 \ (5 \ g/l)$	
PKU-3R	Mixture of 95% PKU-3 and 5%	4 N H ₃ PO ₄	Steel 10,	
	ammonium rhodanide	$(t = 80^{\circ}C)$	$\gamma = 112 (5 \text{ g/l})$	
·	Composite of substituted ammonium	4 N H ₃ PO ₄	Steel St3,	
OB-1	salts, an organobromine compound and a foam maker	$(t = 30-85^{\circ}C)$	$\gamma = 95 - 246 (1.5 \text{ g/l})$	
OR-2	Product of reaction of quinoline bases, benzyl chloride and ammonium rhodanide. Efficient agent – 20% benzylquinolium rhodanide)	H ₃ PO ₄	Carbon steel	
KHOD 1	Composite containing substituted	4 N H ₃ PO ₄	Steel 10,	
KIIOD-4	ammonium salts	$(t = 30 - 85^{\circ}C)$	Z = 97.2 - 99.2% (2 g/l)	
			Steel 20,	
KhOSP-10	Mixture of quaternary ammonium salts, foam maker and synergist	6 M H ₃ PO ₄	$\gamma = 8 - 102 \ (1.5 \ \text{g/l})$	
		$(t = 30 - 90^{\circ}\text{C})$	Steel 40X,	
			$\gamma = 38 - 194 \ (1.5 \ \text{g/l})$	
S-5U	Modified waste of cake and by-	2 N H ₃ PO ₄	Steel St3,	
	product production.	$(t = 50^{\circ}\mathrm{C})$	$\gamma = 13 \; (2.5 \; g/l)$	

Table 1. Assortment of metal acid corrosion inhibitors produced in the USSR and recommended for H_3PO_4 solutions [29, 52].

To date, the assortment of inhibitors of acid corrosion for metals used in the industries of the Russian Federation has been renewed considerably. In TNK-BP enterprises, 12 such domestic inhibitors [54] are reportedly used, but the possibility of using them in H_3PO_4 solutions is not mentioned. To protect steel in hydrochloric acid media in oil and gas sector enterprises, CIs of Aquatec-50 series (manufactured by NPO "Aquatec") [55] are recommended. The possibility of using them in H_2SO_4 and H_3PO_4 solutions is mentioned, but information on the protective effects of the CIs is not provided.

A comprehensive study [56] of the protective properties of a series of CIs (Soling m. Z, Soling m. L, VNPP-2, INVOL-2 m. A, NORUST CM 150 C) used in oil and gas sector enterprises proved their low efficiency in inhibiting corrosion of steels in H_3PO_4 solutions, although in HCl solutions they slowed down the corrosion well. For example, in

2 M of H₃PO₄ (20–100°C) for the studied CIs the maximum decrease in *k* for 08PS steel (content in mass percent, %: 0.08 C, 0.5 Mn, 0.11 Si, 0.035 P, 0.04 S, 0.1 Cr, 0.25 Ni, 0.25 Cu, 0.08 As, remainder Fe) was 5.4-fold. These CIs are equally inefficient in the protection of 70S2KhA high-strength steel (content in mass percent, %: 0.7 C, 0.52 Mn, 1.52 Si, 0.3 Cr, remainder Fe). In 2 M H₃PO₄ (20°C) the biggest decrease in *k* of this steel is 4-fold, while the maximum steel plasticity remains at ~64%, which indicates its strong hydrogenation.

The above data show the actual lack of commercially produced CIs suitable for the protection of metals in H_3PO_4 solutions. Only some of them can provide metal protection in H_3PO_4 after modification with additives. All these facts show the relevance of searching CIs for such media.

Many organic compounds (acetylene derivatives [57], azomethines [58], quaternary ammonium salts (QAS) and N-containing heterocycles [59]) that efficiently inhibit corrosion of steels in HCl solutions and in some cases in H₂SO₄, poorly inhibit it in H₃PO₄ solutions. For example, the γ of propargyl chloride for St3 steel at 25°C in 2M HCl and H₂SO₄ is 10.9 and 18.5 times higher than in 2 M H₃PO₄ [57]. This results from the reduction of propargyl chloride on steel in H₃PO₄ that facilitates the cathodic process. Sometimes an increase in H₃PO₄ content in solution may lead to a substantial protective action of an organic compound. For example, 5 mM of catamine AB at $C(H_3PO_4) = 1-6$ M at 60°C inhibits corrosion of St3 steel no more than 7.2-fold. Under the same conditions, the γ provided by catamine AB in 8 M H₃PO₄ is 32.1 [59].

Numerous compounds considered by the authors as CIs of steels in H₃PO₄ solutions are described in scientific literature. However, from our point of view, this information requires a critical analysis. For example, a group of Kenyan researchers [60] recommend to protect C35E carbon steel (content in mass percent, %: 0.370 C, 0.230 Si, 0.680 Mn, 0.016 S, 0.077 Cr, 0.011 Ti, 0.059 Ni, 0.009 Co, 0.160 Cu, remainder Fe) in 2M of H₃PO₄ (at 30°C) with the additive N-1-naphthylethylenediamine dihydrochloride, which at high C =0.01 M only provides Z = 88.1%. The same poor efficiency in 1 M of H₃PO₄ is shown by benzimidazole (BI) and its 2-substituted derivatives, the most efficient of which, 2-amino-BI, inhibits the corrosion of mild steel 3.3-fold at C = 5 mM [61]. Somewhat better results are shown by 3,5-bis(*N*-pyridyl)-4-amino-1,2,4-triazoles with various structures that provide Z = 92-93% in 3 M H₃PO₄ (at 30°C) at $C_{in} = 0.1$ mM [62].

Many organic compounds are satisfactory in protecting various steels in cold H_3PO_4 , but heating reduces the protective action of CIs. The toxic benzyltriphenylphosphonium chloride (C = 1 mM) in 0.3 M H_3PO_4 at 25°C provides Z = 94%, but increasing the *t* of the solution by 40°C decreases *Z* to 85% [63]. Quaternary salts of pyridinium and quinolinium (1-methyl-4[4'(-N(CH_3)_2)-styryl]pyridinium iodide (QI), 1-methyl-4[4'(-N(CH_3)_2)-styryl]quinolinium iodide (QII), 1-methyl-4[4'(-OCH_3)-styryl]quinolinium iodide (QII)) were studied as corrosion inhibitors of mild steel (content in mass percent, %: 0.02 P, 0.37 Mn, 0.03 S, 0.01 Mo, 0.039 Ni, 0.21 C, remainder Fe) in 2 M H_3PO_4 (at 30°C). The most

