

## Protection of carbon steel against atmospheric corrosion by volatile inhibitors of IFKhAN series at high concentrations of CO<sub>2</sub>, H<sub>2</sub>S and NH<sub>3</sub>

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### Abstract

The protective efficacy of volatile inhibitors (VCI) of IFKhAN-A series (A-8, 112, 114, 118) against atmospheric corrosion of carbon steel St3 was studied at room temperature in air in the presence of corrosion stimulants (CS) at specified concentrations: CO<sub>2</sub> (0.2–0.6) vol.%, H<sub>2</sub>S (10–30) mg/m<sup>3</sup> and NH<sub>3</sub> (20–60) mg/m<sup>3</sup>. The relative humidity was 100%. Corrosion tests were carried out in sealed containers of 7 liters in volume (desiccators) in two versions. In one version, only one CS was introduced into the air atmosphere. In the other, two or all three used CS were simultaneously injected into the gas phase. To create equilibrium concentrations of the CS in the air atmosphere, a special technique has been developed. The duration of the corrosion tests was 240–528 hours. Potentiodynamic polarization measurements were performed at a potential sweep rate of 0.66 mV/s immediately after immersing the electrodes in the solution and after 24 to 96 hours of their stay in the corrosive medium (*in situ*). In the presence of CO<sub>2</sub> in air atmosphere, the protective efficiency of all the VCIs studied is close to 100%. In the presence of NH<sub>3</sub> (20 mg/m<sup>3</sup>), it is within 74% (IFKhAN-8) to 21% (IFKhAN-118). In the presence of H<sub>2</sub>S, the protective effect of the VCIs increases again, amounting to 93–97%. In uninhibited systems containing simultaneously two stimulants of corrosion, intense pitting is observed. When CO<sub>2</sub> and NH<sub>3</sub> are introduced simultaneously, the protective effect of the investigated VCIs is in the range of 76–87%, with CO<sub>2</sub>+H<sub>2</sub>S it is 81% (A-112 and 118) to 100% (A-114), and with H<sub>2</sub>S+NH<sub>3</sub>, it is 67–85%. The most effective is IFKhAN-114, which not only reduces the corrosion rate, but also eliminates pitting (CO<sub>2</sub>+NH<sub>3</sub>). Introduction of IFKhAN-114 allows one to achieve the protective effect of 95% in the presence of all three CS simultaneously. The corrosion rate of steel in the uninhibited background solution is limited by the cathodic reaction. In the presence of (NH<sub>4</sub>)<sub>2</sub>S as an NH<sub>3</sub> and H<sub>2</sub>S reaction

product, the IFKhan-114 inhibitor effectively inhibits the anodic process. As a result, the corrosion potential of steel is increased by 0.070 V. The protective effect of IFKhan-114 obtained from the data of potentiodynamic measurements in this medium immediately after immersing the electrode in the solution, is about 50%. This is lower than the value calculated from the results of gravimetric measurements, due to the different duration of steel aging in the corrosive environment.

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**Key words:** *steel, corrosion, atmosphere, hydrogen sulphide, carbon dioxide, ammonia, volatile inhibitors, protection.*

## Introduction

According to the data of E.N. Kablov and co-workers [1], direct losses from corrosion amount to a fantastic value of \$ 1.8 trillion. In England and Germany, they annually reach 3% of GDP, amounting to 2–6% of the national income in most developed countries. In the Russian Federation, they reach 12% of the national income. The largest losses are for the fuel and energy complex (29%) and agriculture (20%).

At the same time, in agricultural production, due to a number of objective and subjective reasons, volatile corrosion inhibitors (VCIs) are not used, though their application is very effective and technological. Meanwhile, in the atmosphere of cattle-breeding premises where the relative humidity is 100% or close to this value, a multiple increase in CO<sub>2</sub> content with respect to the background, the presence of up to 10 mg/m<sup>3</sup> H<sub>2</sub>S and up to 20 mg/m<sup>3</sup> NH<sub>3</sub> is allowed [2].

At present, there are no methods for investigating VCIs under such conditions, though they can be widely used to protect the electrical equipment of livestock farms, the most important aggregates of internal combustion engines [3], steam boilers during standby and conservation, for the protection of sensor blocks of alarm systems and in control of production processes. VCIs are effective when introduced into gaps and slots that are inaccessible to contact inhibitors under conditions of storage of aggregates and their spare parts.

