Protective ability of volatile inhibitors of IFKhAN series in atmospheric corrosion of brass and copper at high concentrations of CO_2, NH_3 and H_2S in air

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Abstract

The protective efficacy of volatile inhibitors (VCI) IFKhAN-8 (an amino alcohol), IFHAN-112 (a mixture inhibitor based on benzotriazole), IFKhAN-114 (a non-equimolar mixture of a polyamine and a weak organic acid) and IFKhAN-118 (a dimethyl-benzylamine salt) was studied in atmospheric corrosion of M2 copper (99.7 wt.%) and L62 two-phase brass (22.5 wt.% Zn and 67.7 wt% Cu) in the presence of corrosion stimulators (CS): CO_2 (0.2–0.6 vol.%), NH_3 (20–60 mg/m^3) and H_2S (10–30 mg/m^3), either separately or in combination.

In an uninhibited atmosphere with 0.6 vol.% CO_2 + 60 mg/m^3 NH_3 (three times higher than the normally permissible CS concentrations) with a relative humidity of 100%, corrosion of copper and brass has a pronounced local character. In addition, there is a darkening of a significant fraction of the surface of metals (CuO film). The protective efficiency (Z%) of IFKhAN-112, IFKhAN-114, and IFKhAN-118 in relation to the total corrosion is 75% (brass) and 85% (Cu); 82% (brass) and 79% (Cu) and 89% (brass) and 85% (Cu), respectively. In the atmosphere with CO_2 (0.6 vol.%) + H_2S (30 mg/m^3) or H_2S (30 mg/m^3) + NH_3 (60 mg/m^3) in the presence of IFKhAN-114, Z is 75% (brass, copper). With the other inhibitors being studied in the atmosphere, Z is reduced to 13% or even stimulation of corrosion is observed (CO_2 + H_2S).

In the presence of all the three corrosion stimulators, IFHAN-114 with a protective effect of 96% (brass) and 95% (copper) is again the most effective. This VCI hinders the anodic reaction of ionization of the metals both at the initial stage of exposure in the medium and after 96 hours of exposure. IFHAN-114 inhibits the anodic process in the presence of $(NH_4)_2S$ or $(NH_4)_2CO_3$ salts as reaction products of H_2S or H_2CO_3 with NH_3 in the solution, which occurs in the surface phase film of moisture. At the same time, this

volatile corrosion inhibitor completely prevents local damage to brass and copper under all conditions studied.

Introduction

The high efficiency of a number of volatile metal corrosion inhibitors (VCI) under agricultural production conditions was shown earlier in a number of works [1–3]. This is typical of industrial premises, both in the absence of increased amounts of corrosion simulators – air micro components, *viz.*, CO_2, H_2S and NH_3 [1, 4], in comparison with the background concentration, or where they are present separately [2, 3]. At the same time, VCIs can have a significant negative impact under similar conditions. In particular, the presence of IFKhAN-8 volatile inhibitor causes intense corrosion cracking of brass L62 [3]. Therefore, in each specific case, a complex of studies is required to assess the feasibility of using a particular VCI in the specific atmosphere of agricultural premises.

It should be borne in mind that the presence of not one but two or three corrosion stimulators (CS) in the air is characteristic of agricultural production. This situation can have a significant impact on the protective effectiveness of a VCI. The fact is that the interaction of corrosion stimulators can be non-additive. There are possible synergies between the influence of the CSs, that is, a strengthening of their mutual negative impact, as well as a pronounced antagonism, which undoubtedly can affect the protective ability of a VCI. In addition, the presence of CSs in the surface phase film of moisture responsible for the corrosion of structural materials can lead to their chemical interaction, for example, by the reaction:

$$CO_2 + 2NH_3 + H_2O \rightarrow (NH_4)_2CO_3,$$

which can also affect the kinetics of electrode reactions and corrosion of metals as a whole.