efficient of them, QIII, provides Z = 99.95% at $C_{in} = 0.5$ mM. The protective action of the CIs decreases in the series: QIII > QII > QI. Increasing t to 70°C decreases Z_{OIII} to 73.01% [64]. 1-Dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide was studied as a CI of carbon steel (content in mass percent, %: 0.28 C, 0.06 Ti, 1.40 Mn, 0.03 P, 0.03 S, remainder Fe) in 7 M H₃PO₄ by gravimetry, voltammetry and electrochemical impedance spectroscopy (EIS) methods with similar results. As stated above, the protective action of organic CIs in H₃PO₄ solutions with high concentration of the latter is good, but even in this case, the Z value of this CI determined by gravimetric measurements decreases from 97.2 to 87.8% with a t increase from 20 to 80°C [65]. The Sulfapyridine drug [66] also loses its protective action toward C35E carbon steel (content in mass percent, %: 0.370 C, 0.230 Si, 0.680 Mn, 0.016 S, 0.077 Cr, 0.011 Ti, 0.059 Ni, 0.009 Co, 0.160 Cu remainder Fe) in 2 M H₃PO₄ with an increase in t. According to the results of similar studies on mild steel (content in mass percent, %: 0.017 C, 0.007 Si, 0.196 Mn, 0.014 S, 0.043 Cr, 0.013 Ni, 0.015 Mo, 0.196 Mn, remainder Fe), 5% morpholine at 30°C in 2 N H₃PO₄ provides Z = 96.9%, and in 2 N H₂SO₄ it is only 68.5%. However, at 60°C the Z values are 74.7% and 78.4, accordingly [67]. A similar situation is observed in the protection of mild steel with folic acid in $0.5 \text{ M H}_3\text{PO}_4$ [68].

The "environment-friendly" inhibitors specially developed for phosphoric acid media,



(2-isopropyl-5-methylphenol) [70], absinth oil [71], apricot juice [72], extracts of plants *Acalypha indica L*. [73] and *Plectranthus Amboinius L*. [74], extract of bamboo leaves and



alcoholic extract of guayaba leaves [76], are poor inhibitors of mild steel corrosion. Even at ambient *t* these CIs in 0.1-2 M H₃PO₄ do not provide Z > 90% for mild steels.

A better protection of carbon and even highly alloyed steels in phosphoric acid solutions at ambient t is provided by adding relatively hydrophobic S-containing hydrochloride [77], *L*-cysteine methyl ester allylthiourea compounds: [78]. thiosemicarbazide and its derivatives [79], 1-benzoyl-4-phenyl-3-thiosemicarbazide [80], 4-(N,N-diethylamino)benzaldehydethiosemicarbazone [81], 3,4-dimethoxybenzaldehydethiosemicarbazone 2-mercapto-BI 2-mercaptothiazoline [82], [83], [84], 2mercaptopyrimidine [85], benzothiazole derivatives



4-amino-3-hydrazino-5-mercapto-1,2,4-triazole [87], 3-phenyl-4-amino-5-mercapto-1,2,4-

triazole [88], thiophene derivative $\sqrt[5]{c}$ [89], methylthiourea [90]. For example, 4-

amino-3-hydrazino-5-mercapto-1,2,4-triazole [87] in 2M H₃PO₄ (at 30°C) on C35E carbon steel at C = 0.01 M provides Z = 96.8%. However, with increasing *t*, S-containing compounds (*L*-cysteine methyl ester hydrochloride, 4-(*N*,*N*-diethylamino)benzaldehydethiosemicarbazone, 3,4-dimethoxybenzaldehydethiosemicarbazone, 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, thiophene derivative) inhibit corrosion of steels more poorly. For example, for 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole an increase in *t* from 30 to 50°C decreases γ 15-fold [87]. An exclusion here is allylthiourea whose protective action increases somewhat with a *t* increase from 30 to 50°C [78]. Not all Scontaining compounds (thiourea [90], 1,2-bis(thiophen-2-ylidenemethyl)hydrazine [91], 4-

substituted phenacyldimethylsulfonium bromide $\begin{vmatrix} O & CH_3 \\ S & CH_3 \end{vmatrix}$ $Br^- - x = -H, -CH_3, -OCH_3, -CI, -Br, -NO_2$

[93] and Alizarin red (4) (93]) are capable of efficient protection of steel even at ambient temperature.

Unsuccessful attempts to create CIs for H₃PO₄ with the use of acetylacetonate

complexes of Co(II), Cu(II), Zn(II), Mn(II) [94], ruthenium complex



[95]) and inorganic compounds (aluminum phosphate [96]) were also undertaken.

Addition of Cu(II) cations obtained by dissolving CuO in H_3PO_4 , or NO_3^- anions in the form of NaNO₃ is recommended to protect X18H10T chromium–nickel steel in hot H_3PO_4 solutions (up to 130°C). The mechanism of action of these additives that favor the existence of chromium–nickel steel in H_3PO_4 solutions in the passive state was studied [97, 98].

Under conditions of specific corrosion–abrasive wear of an austenitic chromium– nickel steel (content in mass percent, %: 26.75 Cr, 31.43 Fe, 31.85 Ni, 6.6 Mo, 1.5 Mn, 1.21 Cu, 0.193 N, 0.1 Si, 0.005 C, 0.002 S, 0.017 P) in 40% $H_3PO_4 + 4\%$ $H_2SO_4 + 0.42\%$ KCl containing a SiC abrasive (24 g/l, angle of impact of abrasive particles on the surface 90°), addition of 6 g/l clay (content in mass percent, %: 38.86 SiO₂, 10.76 Al₂O₃, 16.48 CaO, 4.42 Fe₂O₃, 3.76 MgO, 1.62 K₂O, 0.31 SO₃, 0.55 TiO₂, 0.04 MnO, 0.18 P₂O₅, 0.017 Na₂O, 0.049 SrO) provides Z = 88% [99].

A more promising method for corrosion protection of metals is to use mixed CIs rather than individual ones [21, 31, 40]. Inhibitor formulations with halide anions [40], among which mixtures containing I may be singled out, are most commonly used for the protection of metals in mineral acids. In some cases, addition of this anion to an organic CI substantially decreases steel corrosion even under extremely drastic conditions of hightemperature corrosion in HCl [100]. Strong inhibition of steel corrosion in H₃PO₄ solutions with KI as an individual additive can only be obtained at high C_{in} values. In 2.5 M H₃PO₄ (30-60°C) on carbon steel (content in mass percent, %: 0.041 C, 0.311 Mn, 0.05 P, 0.007 S, remainder Fe), the presence of 50 mM KI provides Z = 97.1-99.6%. The maximum CI inhibiting efficiency is found at t near 50°C. Reducing the CI content in solution to 20 mM decreases Z to 93.7–98.0% [101]. Formulations of I^- with 6-benzylaminopurine [102], dodecylamine [103], bamboo leave extract and its components (rutin and orientin) [75], as well as the related additive benzyltrimethylammonium iodide [104] in H₃PO₄ solutions were studied. Formulations of I^- with N-containing compounds inhibit corrosion better than the individual mixture components. For example, for 1 mM of 6-benzylaminopurine in 1 M H₃PO₄ (at 20°) on cold rolled steel (content in mass percent, %: 0.07 C, 0.3 Mn, 0.022 P, 0.010 S, 0.01 Si, 0.030 Al, remainder Fe), Z = 63.2%, and for 1 mM 6benzylaminopurine + 1 mM KI, Z = 95.3% [102]. Formulations of I⁻ with dodecylamine [103], bamboo leave extract, rutin and orientin [75] demonstrate a synergistic effect of the components. Mixtures of I⁻ with 6-benzylaminopurine [102], bamboo leave extract, rutin, orientin [75] and benzyltrimethylammonium iodide [104] lose their protective action with an increase in t. Formulations of (4-(2-pyridylazo)resorcin [105] and cetyltrimethylammonium bromide [106]) with chlorides have also been studied. They are substantially inferior to iodide formulations in protective action and are characterized by higher halide concentrations in solution. The degree of protection of formulations containing halide decreases in the series: $I^- > Br^- > Cl^-$ [107]. For example, in 3.5% of H₃PO₄ (at 30°C) the degrees of steel protection (content in mass percent, %: 0.012 C, 0.005 P, 0.017 S, 0.017 Si, 0.07 Mn, remainder Fe) by formulations of $11 \,\mu m$ (E)-N'-(1-(2-hydroxyphenyl)ethylidene)-3-nitrobenzohydrazide and 0.01 M potassium halides are 67.5% (KI), 51.1% (KBr) and 43.8% (KCl).

