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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Protective Properties of Metal Corrosion Inhibitors and Their Formulations in Aqueous-Glycolic Solutions

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Abstract—Contact corrosion of a number of metals in aqueous-glycolic solutions of nitrites, borates, benzoates, and phosphates of alkali metals was studied.

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Modern technology needs a wide variety of liquid heat carriers and working bodies with specific combinations of rheological, thermal, and anticorrosion properties [1]. Ethylene glycol (EG), which provides stable low-temperature properties, is used as the most readily available base component for development and manufacture of promising frost-resistant cooling fluids and heat carriers [2, 3]. An important factor in development of new synthetic fluids is their compatibility with construction materials of cooling systems. A complicated problem is posed by the requirement of simultaneous anticorrosion protection of different construction materials, including contact pairs constituted by metals with opposite electrochemical properties.

Effective anticorrosion properties of a fluid are provided by choosing appropriate corrosion inhibitors. The most readily available and effective inhibitors of metal corrosion in neutral electrolytes are nitrites, borates, phosphates, and benzoates of alkali metals [4]. There is a vast body of detailed evidence about the effect of these inhibitors on the corrosion behavior of both separate metals and multiple-electrode systems. However, these data are mostly available for aqueous electrolytes [5]. Data on the effect of these inhibitors on the behavior of electrochemically dissimilar metals in aqueous-organic media are not so abundant [6, 7]. This suggests that a study of the contact corrosion of metals in aqueous-glycolic solutions of the salts under consideration is both scientifically and practically topical. Despite certain restrictions on their use in cooling fluids for motor cars, introduced by separate countries, these corrosion inhibitors are widely used in manufacture of nonflammable hydraulic and lubricating-cooling fluids and in cooling fluids for heavy-duty vehicles [8, 9].

EXPERIMENTAL

Planar samples of steel 3 [GOST (State Standard) 380], GH-190 cast iron (VAZ Industrial standard 52205), AK6M2 aluminum alloy (GOST 1583), M-1 copper (GOST 859), L-63 brass (GOST 931), and POS-35 solder [TU (Technical Specification) 48-13-10], with dimensions of 50 × 25 × 3 mm, were preliminarily polished and degreased. Corrosion tests were performed in 50 vol % aqueous-glycolic solutions of corrosion inhibitors by the galvanostatic dissolution method [10] and gravimetrically in conformity with GOST 28084 [11]. The corrosion rate was evaluated by weighing metal samples. The following corrosion inhibitors were used: sodium nitrite (GOST 19906) and sodium tetraborate decahydrate (GOST 8429), both of technical grade; sodium benzoate (imported, pure grade); disubstituted sodium phosphate dodecahydrate (TU 2148-021-05761689–98); and a system constituted by monosubstituted potassium phosphate and disubstituted potassium phosphate, produced by titration of an aqueous-glycolic solution of potassium hydroxide with orthophosphoric acid to pH 8.0. Ethylene glycol (GOST 19710, extra quality) was not additionally purified.

As a rule, heat-exchange apparatus and cooling systems of internal combustion engines are multiple-electrode contact systems of metals with different electrochemical properties. In conformity with domestic [11] and foreign [12] standards, corrosion tests of low-freezing cooling fluids are performed with polymetallic aluminum–steel–cast iron and copper–brass–solder contact systems. Therefore, the effect of aqueous–glycolic solutions of the corrosion inhibitors under study on the corrosion behavior of metals was examined for these contact systems.

There is controversial published evidence about anticorrosion properties of sodium tetraborate in aqueous-glycolic solutions. For example, there is an opinion that sodium tetraborate concentrations in the range 0.75–2.0% provide a reliable protection for aluminum and its alloys, steel, copper, brass, and solder [13, 14]. At the same time, data obtained by other researchers [15, 16] indicate that only brass and solder are not subject to a strong corrosive attack by the aqueous-glycolic solution.