The purpose of this work is to study the protective effectiveness of VCIs under conditions of elevated concentrations of CO<sub>2</sub>, H<sub>2</sub>S and NH<sub>3</sub>, separately or together, in the air. The present work is a continuation and development of the concepts characterizing the effectiveness of VCIs under similar conditions, which were originated in our previous studies [4–6].

## Experimental

The following corrosion inhibitors developed at A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of RAS (IPhChE RAS) were studied as VCIs: IFKHAN-8 (an amino alcohol), IFKHAN-112 (mixed inhibitor based on benzotriazole), IFKHAN-114

(a nonequimolar mixture of a polyamine and a weak organic acid), and IFKHAN-118 (a salt of dimethylbenzylamine).

Corrosion tests were carried out in two versions at room temperature in hermetically sealed desiccators (main container) with a volume of 7 liters. In the first version, where the atmosphere was saturated with only one corrosion stimulator ( $\text{CO}_2$ ,  $\text{H}_2\text{S}$  or  $\text{NH}_3$ ), two small auxiliary vessels were placed along with the St3 steel test samples ( $30 \times 15 \times 3$  mm with chemical composition, mass%: C – 0.20, Mn – 0.51, Si – 0.15, P – 0.04, S – 0.05, Cr – 0.32, Ni – 0.21, Cu – 0.23, Fe – 98.29). One of the small vessels contained a VCI being studied (10–15 g), which saturated the gas phase. The other one contained dilute solutions of substances necessary to create in the gas phase the maximum allowable concentrations (MAC) of corrosion stimulators in the air of cattle-breeding premises [2]. In the second variant, where two or three corrosion stimulants (CS) were simultaneously introduced into the air of the desiccator, additional containers with dilute solutions of the initial materials used to prepare the CS were outside the desiccator. Then, the CS obtained was allowed to enter the main tank *via* tubes equipped with shutoff valves and passing through holes in the lid.

To create the necessary equilibrium CS concentration in the gas phase, a special technique has been developed that allows one to reliably calculate the amount of initial substances in solutions based on the specified partial pressure of the CS in the gas phase and their equilibrium concentrations in the liquid, using Henry's law. The solubility of the CS in water as a function of temperature is presented in Table 1 [7].

**Table 1.** Dependence of the solubility criteria of  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  and  $\text{NH}_3$  in water on temperature [7].

Gas	Criteria	Temperature, °C				
		0	10	20	30	40
$\text{H}_2\text{S}$	$\alpha$	4.67	3.90	2.58	2.04	1.66
	$q$	0.707	0.051	0.385	0.298	0.236
$\text{CO}_2$	$\alpha$	1.71	1.19	0.878	0.665	0.530
	$q$	0.335	0.232	0.169	0.125	0.097
$\text{NH}_3$	$\alpha$	1179	857	702	586	–
	$q$	89.5	65.1	53.1	44.0	–

*Note:*  $\alpha$  is the absorption coefficient: the number of gas volumes reduced to 0° C and 760 mmHg, absorbed by 1 volume of water at a partial pressure (gas + water vapor) of 760 mmHg;  $q$  is the mass of gas (g) dissolved in 100 g of  $\text{H}_2\text{O}$  at a total pressure (gas + water vapor) of 760 mmHg.

To obtain the CS in the laboratory, the following reactions were used:



Two series of samples were tested. The duration of corrosion attack on steel was 240 h in the first series and 480–528 h in the second one. Samples of St3 carbon steel were polished to the 6<sup>th</sup> grade and hung up on supports on nylon threads in 8 desiccators. After completion of the experiments, corrosion products were removed with a 10% HCl solution containing 1 g/L KI and 3 g/L hexamethylenetetramine as a mixed contact inhibitor.

The protective effect of the inhibitors ( $Z$ , %) was estimated by the formula:

$$Z, \% = 100(K_0 - K_{\text{Inh}})/K_0$$

where  $K_0$  and  $K_{\text{Inh}}$  are the corrosion rates in the absence and in the presence of the inhibitor, respectively.