Formulations of sodium oleate with Ce(IV) [108] and red tetrazolium $\begin{bmatrix} & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & &$ H₃PO₄ (20–50°C) [109]. However, their protective action also decreases with an increase in *t*.

Protection synergism is observed when Cu(II) cations and NO_3^- anions used as CIs are both present in corrosion medium for the protection of X18H10T chromium-nickel steel in hot H₃PO₄ solutions [110]. The specifics of the synergistic effect of these additives are addressed in [110, 111].

Stainless steel 904L (content in mass percent, %: 0.013 C, 1.84 Mn, 0.145 Si, 0.007 S, 0.029 P, 25.09 Ni, 20.77 Cr, 4.37 Mo, 1.50 Cu, 0.13 W, remainder Fe) in 40% H₃PO₄ + 4% H₂SO₄ + 300 ppm Cl⁻ (80°C) is protected by adding 1,2,3-benzotriazole (BTA). In spite of the fact that in this system the Cl⁻ anion acts as a synergistic additive to BTA, Z = 75% at the maximum concentration $C_{\text{BTA}} = 0.1$ M [112].

Along with two-component mixtures for protection the of steels in phosphoric acid media, patent literature recommends multicomponent formulations (Table 2), containing mandatory components such as urotropine (no less than one third of the inhibiting mixture azomethine (acetylacetone-*o*-aminophenol weight) and [113], acetylacetone-(6brompyrimidyl-5)-sulfanilamide [114], α -naphthal- α -naphthylamine [115], α -hydroxynaphthalisonicotine hydrazide [116], *m*-nitro-benzal-*p*-iodoaniline [117], *p*-dimethylaminosalicylal-*p*-bromaniline [118], p-dipentylaminosalicylal-2-amino-4-nitrophenol [119], and 5-nitro-2-furfural- α -naphthylamine [120]). As additives, these mixtures usually contain relatively hydrophobic components - S-containing organic compounds (dinitrophenylthiocyanate [113], 2,4,6-tris(2-isotioureido)-sim-triazine hydroiodide [116], 2-(thiazolyl-4)-BI [116], 3-ethyl-2[5'-(3'-ethylbenzthiazolinilidene-2'')pentadiene-1,3'yl]benzothiazolium iodide [119], mercazolil [120]), fluoroorganic additives (4trifluoromethyl-2,6-dinitro-3-amino-*N*,*N*-diethylaniline [114], 4,5-dichloro-2-trifluoromethylbenzimidazole [117]) and iodide anions [116, 118, 119]. As accompanying components, some of the mixtures include N-containing molecular (dimethylamino-4hydroxy-5-butyl-6-methylpyrimidin [115], N-(heptylcarbamoyl)-imidazolidinone-2 [118], (indolyl-3)-acetic acid [119]), cationic (iodide methylethyloctyl-phenylammonium [118], 1,1'-dimethyl-4,4'-dipyryliumdi(o-methylsulfate) [120]) or anionic compounds (sodium dimethylaminoazobenzenesulphonate [114]). Regardless of the rather complex and diverse chemical compositions of these formulations, the majority of them [113, 114, 116–120] may, for simplification, be regarded as mixtures of N-containing compounds of different origin with a relatively hydrophobic component, most often an S-containing compound [112, 116, 119, 120]. In practical terms, the use of mixtures containing toxic organofluorine compounds [114, 117] seems unlikely. All the multicomponent CIs studied work in a wide range of media and may be used for inhibiting steel corrosion in H₃PO₄, HCl and H₂SO₄ solutions.

No.	Inhibitor chemical composition, mass %	Application medium	Protected metal	Source
1	Acetylacetone- <i>o</i> -aminophenol – 18.2–29.7; 2,4-dinitrophenylthiocyanate – 22.7–24,3; urotropine – 45.9–59.1.	3 N H ₃ PO ₄ , inhibitor – 3 g/l	Steel, titanium, zinc	113
2	4-Trifluoromethyl-2,6-dinitro-3-amino- <i>N</i> , <i>N</i> - diethylaniline 9.4–11.4; acetylacetone-(6-bromopyrimidyl-5)- sulfanilamide – 14.1–17.1; sodium dimethylaminoazobenzenesulphonate (Methyl Orange) – 20.0–34.3; urotropine – 37.1–56.5.	5 N H ₃ PO ₄ , inhibitor – 3 g/l	Steel, titanium, indium	114
3	 α-Naphthal-α-naphthylamine – 17.5–29.0; dimethylamino-4-oxy-5-butyl-6- methylpyrimidin – 22.9–30.1; urotropine – 59.6–40.9. 	5 N H ₃ PO ₄ , inhibitor – 5.8 g/l	Steel, Z = 94.1-99.6%. Titanium, Z = 45.0-69.2%. Indium, Z = 39.2-54.5%.	115
4	 α-Oxynaphthalisonicotine hydrazide – 11.1–14.7; 2,4,6-tris(2-Isotioureido)-<i>sym</i>-triazine hydroiodide – 15.0–10.3; 2-(Thiazolyl -4)-benzimidazole – 33.4– 25.0; urotropine – 40.5–50.0. 	5 N H ₃ PO ₄ , inhibitor – 5 g/l	Steel, Z = 94.3-99.7%. Aluminum, Z = 71.7-78.7%. Indium, Z = 45.0-55.8%.	116
5	<i>m</i> -Nitro-benzal- <i>p</i> -iodoaniline – 14.8–17.9; 4,5-dichloro-2- trifluoromethylbenzimidazole – 33.3–23.9; Urotropine – 51.9–58.2.	5 N H ₃ PO ₄ . inhibitor – 4.8 g/l	Steel, Z = 94.1-99.4%. Aluminum, Z = 87.0-91.6%. Indium, Z = 48.5-58.9%.	117
6	 <i>p</i>-Dimethylaminosalicylal-<i>p</i>-bromoaniline – 18.1–23.9; <i>N</i>-(Heptylcarbamoyl)imidazolidinone-2 – 11.9–13.7; Methylethyloctylphenylammonium iodide – 16.4–27.3; Urotropine – 40.9–47.8. 	3 N H ₃ PO ₄ . inhibitor – 3.2 g/l	Steel, Z = 95.8 - 99.5%. Zinc, Z = 88.1 - 97.0%. Tin, Z = 70.1 - 73.9%.	118
7	Dipentylaminosalicylal-2-amino-4- nitrophenol – 15.8–12,1;	$5 \text{ N H}_3\text{PO}_4,$ inhibitor $-3,2$ g/l	Steel, Z = 94.5 - 99.7%.	119

Table 2*. Multicomponent inhibitors of metal acid corrosion designed for application in H_3PO_4 solutions.