The purpose of this work was to study the effectiveness of a number of volatile corrosion inhibitors of IFKhAN series under the conditions of corrosion of brass and copper in atmospheres simulating the atmosphere in livestock buildings containing two or all three corrosion stimulators simultaneously, at fixed concentrations and relative humidity (H) equal or close to 100%. The content of CSs was equal to the maximum permissible values according to the regulatory documents for cattle-breeding premises [5, 6], or exceeded them threefold.
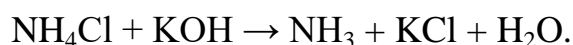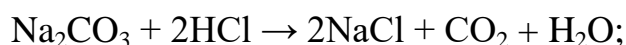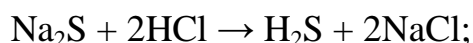
Experimental

Samples of M2 copper (chemical composition, mass%: Al≤0.002; Zn≤0.005; Mn≤0.01; Cr≤0.05; Si≤0.01; Zr≤0.05; Cu 99.7) and two-phase (α + β) brass L62: Zn 22.5, Mn 2.9,

Fe 2.8, Al 4.1, and Cu-rest) with dimensions of $30\times25\times3$ mm, cleaned to 6th class of finish, were used to conduct corrosion tests.

Corrosion inhibitors IFKhAN-8 (an amino alcohol), IFKhAN-112 (a mixture inhibitor based on benzotriazole), IFKhAN-114 (a non-equimolar mixture of a polyamine and a weak organic acid) and IFKhAN-118 (a dimethylbenzylamine salt) developed at A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences (IPCE RAS), were studied as VCIs.

Corrosion tests and polarization measurements were carried out at room temperature in sealed desiccators (basic vessel) 7 liters in volume, in two variants. In the first variant, the atmosphere was saturated with only two corrosion stimulators (CO_2 + NH_3, CO_2 + H_2S or H_2S + NH_3), while in the second variant, all the three CSs were present. The concentrations of CSs are indicated in the text. An additional cell, in which the used VCI (10–15 g) was located, was placed in the basic container. The vessels with dilute solutions in which the reactions of CS synthesis occurred were outside the desiccator, and the atmospheres were saturated with the CSs obtained by means of hoses with overlapping cranes inserted through the hole in the desiccator cover. A special technique was developed that allowed for a specified partial pressure of the CSs in the gas phase and their equilibrium concentrations in the liquid [7], using Henry's law, to accurately calculate the necessary amount of initial substances for the synthesis of CS to create the necessary equilibrium CS concentration in the gas phase. The water solubility of the CSs studied as a function of temperature and partial pressure in the gas phase was borrowed from [8]. The following reactions were used to obtain the SCs in the laboratory:

$$Na_2S + 2HCl \rightarrow H_2S + 2NaCl;$$

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O;$$

$$NH_4Cl + KOH \rightarrow NH_3 + KCl + H_2O.$$

Samples of St3 carbon steel were suspended on nylon threads on special supports in the desiccators. Corrosion products were removed after the experiment with a 10% HCl solution containing additionally 1 g/L KI and 3 g/L hexamethylenetetramine used as a mixed contact inhibitor.

The protective effect of inhibitors was evaluated by the formula:

$$Z = 100[K_0 - K_{\text{Inh}}]/K_0,$$

where K_0 and K_{Inh} are the corrosion rates in the absence and presence of VCIs in the system.

Potentiodynamic measurements with a potential sweep rate of 0.66 mV/s were carried out in a three-electrode electrochemical cell of Pyrex glass with a platinum auxiliary and silver-silver chloride reference electrode using the IPC-Pro MF potentiostat (produced at IPCE RAS) in 0.1 M NaCl solution containing inhibitors and the corresponding salts simulating the presence of the CSs in the atmosphere (an explanation is given below).

All electrochemical measurements were carried out at room temperature. Potentials are given *vs*. the standard hydrogen scale.

Results and discussion

A metallic structural material that corrodes under atmospheric conditions is almost always covered with a surface adsorbed ($H \leq 70\%$) or phase ($80 \leq H \leq 100\%$) moisture film [7], whose thickness in the latter case can reach hundreds of microns. Corrosion stimulators are absorbed by the film. They are partially hydrated and adsorbed on a metal surface in this state or as products of electrolytic dissociation. This leads to a change in the double electrical layer, stimulation of partial electrode reactions and corrosion of metals. Molecules of the active principle of a VCI are first absorbed in such films and then are adsorbed on the corroding surface to inhibit cathodic or anodic reactions, or both simultaneously. In the atmosphere containing 0.6 vol% CO_2 and 60 mg/m^3 NH_3 (hereinafter, unless otherwise specified, the CS concentration is three times higher than the normally permissible one at $H = 100\%$), the overall corrosion rate of brass and copper in the absence of a VCI is 0.010 and 0.014–0.020 g/(m^2·h), respectively. Corrosion has a weakly expressed local character (small rare pits) with darkening of a significant portion of the surface resulting from the formation of a CuO film on it.