Potentiodynamic measurements at a potential sweep rate of 0.66 mV/s were carried out in a three-electrode electrochemical cell made of Pyrex glass with a platinum auxiliary electrode and silver–silver chloride reference electrode using an IPC-Pro MF potentiostat (production of IPhChE RAS) in 0.1 M NaCl solution containing inhibitors and the corresponding salts simulating the presence of CS in the atmosphere. (An explanation is given below.) All electrochemical measurements were carried out at room temperature. Potentials are given *versus* the standard hydrogen scale.

## Results and discussion

In the absence of VCI, the steel corrosion rate ( $K$ ) in the first series of tests (240 h) was 0.64 g/(m<sup>2</sup>·h). Losses of metal within 1 year from 1 m<sup>2</sup> of steel surface in the first case are more than 5.5 kg, in the second – more than 1 kg. Although the formation of a protective solid-phase film in time contributes to the protective action ( $Z$ ) of about 82%, such a situation in livestock premises is unacceptable and requires protection of steel products against corrosion.

The protective effect of inhibitors in the presence of individual corrosion stimulants is shown in Table 2.

**Table 2.** The protective efficiency of VCIs in the presence of corrosion stimulators in the air at  $H = 100\%$ .

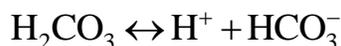
Test duration, h	Z of VCIs, %:								
	IFKhAN-8			IFKhAN-112			IFKhAN-118		
	CO <sub>2</sub> 0.2 vol.%	NH <sub>3</sub> 20 mg/m <sup>3</sup>	H <sub>2</sub> S 10 mg/m <sup>3</sup>	CO <sub>2</sub> 0.2 vol.%	NH <sub>3</sub> 20 mg/m <sup>3</sup>	H <sub>2</sub> S 10 mg/m <sup>3</sup>	CO <sub>2</sub> 0.2 vol.%	NH <sub>3</sub> 20 mg/m <sup>3</sup>	H <sub>2</sub> S 10 mg/m <sup>3</sup>
240	~100	58	94	~100	43	97	~100	43	95
528 (480*)	~100	74	96	~100	61	96	~100	21	93

\* –the medium containing H<sub>2</sub>S.

Thus, all the VCIs studied almost completely suppress corrosion at CO<sub>2</sub> content many times greater than the background atmospheric concentrations (~ 0.003% [8]). We note that, in view of the substantial shift of equilibrium



to the left, the dissolved CO<sub>2</sub> in the aqueous solution is predominantly in the oxide form: out of 296 CO<sub>2</sub> molecules, only one forms carbonic acid [9], which dissociates in the first stage according to the equation

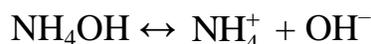
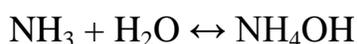


with acidification of aqueous phase to pH ≈ 5.6 [9].

In the presence of hydrogen sulphide at a concentration 1000 times higher than the background one in rural areas (10<sup>-2</sup> mg/m<sup>3</sup> [9]), the protective effect of VCI is also high enough, and hydrogen sulfide in the phase moisture film is almost completely in molecular form. The 1<sup>st</sup> constant of electrolytic dissociation of hydrogen sulphide at 20°C is ~ 9·10<sup>-8</sup> [7].

And only in the presence of ammonia at a concentration exceeding the background one (5·10<sup>-3</sup> mg/m<sup>3</sup> [9]) 4000-fold, the protective effect of inhibitors is sharply reduced and is from 74% (IFKhAN-8) to 21% (IFKhAN-118).

It is of fundamental importance that several equilibria occur in solution as a result of interaction of NH<sub>3</sub> with water [8].



with an effective value of  $K_{\text{diss}} = 1.8 \cdot 10^{-5}$  [7]. They basify the aqueous phase to pH 8.5.

However, usually the air of cattle-breeding premises simultaneously contains several corrosion stimulants studied. The presence of two, and especially three, microcomponents of air can significantly affect the absorption of each of them by the surface phase film of moisture present on the steel, as well as the possibility of formation of solid phase surface films and adsorption of VCIs.

In view of the above, we present experimental data characterizing the protective efficacy of the studied inhibitors when two stimulants of corrosion are simultaneously present in the air. Moreover, we consider both the cases (i) where the CS concentrations are triple with respect to the normally permissible ones, and (ii) where they completely match the admissible values. In all cases, the duration of the corrosion tests was 240 hours (conditionally).