No.	Inhibitor chemical composition, mass %	Application medium	Protected metal	Source
	(Indolyl-3)acetic acid – 10.3–15.0; 3-Ethyl-2 [5'-(3'-ethylbenzthiazolinilidene- 2'')pentadiene-1,3'-yl]benzothiazolium iodide – 25.9–32.3; Urotropine – 48.0–40.6.		Titanium, Z = 80.1-93.0%. Indium, Z = 46.9-58.0%.	
8	5-Nitro-2-furfural-α-naphthylamine – 8.7–10.5; di(<i>o</i> -Methylsulfate)-1,1'- dimethyl-4,4'- dipyrylium – 12.9–23.0; Mercazolilum – 29.1–33.6; Urotropine – 49.3–32.9.	0,03÷5 N H ₃ PO ₄ , inhibitor – 2,5 g/l	Steel, Z = 94.5-99.7%. Titanium, Z = 48.1-57.0%. Aluminum, Z = 63.3-79.2%.	120

* results of measurements performed at 20°C and 90°C.

Article [121] describes a failed attempt of mild steel protection in 40% H₃PO₄ (40°C) with composite CIs containing 10 mM of an S-containing amino acid (methionine, cystine, cysteine, *N*-acetylcysteine), Cl⁻ and F⁻, Fe(III). Such formulations provide $Z_{max} = 78\%$, while for a binary amino acid mixture with Cl⁻, $Z_{max} = 87\%$.

Binary CIs including N-containing organic compounds and S-containing ones capable of protection even in hot acid solutions are interesting for H_3PO_4 solutions. In 2 M H_3PO_4 (60°), adding 5 mM of citralidenebenzylamine + 5 mM KNCS decreases the corrosion rate k of St3 steel 96-fold, while addition of 5 mM sodium diethyldithiocarbamate (DDTC) decreases the k value 84-fold [58]. Under the same conditions, the mixture of 5 mM of N-(2-chlorophenyl)-1,3,5-triazine-2,4-diamine derivatives with the formula:



with 0.5 mM KNCS inhibits corrosion 29–41 fold [122]. On steel 10 in 4 N H₃PO₄ (at 80°) for a series of formulations of waste from industrial production of morpholine with captax or thiocarbamide (3 g/l), Z = 97.7-99.2% according to 1-hour tests [123].

In practical terms, the use of mixtures of triazole derivatives with S-containing compounds seems promising. Such formulations based on 3-substituted 1,2,4-triazole, the IFKhAN-92 CI, efficiently inhibit low carbon steel corrosion [11, 124, 125], although individual components of these mixtures do it poorly (Figure 1). Mixtures of this triazole with anionic sulphur-containing additives (KNCS, DDTC, Na₂S) give the maximum reduction of corrosion: they provide at least 10 times smaller k values than KI-containing formulations.



* DDTC - sodium diethyldithiocarbamate

Figure 1. Steel corrosion inhibition factors for St3 steel in 2 M H₃PO₄ ($t = 60^{\circ}$ C) by sulphurcontaining compounds (0.5 mM) and their mixtures with 5.0 mM IFKhAN-92. Test duration – 2 h.

Using mixtures of a 3-substituted 1,2,4-triazole with KNCS and captax as an example (Figure 2), the possibility of protecting low carbon steel in H₃PO₄ solutions within a wide range of concentrations (2.0–8.0 M) and temperatures (0–95°C) was shown [11, 124, 125]. A systematic growth in γ_{mix} with an increase in *t* is observed. The temperature maximum of the mixtures' efficiency is not reached at least up to 95°C, which allows one to consider them as "high-temperature CIs" [29]. In solutions with these additives the average *k* of St3 steel goes down with increasing duration of corrosion testing. In case of the 5 mM triazole + 0.5 mM KNCS mixture, the resulting $\gamma = 233$ in a 6 h test, or 59 in a 0.5 h test.

The resistance of CIs for acid corrosion of steels to the impact of iron cations is an important process parameter allowing their use under real industrial conditions where the etching solutions necessarily contain iron salts, but in such media the vast majority of compounds inhibiting corrosion of steels lose the capacity to protect the metal. The formulation of triazole with KNCS maintains a high protective action in H_3PO_4 solution containing Fe²⁺ as well as Fe³⁺ ions (Figure 3) due to inhibition of their cathodic reduction occurring in diffusion mode, which is unique among CIs [126].



Figure 2. Steel corrosion inhibition factors for St3 steel in H_3PO_4 solutions by combinations of IFKhAN-92 with KNCS and captax at various temperatures (*a*) and acid concentrations (*b*). Test duration – 2 h.



Figure 3. Influence of Fe(III) and Fe(II) cations (C = 0.10 M) on corrosion inhibition of St3 steel in 2 M H₃PO₄ by combination of 5.0 mM IFKhAN-92 and 0.5 mM KNCS. Test duration - 2 h.