The experimental results characterizing the protective efficiency are given in Table 1.

Table 1. The protective effect of VCI (*Z*, %) in atmospheres containing simultaneously two corrosion stimulators. Numerator: a threefold excess of the CS relative to the normative concentration in air, denominator: the CS concentration is equal to the normative one.

Inhibitor	Metal	CS in the air		
		$CO_2 + NH_3$	$CO_2 + H_2S$	$H_2S + NH_3$
IFKhAN-112	Brass	75/–	13/–	75/–
	Copper	85/–	< 0 (S*)/–	10/–
IFKhAN-114	Brass	82/74	75/~100	75/90
	Copper	79/95	75/~100	30/90
IFKhAN-118	Brass	89/–	13/–	84/–
	Copper	85/–	< 0 (S*)/–	30/–

S* – stimulation.

It is easy to see that all the VCIs studied have similar efficiencies under the conditions studied, and the darkening of the metal surface caused by the formation of copper(II) oxide on the surface is practically not observed, nor are traces of local metal damage.

Both corrosion stimulators (CO_2 and H_2S) simultaneously present in the air are acidic. Carbonic acid formed by the reaction:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
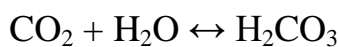
is noticeably stronger than hydrosulphuric acid, which, in principle, should lead to a decrease in the pH of the surface phase moisture film to 5.6–5.8.The darkening of ~25% of the surface is observed on brass after 240 h of exposure in the presence of these CSs in the gas phase simultaneously, but corrosion is uniform. The protective effect was reduced to 13% in the presence of volatile inhibitors IFKhAN-112 and IFKhAN-118, and copper corrosion is generally stimulated. It should be noted that IFKhAN-118 causes a significant deterioration of the state of the surface of brass and copper. In 240 h the entire copper surface becomes dark. Only IFKhAN-114 retains a significantly high protective efficiency with respect to both metals (Table 1). In the atmosphere with H_2S and NH_3 at $H = 100\%$ the picture is almost identical to the previous one in the presence of IFHAN-112, but IFHAN-118 is much more effective in the corrosion of brass (Table 1). Only IFKhAN-114 retains its protective ability in the case of brass corrosion.

Because of the greater versatility of the action of IFKhAN-114, further investigations in the presence of CSs with a concentration in the atmosphere equal to the normally permissible one were carried out only with this inhibitor. A threefold decrease in C_{CS} markedly increases the protective effect of this VCIs (Table 2). Some decrease in the value of Z is observed (for 240 hours of corrosion) only for brass in the presence of CO_2 and NH_3, but even in this case the corrosion rate can be reduced almost 4-fold. The protective effect of the studied VCIs in the presence of all three CSs is shown in Table 2. This is the most likely variant of the influence of corrosion stimulators characteristic of cattle-breeding premises.

Table 2. The protective effect of VCIs in the presence of all three corrosion stimulators simultaneously in the air. Numerator: a threefold excess of the CS concentrations with respect to the permissible values for cattle breeding farms; denominator: the concentrations of the CSs are equal to the permissible values. The duration of corrosion attack is 240 h, $H = 100\%$.