It was found that, at a 0.3% concentration, sodium tetraborate protects steel and cast iron from corrosion to some extent (degree of protection z = 50 and 70%, respectively). For other metals, only a slight inhibiting effect is observed, the degrees of protection for solder, brass, and aluminum are 4–8%, and the corrosion loss of copper substantially increases (Fig. 1a). As the sodium tetraborate concentration is raised to 2.0%, the corrosion resistance of solder sharply decreases, but the corrosion rates of copper and brass substantially increase and the corrosion of aluminum is completely suppressed. As regards the corrosion behavior of steel and cast iron, it can be stated that their degrees of protection remain almost unchanged as the inhibitor concentration increases. In this case, a passivating oxide is formed on the surface of iron by oxygen from hydroxide ions [5] additionally supplied by salt hydrolysis. Because the pH value of the buffer solution is almost independent of its concentration, this is probably the reason why the degree of protection of ferrous metals does not increase as the content of sodium tetraborate in solution is raised. However, it is necessary to take into account, in addition to the effect of hydroxide ions on the formation of passivating layers, the ability of borate anions to form difficultly soluble compounds on the surface of metals. At low sodium tetraborate concentrations, a metal is only partially passivated. This may lead to an increase in the rate of the anodic reaction, which is clearly manifested in that the corrosion of copper is initiated (Fig. 1a, curve *2*).

A study of the corrosion behavior of metals in solutions of potassium nitrite demonstrated that, at a concentration of 0.1%, this inhibitor provides a nearly full protection of steel and cast iron (z 98.5 and 92.5%), but corrosion of solder, copper, brass, and aluminum is initiated (Fig. 1b). As the concentration of potassium nitrite is raised to 0.5%, the corrosion rate slightly decreases for copper and brass, increases for solder, and remains unchanged for aluminum. The inhibiting properties of nitrite ions are attributed by most of researchers to the formation of an oxide film of Fe_2O_3 on the surface of steel and cast iron, which hinders the anodic dissolution of iron. The presence of such an oxide has been confirmed experimentally [5],

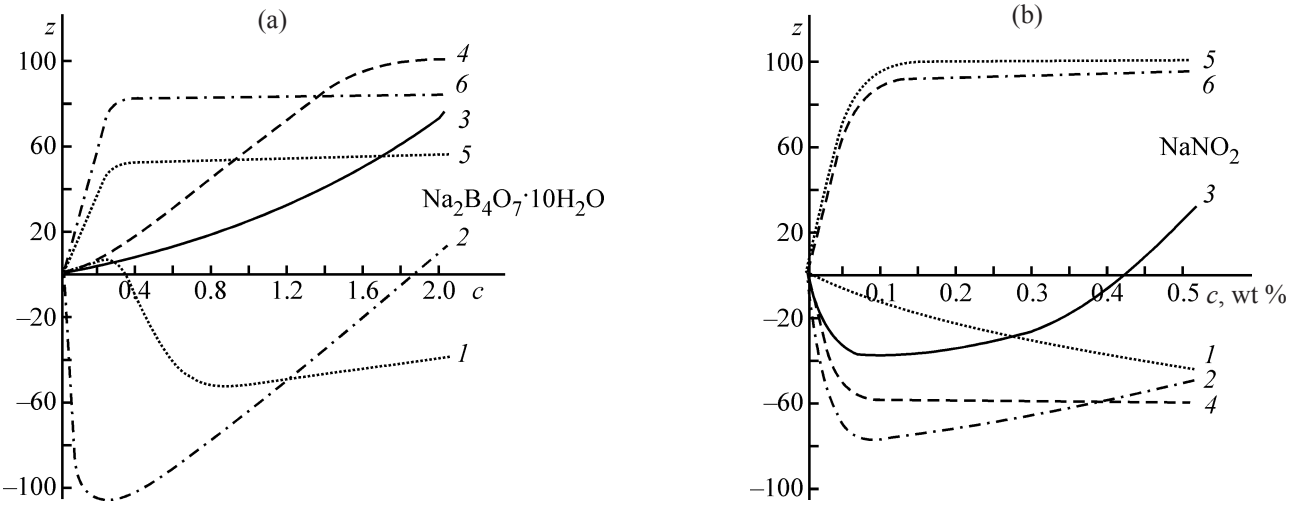


Fig. 1. Effect of the concentration c of (a) sodium tetraborate and (b) sodium nitrite on the degree of metal protection, z, in an aqueous solution of ethylene glycol. (*1*) Solder, (*2*) copper, (*3*) brass, (*4*) aluminum, (*5*) steel, and (*6*) cast iron; the same for Figs. 2 and 3.