Examples of protection of nonferrous metals by organic CIs in H₃PO₄ solutions are also known. For example, for pure *aluminum* in 1 M H₃PO₄ the mixture of 10 mM purine with 0.1 mM KI (25°) provides Z = 92% [127]. Formulations of unsaturated ketones (benzalacetophenone, dibenzalacetone, dibenzal-1,4-diacetylbenzene) with halide anions [128] are less efficient in this respect. The protective action of such mixtures on aluminum (content in mass percent, %: 0.483 Si, 0.180 Fe, 0.001 Cu, 0.405 Mg, 0.017 Zn, 0.015 Ti, 0.004 Cr, 0.005 Ni, remainder Al) in 1 M H₃PO₄ (30°) decreases in the series: $\Gamma > Br^- >$ Cl⁻. For the most efficient formulation, 11 µm dibenzal-1,4-diacetylbenzene + 10 mM KI, Z = 80%. For a similar mixture containing KBr, Z = 76%, and Z = 70% for the mixture containing KCl. An aqueous extract of coriander (Coriandrum sativum L.) seed was offered as an "environment-friendly" CI for aluminum (content in mass percent, %: 0.120 Si, 0.270 Fe, remainder Al) and 6063 alloy (content in mass percent, %: 0.41 Si, 0.11 Fe, 0.05 Cu, 0.49 Mg, remainder Al) [129, 130]. According to the results of voltammetry and electrochemical impedance spectroscopy (EIS), the extract of coriander seeds (up to 0.05%) in H₃PO₄ (30–50°C) provides $Z \le 75\%$. A similar effect ($Z \le 79\%$) for aluminum protection, according to voltammetry and EIS data, is provided by adding 10 mg/l of essential oil from Mentha Pulegium leaves to 2 M H₃PO₄ (25°C) [131]. A less efficient extract from leaves of Dendrocalamus brandisii [132] on aluminum (content in mass percent, %: 0.25 Si, 0.35 Fe, 0.05 Cu, 0.03 Mg, 0.05 Zn, 0.03 Ti, 0.05 V, remainder Al) in 0.5–3 M H₃PO₄ (20–50°C) gives Z < 50%. The protective action of this extract decreases with increasing t and increasing C_{H3PO4} . In very dilute solutions (0.033–0.167 M H₃PO₄, 30°C), the corrosion of B26S copper-aluminum alloy (content in mass percent, %: 3.88 Cu, 0.87 Mn, up to 0.59 Si, up to 0.71 Fe, up to 0.32 Mg, remainder Al) is inhibited by aniline derivatives (up to 0.5 g/l), of which *p*-toluidine provides the best protective effect, in some cases almost totally suppressing corrosion [133]. The impact of aniline derivatives on aluminum corrosion in this medium is based on its ability of partially neutralizing highly dilute solutions of the acid.

For inhibition of aluminum corrosion, patent literature (Table 2) recommends several aforementioned multicomponent inhibitor formulations, which include urotropine and azomethine with addition of an S-containing compound [116, 120] or a fluoroorganic compound [117].

Inorganic compounds are used for the protection of aluminum alloys in phosphoric acid media along with organic CIs. For example, adding Na₂MoO₄ ($C \le 20$ mM) to 1 M H₃PO₄ (25°) allows inhibiting the corrosion of an aluminum alloy (content in mass percent, %: 0.25 Si, 0.35 Fe, 0.05 Cu, 0.03 Mn, 0.03 Mg, 0.05 Zn, 0.03 Ti, 0.05 V, remainder Al) with $Z \le 90\%$ [134]. The corrosion of A383 aluminum-silicon alloy (content in mass percent, %: 10.6 Si, 0.918 Fe, 2.52 Cu, 0.21 Mn, 0.057 Mg, 0.052 Sn, 2.91 Zn, 0.05 Ni, 0.069 Cr, 0.052 Pb, 0.041 Na, 0.038 Ti, remainder Al) in 0.5 M H₃PO₄ can be inhibited (Z = 95%) by using the 0.1 M K₂CrO₄ additive [135, 136].

For *zinc* protection in dilute H₃PO₄ solutions (0.01–0.15M) at ambient *t*, aniline [137], urotropine [138] and 4-aminoantipyrine [139] are used. In 1 M H₃PO₄ (25°), zinc corrosion is inhibited by adding 0.5–7.0 mM 2-thiophenecarboxaldehyde (TPhCA) with Z = 53-96% [140]. Increasing *t* to 65°C weakens metal protection by the inhibitor, and at 1 mM TPhCA, the *Z* value decreases from 65 to 35%. Better inhibition of the corrosion of zinc (spectroscopically pure, 99.9%)) in 1 M H₃PO₄ (25°) is provided by 2 mM 2-mercapto-BI, Z = 98% [141]. The use of a mixture of acetylacetone-*o*-aminophenol, dinitrophenyl-thiocyanate and urotropine (3 g/l) decreases the zinc corrosion rate in 1 M H₃PO₄ (20°C)

only 13-fold [113]. More promising for the protection of this metal is the use of substituted triazole IFKhAN-92, which, at a concentration of 5 mM in 2 M H₃PO₄ (25–60°C), slows down the corrosion of Ts1 zinc 15–26 fold [142]. In 1 M H₃PO₄ (20–90°C), 3.2 g/l of a four-component mixture (*p*-dimethylaminosalicylal-*p*-bromoaniline + *N*-(heptyl-carbamoyl)-imidazolidinone-2 + methylethyloctylphenylammonium iodide + urotropine) [118] provides Z = 88.1-97.0% on zinc.

In the protection of *copper alloys* in phosphoric acid solutions, 3-mercapto-1,2,4-triazole, benzotriazole, thiophene, tetrahydrothiophene [143], 1-butyl-4-methylpyridinium tetrafluoroborate [144], oil of *Artemisia Astéracées* plant [145] and extract of sea algae *Sargassum wightii* [146] demonstrate weak inhibiting properties. Multicomponent mixtures (Table 2) containing urotropine, azomethine and an additive of hydrophobic origin are capable of preventing corrosion of *titanium* [113–115, 119, 120], *indium* [114–117, 119] and *tin* [118] in 1 M H₃PO₄.

Let us separately consider the CIs introduced into acidic phosphate formulations to remove products of atmospheric corrosion (rust converters, RC) from the surface of steels. For example, adding 0.5–1% catapin KI-1 prevents the undesirable dissolution of the surface of 20X13 and 40X13 stainless steels with low chromium content when treated with RC with the following composition, g/kg: H₃PO₄ 200–300, oxalic acid 5–10, surfactant 1– 6, silicon dioxide 40–75, water up to 1 kg [147]. Triethanolamine (0.2–0.3%) is added to decrease the corrosivity of a frost-resistant RC (content in mass percent, %: H₃PO₄ 3.0– 5.0, alcohol C₁–C₄ or their mixtures 79.5–86.0, water 11.0–15.0) [148].

In some cases, H_3PO_4 added to an HCl solution can itself play the role of a corrosion inhibitor. For example, adding 1% H_3PO_4 to 1 M HCl (at ambient *t*) allows the corrosion rate of X18H10T steel to be reduced 70-fold [149]. However, this effect is unstable and depends on the composition of the solutions and the corrosion duration. The corrosion of low-carbon steel (content in mass percent, %: 0.16 C, 0.16 Si, 0.53 Mg, remainder Fe) in 1 M HCl (30°C) is decreased by adding 0.015% of a combination of tannin and H_3PO_4 (1:1) with Z = 61%, against 72 and 55% for tannin and H_3PO_4 themselves. The presence of H_3PO_4 in etching solution gives steel samples resistance to corrosion in the atmosphere and prevents corrosion damage from appearing on their surface for 3 weeks, against on the 1st week for samples kept in the acid inhibited solely by tannin [150].

Analysis of literature shows that at present no CIs of metals for H_3PO_4 solutions are commercially produced in the RF. Except for S-containing compounds, individual organic CI weakly inhibit steel corrosion in H_3PO_4 solutions. S-containing compounds substantially lose protective properties upon rising *t* even to 50°C. Mixed CIs consisting of N-containing compounds and relatively hydrophobic S-containing compounds have a better protective action in H_3PO_4 . More promising are mixtures of triazole derivatives and S-containing compounds that can substantially reduce the *k* of metals even in hot acid solutions (*t* up to 100°C), and in the case of steels are capable of maintaining protective action in the presence of Fe(II) and Fe(III) cations. It is very important for CIs used in acid etching of steels.