Inhibitor	The protective effect of VCI in the corrosion of:	
	Brass	**Copper**
IFKhAN-112	56/–	90/–
IFKhAN-114	96/60	95/99
IFKhAN-118	44/–	88/–

According to the experimental data obtained, in this case IFKhAN-114 remains the most effective VCI of all the studied ones. Therefore, only its protective effect was evaluated at a CS concentration lowered to the normative value. It was higher than in the presence of the $NH_3 + H_2S$ binary system and comparable with the influence of IFKhAN-114 in the binary systems with $CO_2 + NH_3$ and $CO_2 + H_2S$ corrosion stimulators. As noted above, electrochemical measurements in the presence of IFKhAN-114 were carried out in a

0.1 M NaCl solution. In the first series of experiments, the inhibitor at a given concentration was injected directly into the background solution with the said composition that did not contain any CSs. The measurements were carried out immediately after immersing the electrodes into the solution and after 24, 48, 72 and 98 h of immersion. The corresponding data are shown in Figure 1. The use of different electrode exposure times in the solution allowed us to specify the time of establishment of the stationary state during adsorption of the active principle of the inhibitor. Immediately after immersion of the electrode into the solution, the anodic reaction is significantly inhibited, while the cathodic reaction is accelerated as a result of adsorption of the inhibitor on brass (Figure 1, curves 1 and 2). However, an increase in the value of E_{cor} by 0.050–0.060 V indicates that corrosion of brass is determined by the kinetics of metal ionization. After that, during 24–48 h the anodic process slows down even more (Figure 1, curves 3 and 4). However, this process stops at 72 hours and the rate of anodic ionization increases to reach a value characteristic of the initial stage of the process (Figure 1, curves 4 and 5). This effect can be explained by partial displacement of particles of the active principle of the inhibitor from active surface centers by water molecules. Apparently, the equilibrium with H_2O is achieved much more slowly than with the molecules of the IFKhAN-114 inhibitor or the products of their transformation as a result of adsorption.
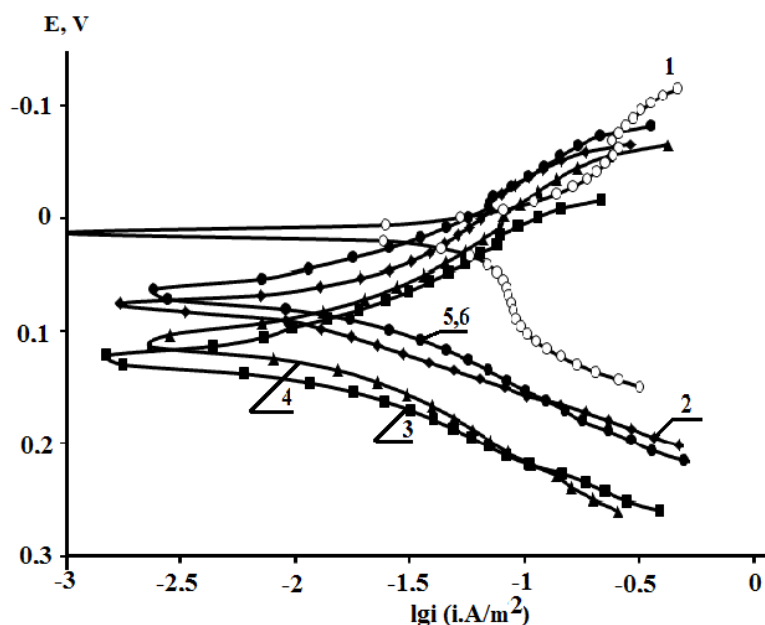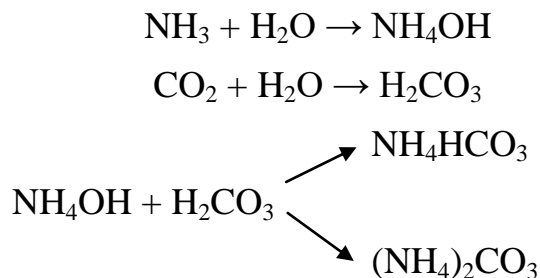

Figure 1. Potentiodynamic polarization curves of L62 brass in 0.1 M NaCl solution in the presence of 100 mg/L IFKhAN-114. Duration of electrode exposure in a corrosive environment, h: 1 – no inhibitor, 2 – 0.20; 3 – 24; 4 – 48; 5 – 72; 6 – 96. Air atmosphere, room temperature, fixed electrode.