and only the problem of its origin remains debatable. The most plausible is the standpoint according to which the passivating oxide is formed on the metal surface via oxidation of a lower oxide to a higher oxide by oxygen from water. However, according to [18], the passivating mechanism consists in oxidation of ferrous oxide hydrate by nitrite ions and its deposition on the surface of iron.

An examination of the effect of sodium benzoate on the metals under study demonstrated that, as the content of this inhibitor in aqueous-glycolic solutions increases, the corrosion loss of solder, brass, steel, and cast iron substantially decreases. In a 2.0% sodium benzoate solution, the degrees of protection of these metals were 92.5, 82, 99.5, and 99%, respectively, in good agreement with published data [4, 19]. At the same time, this inhibitor initiates corrosion of copper, and, at concentrations exceeding 0.75%, also that of aluminum. Such an ambiguous manifestation of the protecting effect of sodium benzoate in aqueous-glycolic solutions is presumably accounted for by the different solubilities of benzoates of the metals under study, formed on their surface. One more reason why the degree of protection of steel and cast iron is high is that the benzoic acid anion strongly affects the rate of anodic dissolution of iron by shifting the passivation potential in the positive direction. This leads to a decrease in the passivation current by approximately two orders of magnitude [20].

It is known that joint use of sodium tetraborate and sodium nitrate in aqueous-glycolic solutions provides an effective anticorrosion protection of iron [4]. As, however, can be seen from the data in Table 1, the degree of protection increases when this inhibiting complex is used not only for ferrous metals (steel, cast iron), but also for aluminum and copper. The maximum anticorrosion efficiency of sodium benzoate is observed at electrolyte pH 7.5–8.5 [21], and, therefore, it was of interest to study the corrosion behavior of metals in a wide range of sodium benzoate concentrations in a buffer solution of sodium tetraborate. At a sodium tetraborate content of 0.7% in an aqueous-glycolic solution (pH 7.8), raising the sodium

Table 1. Corrosion loss of metals in an aqueous-glycolic solution in relation to the nature of an inhibiting complex

Content, %	Degree of metal protection, %					
	solder	copper	brass	aluminum	steel	cast iron
Sodium nitrite 0.1	–14.4[a]	–81.3	–52.9	–62.8	99.5	92.5
Sodium tetraborate 0.7	–51.7	–90.6	11.8	34.9	49.8	80.3
Sodium nitrite 0.1, Sodium tetraborate 0.7	–46.6	–34.3	–35.3	58.2	100.0	96.6

[a] Initiation of corrosion.

Table 2. Corrosion loss of metals in a 0.7% aqueous-glycolic solution of sodium tetraborate at different sodium benzoate concentrations

Content of sodium benzoate, %	Degree of metal protection, %					
	solder	copper	brass	aluminum	steel	cast iron
0.00	–51.7	–90.6	11.8	34.9	49.8	80.3
0.35	46.0	–43.8	5.9	34.9	76.5	85.9
0.70	74.7	–9.3	73.5	18.6	85.1	94.2
1.00	94.8	50.0	70.6	–16.2	95.9	97.8
1.50	93.7	50.0	73.5	–34.9	99.6	98.5
2.00	94.4	53.1	70.6	–65.1	99.6	99.1
2.00[a]	95.4	75.0	76.5	100.0	88.2	95.4

[a] Sodium tetraborate concentration 2.0%.