Attention should be paid to the group of metal CIs for H_3PO_4 claimed to be "environment-friendly". They are often produced by extraction from various parts of plants. They all show poor results in metal protection, and their effect cannot be substantially improved even by combining them with such a well-known synergist as the iodide anion.

2. The specifics of the mechanism of inhibitor action in mixtures of triazoles and sulphur-containing compounds on steels in phosphoric acid solutions

As a rule, the reasons for the low efficiency of organic CIs toward steels in H_3PO_4 solutions are not discussed. It is probably caused by build-up of insoluble surface phosphates on a metal that prevent the adsorption of CIs. As a result, compounds capable of only physical interaction with the steel surface are poorly adsorbed on the metal surface and weakly protect steel. This is proved by the fact that many of these CIs (acetylene derivatives [57], azomethines [58], quaternary ammonium compounds (QAC) [59], N-containing heterocycles [11, 31, 59, 124, 125]) show higher protective effects in other mineral acids and, in particular, in HCl. In addition, propargyl alcohol [151], some QAC and triazoles [11, 59, 124, 125] improve efficiency on transition to concentrated H_3PO_4 solutions where soluble acid iron phosphates emerge, thus freeing the metal surface. It is logical to assume that high protection of steels can only be obtained here by CIs chemically interacting with steel and competing in adsorption with iron phosphates. The situation may be made clear by analyzing the regularity in the adsorption of organic CIs on steels in H_3PO_4 .

The adsorption of individual organic compounds (N-1-naphthylethylenediamine dihydrochloride [60], barbiturates [69], 2-isopropyl-5-methylphenol [70], rutin, orientin [75], 6-benzylaminopurine [102], benzyltrimethylammonium iodide [104]) on steel in H₃PO₄ solutions is described by the Langmuir isotherm, that of BI derivative is described by the Flory–Huggins isotherm [61], that of benzyltriphenylphosphonium chloride [63], quaternary salts of pyridinium and quinolinium [64] is described by the El Avadi isotherm, and that of sodium oleate is described by the Temkin isotherm [108]. The free energy of their adsorption ($-\Delta G_{ads}$) on steels is substantially lower than 40 kJ/mol that could allow chemisorbtion of a CI on steel to be assumed. This result well agrees with the low efficiency of these compounds in corrosion inhibition of steel in H₃PO₄. Adsorption of I⁻ (inorganic additive) also complies with the Langmuir isotherm with ($-\Delta G_{ads}$) = 29.6 kJ/mol [101]. Addition of this ion to rutin, orientin, 6-benzylaminopurine, as well as addition of Ce(IV) ions to sodium oleate increases the adsorption energy of organic compounds, although the value of ($-\Delta G_{ads}$) = 40 kJ/mol is not reached. Only in the absorption of 1-dodecyl-5-methyl-1*H*-benzo[d][1,2,3]triazol-1-ium bromide on carbon steel described by

the Langmuir isotherm, a high value of $(-\Delta G_{ads}) = 37-42$ kJ/mol [65] is observed, which allows chemical interaction of this BTA derivative with steel surface to be assumed.

Stronger interaction of steel surface and inhibitor is observed for S-containing compounds, such as allylthiourea (($-\Delta G_{ads}$) = 37.6–40.4 kJ/mol) [78], 4-(N,Ndiethylamino)benzaldehydethiosemicarbazone (32-34 kJ/mol) [81], thiosemicarbazide and 1,2-bis(thiophen-2-ylidenemethyl)hydrazine derivatives (38-40 kJ/mol)[79], its (38 kJ/mol) [91], 3,4-dimethoxybenzaldehydethiosemicarbazone (40–43 kJ/mol) [82], benzothiazole derivatives (44.5-52.2 kJ/mol) [86], 4-amino-3-hydrazino-5-mercapto-1,2,4triazole (38.3 kJ/mol) [87], 3-phenyl-4-amino-5-mercapto-1,2,4-triazole (36.1 kJ/mol) [88], a thiophene derivative (38.3 kJ/mol) [89], that also inhibit steel corrosion better. The adsorption of these compounds obeys the Langmuir isotherm. Judging from the high adsorption energy $(-\Delta G_{ads}) \ge 40$ kJ/mol, we can assume with high probability that BTA some 3,4-dimethoxybenzaldehydethiosemicarbazone, thiosemicarbazide derivatives. derivatives and allylthiourea are chemisorbed on steel surface.

Data on the adsorption of organic CIs on nonferrous metals in H₃PO₄ are fragmentary, but they exclusively support the absence of chemisorption interaction of these metals with the compounds in question. Low $(-\Delta G_{ads})$ values of organic CIs on aluminum are observed in H₃PO₄ solutions where they are not efficient. $(-\Delta G_{ads}) = 17.3$ kJ/mol for the mixture of compounds produced from the *Dendrocalamus brandisii* plant [132], and even lower (4.7–5.8 kJ/mol) for unsaturated ketones [128]. Better adsorption is observed for TPhCA on zinc with $(-\Delta G_{ads}) = 28.9$ kJ/mol [140] and for 1-butyl-4-methylpyridinium tetrafluoroborate on copper (23.3–24.7 kJ/mol) [144]. In all the cases, adsorption is described by the Langmuir isotherm.

Mixtures of triazoles with S-containing additives have high protective effects on steel corrosion in H_3PO_4 , including hot solutions (t up to 100°C). It is logical to expect that the components of these mixtures interact with the metal surface in a chemisorption manner, thus ensuring substantial corrosion inhibition. In fact, it has been shown that adsorption of a 3-substituted 1,2,4-triazole on cathodically polarized low-carbon steel from acid solutions is described by the Temkin isotherm (Figure 4) with a relatively high free adsorption energy $(-\Delta G_{ads}) = 51 \pm 1$ kJ/mol, indicating the chemical nature of binding inhibitor molecules with the metal surface atoms [152]. Its adsorption kinetics is described by the Roginsky-Zeldovich equation (Figure 5), which is also in favor of CI chemisorption. Addition of KNCS to an H₃PO₄ solution speeds up the adsorption of the triazole on steel, which is evidenced by an increase in the rate constant in this equation in the presence of this compound. This explains the higher efficiency of the mixed CI in steel corrosion inhibition in H₃PO₄ in comparison with the triazole itself. Probably, the NCS⁻ anions that are adsorbed on the metal decrease the positive charge on the steel surface. As a result, the adsorption of the triazole present in the form of an organic cation accelerates. Ultimately, this allows a higher protection effect to be obtained than by the triazole itself,

even under mode drastic conditions in the absence of cathodic protection at the free corrosion potential, E_{cor} [152].



Figure 4. Adsorption isotherm of IFKhAN-92 (1) and its mixture with 0.5 mM KNCS (2) on St3 steel (E = -0.30 V) from 2 M H₃PO₄ (22°C). Points – measured values, straight line – theoretical dependence for the Temkin isotherm.