In the second series of experiments, polarization measurements were carried out in 0.1 M NaCl solution containing ammonium sulphide or ammonium carbonate. The point is

that in the presence of CS in the liquid phase, whether it is a phase surface moisture film or the bulk of the background solution, the picture can significantly change. Consider this for the situation where H_2S and NH_3 are present in the gas phase as an example. The adsorption of both CSs in the phase surface moisture film to form hydrogen sulphide and ammonium hydroxide is possible in this case. The following processes will occur in the film:

$$NH_3 + H_2S \rightarrow NH_4HS;$$

$$2NH_3 + H_2S \rightarrow (NH_4)_2S.$$
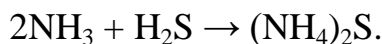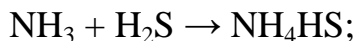
In this connection, it would be necessary to carry out polarization measurements in a solution containing, for example, ammonium sulphide. However, $(NH_4)_2S$ is a salt of a weak base and a weak acid, and it almost completely hydrolyses in solutions into the acid and the base. Therefore, polarization curves were taken in 0.1 M NaCl solution containing ammonia and hydrogen sulfide in concentrations allowing formally to obtain 50 mg/L $(NH_4)_2S$. They were also added at specified concentrations to the background solution along with IFNAN-114 to evaluate the effect of the inhibitor. In turn, ammonia and carbon dioxide adsorbed by the phase film of moisture can enter into reactions to give ammonium carbonates according to the scheme:

$$NH_3 + H_2O \rightarrow NH_4OH$$

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$NH_4OH + H_2CO_3 \begin{array}{c} \nearrow NH_4HCO_3 \\ \searrow (NH_4)_2CO_3 \end{array}$$

Therefore, ammonium carbonate was introduced into the solution, since this salt does exist in solutions [6].

Polarization curves obtained on brass under similar conditions are shown in Figure 2. The presence of ammonium carbonate significantly inhibits the anodic reaction of brass near the corrosion potential at the initial stage of the process (Figure 2a, curves 1 and 2). The presence of the IFKhAN-114 inhibitor enhances this process even more. In both cases, E_{cor} increases by 0.080 and 0.100 V, respectively.

The presence of ammonium sulphide in the form of NH_4OH and H_2S exerts a quantitatively similar action (Figure 2b, curves 1 and 2). IFKhAN-114 acts in a similar way, but in this case its effect is much stronger.