Table 3. Degree of metal protection in a 0.1% aqueous-glycolic solution of sodium nitrite at different sodium benzoate concentrations

Content of sodium benzoate, %	Degree of metal protection, %					
	solder	copper	brass	aluminum	steel	cast iron
0.00	–51.7	–90.6	11.8	34.9	49.8	80.3
0.35	46.0	–43.8	5.9	34.9	76.5	85.9
0.70	74.7	–9.3	73.5	18.6	85.1	94.2
1.00	94.8	50.0	70.6	–16.2	95.9	97.8
1.50	93.7	50.0	73.5	–34.9	99.6	98.5
2.00	94.4	53.1	70.6	–65.1	99.6	99.1
2.00 [a]	95.4	75.0	76.5	100.0	88.2	95.4

[a] Boldface designates the corrosion-inhibiting formulation with the highest degree of protection for all the metals under study; the same for Table 4.

Table 4. Degree of metal protection in a 0.1% aqueous-glycolic solution of sodium benzoate at different sodium nitrite concentrations

Content of sodium nitrite, %	Degree of metal protection, %					
	solder	copper	brass	aluminum	steel	cast iron
0.0	92.0	4.7	1.6	6.3	1.2	1.1
0.1	63.2	18.8	38.1	11.7	100.0	87.6
0.2	71.9	–15.6	–11.8	–30.2	100.0	84.4
0.5	73.0	–56.3	–32.4	–39.6	100.0	81.8

benzoate concentration to 1.0–1.5% leads to a substantial rise in the degree of protection of all the metals except aluminum (Table 2). Further increase in the content of sodium benzoate in solution does not noticeably affect the behavior of the metals. The corrosion of aluminum can be completely precluded by raising the content of sodium benzoate to 2.0%; however, this leads to a certain decrease in the corrosion resistance of cast iron and steel (Table 2). It should also be noted that, with this inhibiting complex used, the degree of copper protection is as high as 75%, whereas taken separately, both the components initiate the corrosion of the metal (Table 2; Figs. 1a, 2b).

There is an ample body of data on the anticorrosion properties of corrosion inhibitors based on benzoates and nitrites of alkali metals; however, different researchers disagree on estimates of both the concentrations of the inhibitor components, which provide an effective anticorrosion protection, and their relative amounts [22, 23]. A detailed study of the anticorrosion properties of the benzoate-nitrite complex revealed its high inhibiting capacity toward the metals under study at the optimal component concentrations of 1.0–1.5% and 0.1%, respectively (Tables 3, 4). It is known [21] that the protective properties of sodium benzoate become substantially stronger in the presence of oxygen, and, therefore, it is rather probable that, being an oxidizing agent, sodium nitrite exerts a similar influence.

In view of the high protective capacity of the benzoate-borate complex toward nonferrous metals (Table 2) and of the nitrite-borate complex toward aluminum and ferrous metals (Table 1), it was assumed that addition of sodium tetraborate to the benzoate-nitrite system will provide effective protection for all the metals being tested. Indeed, an addition of 0.7% sodium tetraborate to an aqueous-glycolic solution containing a mixture of sodium benzoate and sodium nitrite resulted in an increase in the degree

Table 5. Degree of metal protection in an aqueous-glycolic solution in relation to the inhibitor nature

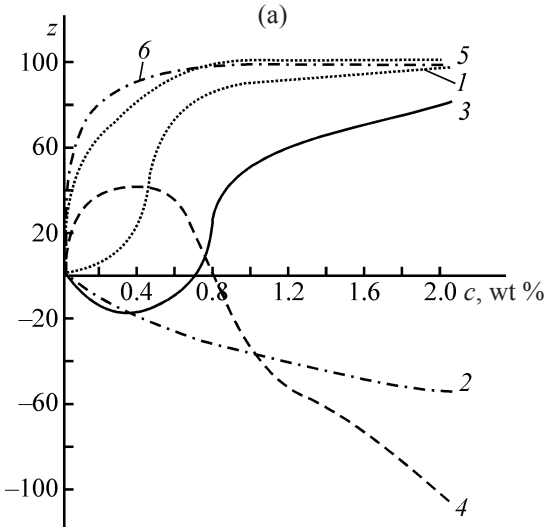
Content of inhibitor, %	Degree of metal protection, %					
	solder	copper	brass	aluminum	steel	cast iron
C_6H_5COONa 1.0, $NaNO_2$ 0.1	63.2	18.8	38.1	11.7	100.0	87.6
C_6H_5COONa 1.0, $NaNO_2$ 0.1, $Na_2B_40_7 \cdot 10H_2O$ 0.7	79.9	5.7	30.0	41.9	100.0	92.5

of protection for all the metals except copper and brass, whose corrosion rates somewhat increase (Table 5).