Let us consider the results obtained in the presence of both CO<sub>2</sub> and NH<sub>3</sub>. When their concentrations exceed the normatively admissible values three-fold in the absence of a VCI, the rate of general corrosion of the steel is about 0.01 g/(m<sup>2</sup>·h). Its value is between the  $K_{0i}$  in the presence of NH<sub>3</sub> or CO<sub>2</sub> only:

$$K_{0,\text{CO}_2} > K_{0,\text{CO}_2+\text{NH}_3} > K_{0,\text{NH}_3}$$

Corrosion has a pronounced local character with ulcerous formations on the surface of the metal.

Data on the protective efficacy of all the VCIs studied are shown in Table 3.

**Table 3.** Protective efficiency ( $Z$ , %) of the studied VCIs in relation to the corrosion of steel in the presence of simultaneously two corrosion stimulators in the air. The numerator is  $Z$  for the threefold excess of the maximum permissible concentration of CS in the air, while the denominator is  $Z$  for the CS concentration corresponding to the MPC.

VCI	Z in the presence of CS		
	CO <sub>2</sub> + NH <sub>3</sub>	CO <sub>2</sub> + H <sub>2</sub> S	H <sub>2</sub> S + NH <sub>3</sub>
IFKhAN-112	76/–	81/–	70/–
IFKhAN-114	86/87	94/100	83/85
IFKhAN-118	85/–	81/–	67/–

If there are both CO<sub>2</sub> and NH<sub>3</sub> in the air, IFKhAN-114 is the most effective. In its presence, the corrosion of steel is uniform, without traces of local surface lesions.

If both CO<sub>2</sub> and H<sub>2</sub>S are present simultaneously in the uninhibited gas phase and their concentrations exceed the normatively admissible values three-fold, the rate of general steel corrosion is 0.07 (g/m<sup>2</sup>·h), and the corresponding series is:

$$K_{0,\text{CO}_2} > K_{0,\text{CO}_2+\text{H}_2\text{S}} > K_{0,\text{H}_2\text{S}}$$

An intense local lesion of the metal surface with intense pitting is again observed. The protective effect of VCIs is quite high (Table 3), but in the presence of IFKhAN-118, pitting is observed again. Let us note one more row observed:

$$Z_{\text{CO}_2} > Z_{\text{H}_2\text{S}} > Z_{\text{CO}_2+\text{H}_2\text{S}},$$

where the lower index indicates the nature of corrosion stimulants present in the air. It can be assumed that the protective effect of the “FeCO<sub>3</sub> + FeS<sub>n</sub> + inhibitor” system is lower than that of “FeCO<sub>3</sub> + inhibitor” and “FeS<sub>n</sub> + inhibitor” ones, but it still remains relatively high. Again, IFKhAN-114 is most effective.

If both NH<sub>3</sub> and H<sub>2</sub>S are present simultaneously in the uninhibited gas phase and their concentrations exceed the normatively admissible values three-fold, the rate of general steel corrosion is 0.03 (g/m<sup>2</sup>·h) and pronounced local destruction of metal surface is observed. Consequently, equipment made of carbon steel can not be left without effective protection under similar conditions. The series observed in this case is:

$$K_{0,\text{H}_2\text{S}} > K_{0,\text{H}_2\text{S}+\text{NH}_3} > K_{0,\text{NH}_3}$$

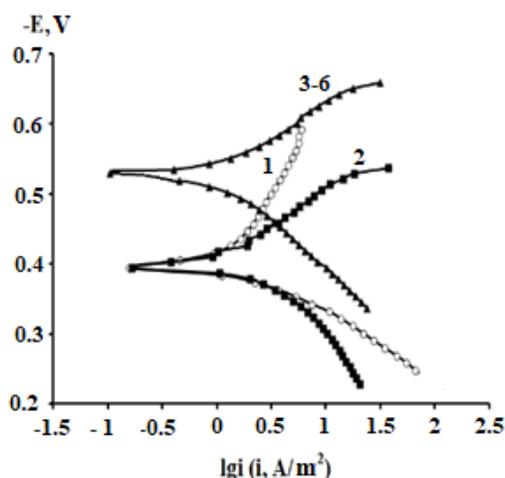
The protective efficacy of the studied VCIs in this atmosphere is shown in Table 3. In the presence of IFKhAN-114, it is the highest, and the  $Z$  of IFKhAN-118 is markedly lower (Table 3).