The effect of added salts and IFKhAN-114 in the presence of these salts at the initial stage of copper corrosion is shown in Figure 3. Ammonium carbonate significantly inhibits the anodic reaction at the initial stage of corrosion, as a result of which E_{cor} increases by 0.040–0.050 V (Figure 3a, curves 1 and 2). The presence of IFKhAN-114 reduces the inhibition of copper ionization at the initial stage of the process, but still this reaction remains slower than in the background solution (Fig. 3a, curves 1 and 3).
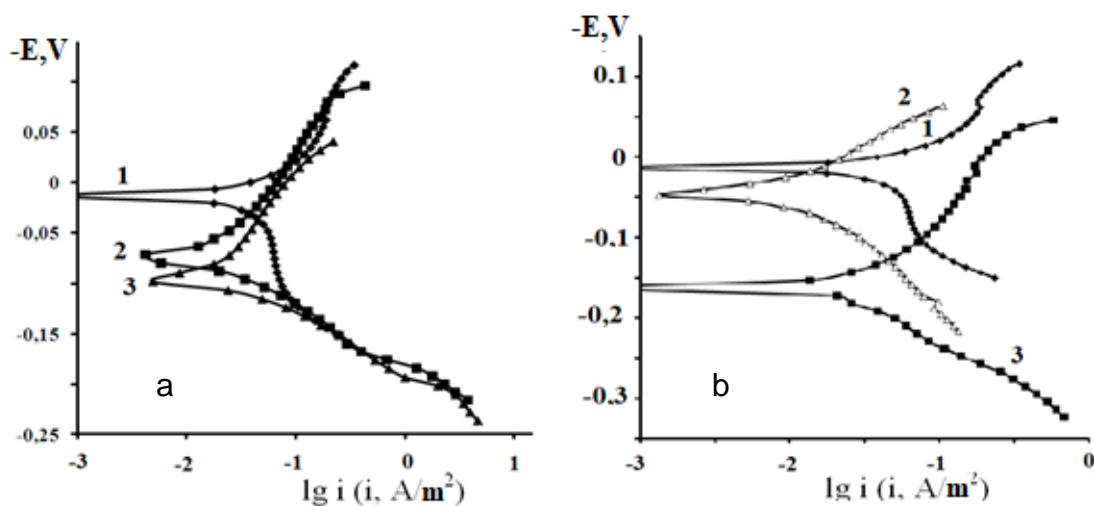
Figure 2. Potentiodynamic polarization curves of brass L62 in a 0.1 M NaCl solution in the absence (1) and in the presence of additives (2, 3): a – carbonate, b – ammonium sulfide (2) and simultaneously 100 mg/L IFKhAN-114 (3). Room temperature, fixed electrode.
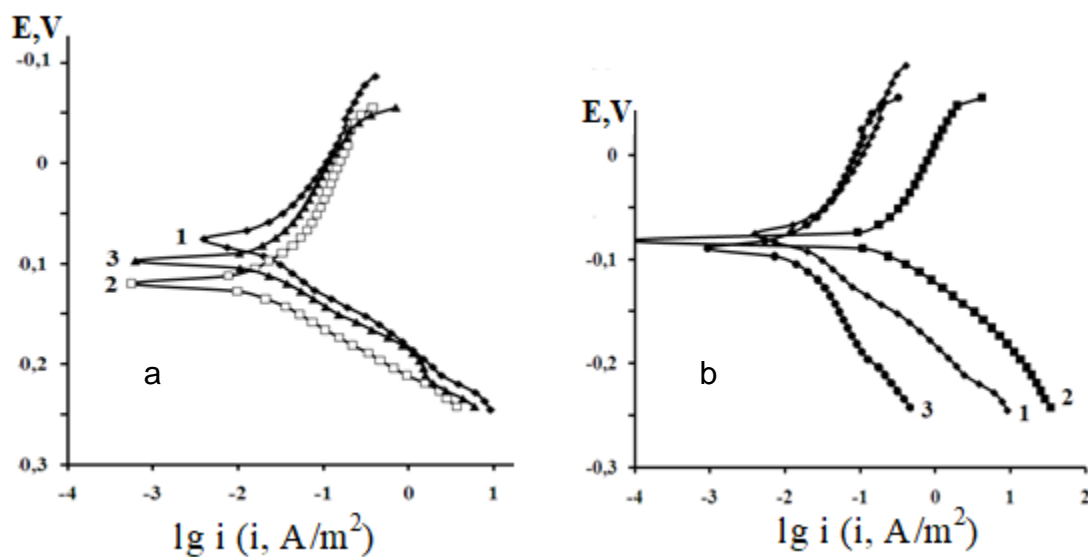
Figure 3. Potentiodynamic polarization curves of M2 copper in a 0.1 M NaCl solution in the absence (1) and in the presence of additives (2, 3): a – ammonium carbonate (2, 3); b – ammonium sulphide (2) and simultaneously 100 mg/L IFKhAN-114 (3). Room temperature, fixed electrode.

Ammonium sulphide stimulates both electrode reactions at the initial stage of the corrosion process, as a result of which the value of E_{cor} practically does not change (Figure 3b, curves 1 and 2). The presence of IFKhAN-114 inhibits the anodic and cathodic reactions even more (Figure 3b, curves 2 and 3). As a result, E_{cor} increases by 0.010–0.015 V.

Conclusion

1. The nature of the medium containing simultaneously two stimulators of corrosion significantly affects the protective ability of VCIs. In fact, the protective ability of all VCIs is between 74 and 95% under the conditions of brass and copper corrosion in the presence of CO_2 and NH_3 simultaneously. Replacing NH_3 with H_2S reduces the protective efficiency of IFKhAN-112 and IFKhAN-118 to 13% (brass) or even leads to stimulation of corrosion (copper). In the presence of NH_3 and H_2S, the protective efficacy of all inhibitors is maintained at 75–84% (brass) or reduced to 10–30% (copper, IFKhAN-112 and IFKhAN-118). IFKhAN-114 in the presence of all binary systems of stimulators retains a high protective ability (at $H = 75-90\%$).
2. In the ternary system $CO_2 + NH_3 + H_2S$, IFKhAN-114 retains a high protective ability in atmospheric corrosion of both brass (96%) and copper (88–99%).

Acknowledgment

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