Inorganic phosphates are widely used as corrosion inhibitors for ferrous metals in water-supply engineering, cooling systems, and power installations [24]. It was found that, at concentrations of 1.0–1.5%, the inhibiting complex $KHPO_4$–K_2HPO_4 provides a reliable anticorrosion protection of solder (z = 97%), steel (z = 100%), cast iron (z = 99.7%), and aluminum (z = 91%). As regards copper and brass, the anticorrosion properties of this inhibitor are not so fully pronounced (Fig. 2b). With disubstituted sodium phosphate dodecahydrate used as corrosion inhibitor, the corrosion behavior of the metals under study is similar to that for aqueous-glycolic solutions of mixtures of mono- and disubstituted potassium acid phosphates. Comparison of the experimental data in Figs. 2b and 3 shows that, at the same concentrations (in terms of substituted phosphate anions), disodium phosphate exhibits a stronger protective effect, compared with a mixture of partial potassium phosphates. This is probably accounted for by the fact that monosubstituted potassium phosphate is a weak inhibitor [24] and, when present in substantial concentrations, it can initiate corrosion because of the acidification of the medium as a result of its hydrolysis.

At concentrations that cannot provide full protection (c d" 0.2%), disubstituted sodium (potassium) phosphates can raise the corrosion rate of ferrous metals. This is probably due to a partial passivation of an electrode, which shifts the electrode potentials in the positive direction [25]. However, this shift is insufficient for bringing the potentials of steel and cast iron outside the of full passivation range, and, therefore, the corrosion rate increases. At sufficient phosphate concentrations, the corrosion terminates (Figs. 2b and 3). An electron diffraction analysis of the composition of protective films formed on the surface of steel in the presence of disodium phosphate demonstrated that these films are composed of a mixture of γ-Fe_2O_3 and $FePO_4 \cdot 2H_2O$ [26].

It has been stated in most of reports devoted to the mechanism of the anticorrosion protection of iron and its



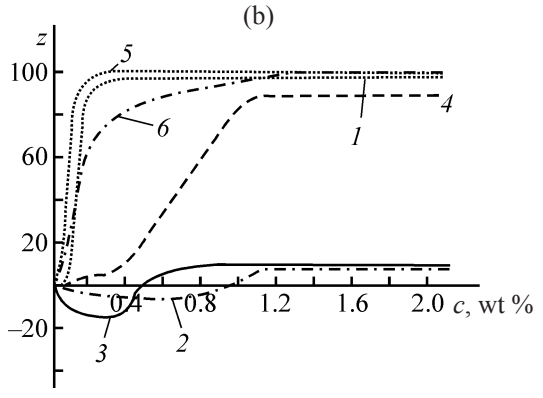


Fig. 2. Effect of the concentration c of (a) sodium benzoate PhCOONa and (b) mixture of partial potassium phosphates KH_2PO_4–K_2HPO_4 on the degree of metal protection, z, in an aqueous solution of ethylene glycol.