Figure 5. Dependence of the coverage of St3 steel surface with inhibitor (E = -0.30 V) on the logarithm of its adsorption time in 2 M H₃PO₄ (22°C) containing IFKhAN-92 (*a*) and its combination with 0.5 mM KNCS (*b*), with concentrations in μ m: 1 – 2.5, 2 – 5.0, 3 – 10. Points – observed dependences. Straight lines – theoretical dependence for the Roginsky–Zeldovich equation.

It has been shown by X-ray photoelectron spectroscopy that upon adsorption from H_3PO_4 solutions on the steel surface at E_{cor} , formulations of the 3-substituted 1,2,4-triazole and KNCS form a polymolecular protective layer more than 4 nm thick, presumably consisting of a complex combination of triazole molecules, Fe(II) cations and NCS⁻ that has a polymeric nature. This layer is chemically bound to the steel surface, which determines its ability to remain on the metal even during its ultrasonic cleaning. In background acid solutions such CI layers provide high protection of steel (Figure 6) [153].



Figure 6. Protective after-effect of inhibitor layers formed on the surface of St3 steel in 2 M $H_3PO_4 + 5$ mM IFKhAN-92 + 5 mM KNCS (20°C) in 2 M H_3PO_4 solution (2 h). 1 – samples after preliminary inhibitor adsorption (24 h), 2 – samples after preliminary inhibitor adsorption (24 h) followed by ultrasonic washing, 3 – samples without preliminary inhibitor adsorption.

The protective CI layers formed by the formulation of the triazole and KNCS on the steel surface strongly inhibit the electrode reactions of steel in H₃PO₄ solution at $t \le 95^{\circ}$ C, thus enabling efficient protection of steel under these conditions [154].

Therefore, the high efficiency of mixtures of triazoles and KNCS in the corrosion of steel in H_3PO_4 solutions results from the capability of such heterocycles to be chemisorbed on steel and form on its surface, jointly with Fe(II) and NCS⁻, protective layers similar in structure to polymeric complexes. This mechanism of protective action of the mixed CI is largely determined by the unique structure of the triazole is one of the mixture components and that exhibits the properties of a bidentate ligand. As a result, the CI is not only chemisorbed but also forms a polymeric protective layer on steel [153].

In addition, rhodanide anions speed up the adsorption of triazoles on steel, thus contributing to the inhibitive effect of the mixture. It is important to note that often in studying the protection mechanism of CIs is acids, the role of kinetics of their adsorption on metals is not taken into account, although, as shown in [152], this factor can play the predominant role in metal protection.

3. Inhibited acid solutions based on H₃PO₄ resistant to accumulation of Fe(III) salts

Etching of steels in solutions of mineral acids is accompanied by the accumulation of Fe(III) salts due to dissolution of scale of Fe(II) salts formed in the reactions between the scale and the metal with the acid and their oxidation with air oxygen [51, 155]. For example, in an etching solution operating in periodical etching mode (initial HCl content 220 g/l, t = 40°C, etching time up to 60 min), when 3/4 of the initial acid content is consumed, the concentration of FeCl₃ may reach 0.1 M [51]. Accumulation of Fe(III) salts

results in the occurrence of an additional depolariser with a high oxidation potential $(E^{0}_{Fe(III)/Fe(II)} = 0.771 \text{ V} [156])$ in the solution, which substantially increases the system corrosivity toward steel. In acid solutions containing Fe(III), dissolution of steels occurs not only due to reaction of iron with the acid:

$$Fe + 2 H^+ = Fe^{2+} + H_{2}$$

but also as a result of a parallel reaction of the metal with the Fe(III) salt:

$$Fe + 2 Fe^{3+} = 3 Fe^{2+}$$
.

It is stated in [157] that in HCl solutions with high FeCl_3 content, corrosion of steel occurs mostly because of the metal oxidation with Fe(III) cations, which can in practice suppress the evolution of hydrogen gas formed in the course of the reaction of steel with HCl.

Fe(III) cations substantially decrease the protective action of CIs added to an etching solution [158]. It is noted that the presence of FeCl_3 in inhibited hydrochloric acid solutions used at the plants of the oil producing sector drastically increase their corrosivity to steel equipment [1, 56]. Among the reasons of reduced efficiency of CIs by Fe(III) cations we should note their removal from the corrosive medium due to coagulation [28] and the weak hindrance of Fe(III) reduction occurring diffusion mode by these compounds [126].

Almost no efficient way for reducing the adverse effect of Fe(III) on the corrosion of steels in acids is reported in literature. Addition of 15 g/l SnCl₂·2 H₂O is recommended for protection of steel in 5.9% HCl + 6.9 g/l Fe(III) (at 60°C). It slows down steel corrosion 18-fold [159]. The poor performance of this additive is evident. It is very likely that its effect is based on the reduction of Fe(III) to Fe(II) by Sn(II) cations. As a result, the effect of the additive will be unstable due to its consumption. In addition, SnCl₂ will be reduced on steel to Sn⁰, producing micro-galvanic pairs on its surface, which will result in local corrosion of a steel product during its further operation. To improve the efficiency of the PB-5 inhibitor for protection of steels in hot 4% HCl solutions containing 1.5 g/l FeCl₃, addition of urotropine is suggested, although its effect is small [158].

Improvement of CI protective action in solutions of acids containing Fe(III) salts is possible by means of reducing the total corrosivity of such a medium. This can be achieved using solutions of acids which upon dissociation generate anions capable of binding Fe(III) cations into strong complex ions with a weaker oxidation capability compared to Fe(III) aquacomplexes. Analysis of literature data on the stability of Fe(III) complexes with anions of mineral acids shows (Table 3) that solutions of H_3PO_4 and, in particular, HF are most promising in terms of reducing the oxidation capability of Fe(III) salts. It may be assumed that the oxidation capability of Fe(III) cations will be minimized in their solutions.

Ligands	р <i>К</i> _{і1}	р <i>К</i> _{і1.2}	р <i>К</i> _{і1-3}	р <i>К</i> і1-4	р <i>К</i> _{і1–5}	р <i>К</i> _{і1-6}	Ref.
ClO_4^-	1.15	_	_	_	_	_	160
	1.0	_	_	_	_	_	161
SO_4^{2-}	4.18	7.4	_	_	_	_	160
	4.02	5.38	—	—	—	_	162
HSO_4^-	2.48	_	_	—	—	_	163
HPO_4^{2-}	3.5	_	_	9.15	_	_	160
$H_2PO_4^-$	9.75	_	_	_	_	_	160
F^-	6.04	10.74	13.74	15.74	16.10	~16.10	160
CI⁻	1.45	2.10	1.10	-0.85	_	_	160
	1.52	2.22	_	_	_	_	161
	1.48	2.13	1.13	_	_	_	164
Br^-	0.55	0.82	_	_	_		160

Table 3. The instability constants (p K_i) of Fe(III) complexes with some inorganic ligands. $t = 20-30^{\circ}$ C.