Table 6. Corrosion behavior of metals in an aqueous-glycolic solution containing various inhibitors[a]

Corrosion inhibitor	Solder	Copper	Brass	Aluminum	Steel	Cast iron
$Na_2B_4O_7 \cdot 10H_2O$	–	–	++	+++	+	++
Na_2NO_2	–	–	+	–	+++	+++
C_6H_5COONa	+++	–	++	–	+++	+++
KH_2PO_4–K_2HPO_4	+++	+	+	+++	+++	+++
$Na_2HPO_4 \cdot 12H_2O$	+++	+	–	+++	+++	+++
$Na_2B_4O_7$–$10H_2O$–Na_2NO_2	–	–	–	++	+++	+++
$Na_2B_4O_7 \cdot 10H_2O$–C_6H_5COONa	+++	++	++	+++	+++	+++
C_6H_5COONa–$NaNO_2$	++	+	+	+	+++	+++
C_6H_5COONa–$NaNO_2$– $Na_2B_4O_7$	++	+	+	+	+++	+++
KH_2PO_4–K_2HPO_4– $Na_2B_4O_7 \cdot 10H_2O$	–	+	+	+++	+++	+++
C_6H_5COONa–$Na_2HPO_4 \cdot 12H_2O$	+++	+	++	+++	+++	+++

[a] Designations: "–"initiation of corrosion, "+" $z \le 50\%$, "++" $50\% < z < 90\%$, "+++" $z \ge 90\%$.

alloys by phosphates that the phosphate layer is deposited from the electrolyte and the passivating oxide appears via interaction of a metal with oxygen. The role of the phosphate secondarily deposited from the electrolyte consists in lowering the dissolution rate of the oxide layer [27, 28]. Thus, the poorly soluble iron phosphate accumulates on the surface of the metal, which creates favorable conditions for the oxide passivation. Aluminum, solder, and copper and its alloys are probably protected by insoluble phosphates that are formed on their surface and hinder the transfer of metal cation into solution [6]. Joint use of partial sodium (potassium) phosphates with sodium tetraborate initiates corrosion of solder, and their presence in insignificant concentrations (0.05–0.1%) in aqueous-glycolic solutions of sodium benzoate enables an almost full protection of aluminum ($z > 90\%$). The corrosion behavior of the rest of the metals is not noticeably affected by the corrosion inhibitor combinations studied (Table 6).

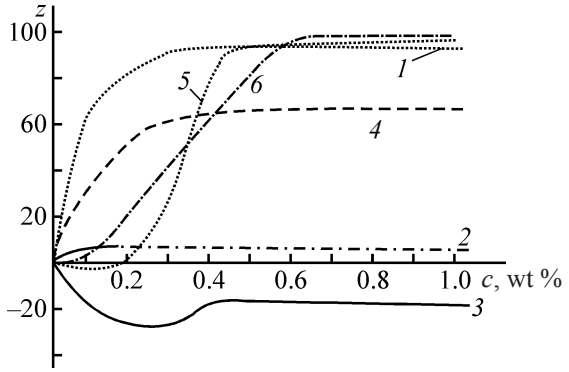


Fig. 3. Effect of the concentration c of disubstituted sodium phosphate $Na_2HPO_4 \cdot 12H_2O$ on the degree of metal protection, *z*, in an aqueous solution of ethylene glycol.

The results obtained in the study of the effect of inhibitors on the corrosion behavior of the metals in aqueous-glycolic solutions are listed in Table 6. It can be clearly seen that, as a rule, the anticorrosion properties of separately taken inhibitors exhibit additivity in their joint use. The exceptions are the benzoate–borate, benzoate–nitrite, and benzoate–nitrite–borate inhibiting complexes, which exhibit a protective effect toward copper, whereas any of their constituents initiates corrosion of this metal. A similar protective effect is exhibited by the benzoate–nitrite complex toward aluminum. By contrast, sodium nitrite and sodium tetraborate exhibit protective properties for brass, but initiate its corrosion when used together (Table 6).

CONCLUSIONS

(1) Results obtained in a study of the corrosion

behavior of metals in the aluminum–steel–cast iron and copper–brass–solder contact systems in aqueous-glycolic solutions with inhibitors, individual substances and inhibiting formulations on their basis, are presented.

(2) It is shown that, as a rule, the anticorrosion properties of separately taken inhibitors exhibit additivity in their joint use.

(3) Compositions of inhibiting formulations providing a good performance in corrosion protection of ferrous and nonferrous metals are suggested.

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