In fact, a potentiometric study of $E_{Fe(III)/Fe(II)}^{0}$ in various acids confirmed this. For mineral acids containing Fe(III), the oxidation capacity decreases in the series HClO₄ > HBr > H₂SO₄ > HCl > H₃PO₄ > HF [165]. The prospects of practical use of HF for reducing the oxidation capability of media containing Fe(III) are very limited due to the high toxicity of this acid. In H₃PO₄ solutions (20–95°C), the values of $E_{Fe(III)/Fe(II)}$ are lower by 0.33–0.40 V than the standard value. Such a reduction in the system oxidation capability is sufficient for making some CIs efficient in steel protection in this medium. As discussed earlier, the combination of IFKhAN-92 and KNCS can efficiently inhibit corrosion of low-carbon steel in H₃PO₄ solutions containing FePO₄ [126].

It is important that addition of H_3PO_4 to solutions of acids (HCl and H_2SO_4), which do not considerably decrease the oxidation properties of Fe(III) cations, significantly decreases the oxidation capacity of these systems. In solutions of acid mixtures (HCl + H_3PO_4 or $H_2SO_4 + H_3PO_4$) containing Fe(III) salts, the oxidation capability decreases with an increase in the relative content of H_3PO_4 in the system [165, 166]. In addition, examination of the system $H_2SO_4-H_3PO_4-H_2O-Fe(III)$ by cyclic voltammetry (CVA) shows that binding Fe(III) ions into phosphate complexes significantly decreases the rate of their diffusion in a corrosion environment [167]. This plays an important role in inhibiting Fe(III) reduction on the surface of corroding steel because this process is diffusion-controlled [126].

The change in the properties of HCl and H_2SO_4 solutions containing Fe(III) after H_3PO_4 addition is sufficient to efficiently inhibit steel corrosion in such media by using CIs having

high protective action. For example, in 2 M $H_2SO_4 + H_3PO_4 + 0.05$ M Fe(III), a formulation of 4.5 mM IFKhAN-92 + 0.5 mM KNCS efficiently inhibits the corrosion of low-carbon steel in solutions containing up to 50% H_2SO_4 (Figure 7) [168]. In the same medium, the three-component formulation of 4.5 mM IFKhAN-92 + 0.5 mM KNCS + 0.2 M urotropine protects low-carbon steel better. Satisfactory protective action of a three-component formulation of CIs on steel corrosion is observed in acid mixtures with higher H_2SO_4 content (up to 60%) [169]. In 2 M HCl + $H_3PO_4 + 0.05$ M Fe(III), the formulation of 4.5 mM IFKhAN-92 + 0.5 mM KNCS is not that efficient in inhibiting steel corrosion as in 2 M $H_2SO_4 + H_3PO_4 + 0.05$ M Fe(III). However, addition of 4.5 mM IFKhAN-92 + 0.5 mM KNCS + 0.2 M urotropine to this corrosion medium allows one to provide satisfactory inhibition of steel corrosion in solutions of acid mixtures containing up to 60% HCl [170]. In actual use, inhibited solutions of acid mixtures resistant to accumulation of Fe(III) are more practical than similar solutions of individual H_3PO_4 due to a reduction in the solution cost.



Figure 7. Steel corrosion inhibition factors for 08PS steel in 2 M $H_2SO_4 + H_3PO_4$ and 2 M $HCl + H_3PO_4$ with addition of 0.05 M Fe(III) containing 4.5 mM IFKhAN-92 + 0.5 mM KNCS (1) and 4.5 mM IFKhAN-92 + 0.5 mM KNCS + 0.20 M urotropine (2), with various molar fractions of H_3PO_4 in solutions. Experiment duration – 2 h. $t = 60^{\circ}C$.

The use of potentiometry and CVA methods for studying $HCl-H_3PO_4-H_2O$ and $H_2SO_4-H_3PO_4-H_2O$ systems containing Fe(III) allowed the reasons of maintaining the protective effect in mixed CIs based on IFKhAN-92 in case of steel corrosion in such media to be found out. Phosphate ions bind the strong oxidant, *i.e.*, Fe(III) cations present in the solution, into strong complexes. These complexes have a weaker oxidation capability and are less mobile compared to Fe(III) complexes existing in acid chloride or sulphate solutions. Adding H_3PO_4 affects the thermodynamics of the system by reducing its oxidation capability. This additive also changes the kinetic parameters of reduction of Fe(III) cations on steel, which is diffusion-controlled. A decrease in the diffusion rate of Fe(III) cations should slow down their reduction. Evidently, such a complex effect should be sufficient so that the mixed CI based on IFKhAN-92 can, jointly with the hindrance of proton reduction, suppress the reduction of Fe(III) cations. An important role in the

observed effect belongs to IFKhAN-92 itself. It is capable of forming mono- and polymolecular protective layers on metals in solutions of acids. These layers are bound to a metal surface by strong chemical bonds, which allows a maximum protective effect to be obtained in such highly corrosive media as acids containing Fe(III) cations. Adding urotropine to such media additionally binds Fe(III) into complexes, thus reducing the content of its remaining non-complexed ions that are most corrosive to the metal.

Therefore, in the etching of steels or acid rinsing of steel equipment, in case of potential accumulation of Fe(III) salts that accelerate metal corrosion in such media, no solutions of individual mineral acids (HCl or H_2SO_4) should be applied but mixtures on their basis containing no less than 40% H_3PO_4 and an IFKhAN-92 + KNCS + urotropine combination (molecular ratio of components 9:1:400), because in such solutions steel corrosion due to its interaction with Fe(III) compounds is minimized.

Conclusion

 H_3PO_4 solutions are widely used in various fields of technology. A more extensive practical use of this acid is mainly limited by its corrosivity toward some metals, especially at elevated *t*, as well as by the lack of efficient means of their inhibitor protection in this medium. The overwhelming majority of individual organic compounds and mixed CIs offered for protection of metals in phosphoric acid media are of low efficiency due to their weak adsorption on metal surfaces. Low adsorption capacity of these compounds on steels is a consequence of their competition with iron phosphates in this process.

A promising method for the protection of steels in H_3PO_4 media involves the use of formulations of triazoles with S-containing additives. Components of these mixtures can compete in adsorption with iron phosphates formed on the metal surface, and create polymolecular protective layers with high efficiency in inhibiting corrosion on it.

An important property of these protective layers is a strong chemical bond of the inhibitor molecules with the metal surface and with each other inside the layer. It is the formation of these layers on the steel surface that allows efficient protection of steels in highly corrosive media – hot H_3PO_4 solutions, as well as solutions of this acid containing Fe(III) cations.

Inhibited acid solutions resistant to accumulation of Fe(III) salts in them created with the use of phosphoric acid may become a new and promising field of application of H_3PO_4 . Such solutions are necessary for etching steels or acid rinsing of steel equipment in case of potential accumulation of Fe(III) salts accelerating metal corrosion in such media.

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