Due to the fact that IFKhAN-114 is the most effective of inhibitor studied, tests in air environments with a normatively permissible concentration of corrosion stimulators were conducted only with this inhibitor, especially since this VCI possesses the lowest saturated vapor pressure (below  $10^{-3}$  mmHg or  $< 0.133$  Pa). Consequently, it is characterized by the lowest concentration of saturation in the air, which is important for ecological reasons, and the lowest consumption coefficient.

With a decrease in the concentration of corrosion stimulators to the normative value for livestock premises, the protective effect of IFKhAN-114 increases somewhat, and to the greatest extent in the presence of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  (Table 3).

Of undoubted interest is the evaluation of the efficiency of VCI in atmospheres containing simultaneously all three corrosion stimulators. In this case, one could expect both a synergistic (increase in the  $Z$  value) and antagonistic effects. When the micro-components are present in concentrations of 0.6 vol.%  $\text{CO}_2$  + 60 mg/m<sup>3</sup>  $\text{NH}_3$  + 30 mg/m<sup>3</sup>  $\text{H}_2\text{S}$ , the protective effect of IFKhAN-114 is 95%. With a decrease in their content to the normally permissible value, the value of  $Z$  remains practically at the same level.

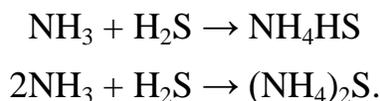
The electrochemical measurements in the presence of IFKhAN-114 were carried out in 0.1 M NaCl solution. In the first series of experiments, the inhibitor at a given concentration was introduced directly into the background solution with the indicated composition without a CS. The measurements were carried out immediately after the electrode was immersed in the solution and *in situ* at 24, 48, 72, and 98 h. The results of similar polarization measurements are shown in Figure 1 with  $C_{\text{IFKhAN-114}} = 50$  mg/L. The polarization curves in the background and inhibited solutions (Figure 1, curves 1 and 2) near the corrosion potential close to  $-0.400$  V practically coincide.



**Figure 1.** Potentiodynamic polarization curves of St3 steel in a 0.1 M NaCl solution in the absence (1) and in the presence of 50 mg/L of IFKhAN-114 (2–6). Duration of exposure of the electrode in the corrosive environments, h: 1, 2 – 0.25; 3 – 24; 4 – 48; 5 – 72; 6 – 98.

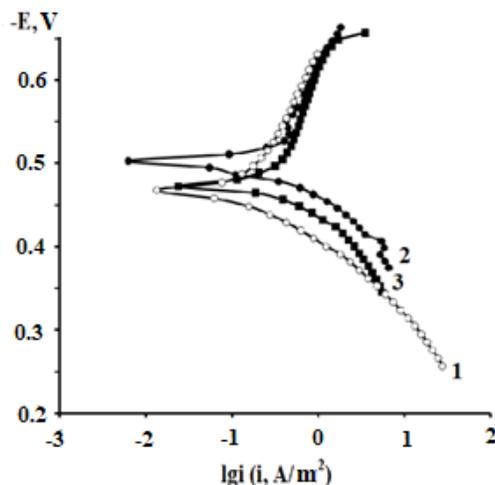
However, after one day in the inhibited media,  $E_{\text{cor}}$  shifts to the cathodic region to  $-0.510 \dots -0.520$  V due to significant inhibition of the cathodic reaction (with simultaneous acceleration of the anodic one). But the first process is obviously the limiting one. Correspondingly, the rate of corrosion decreases somewhat.

In the presence of CS, the picture can change significantly. Let us consider the example where  $\text{H}_2\text{S}$  and  $\text{NH}_3$  are present in the gas phase. In this case, both CS can be absorbed in the phase surface moisture film to form hydrogen sulphide and ammonium hydroxide (ammonia hydrate). In this case, the following processes will occur:



In this connection, it would be necessary to carry out polarization measurements in a solution containing, for example, ammonium sulphide. But this is the salt of a weak base and a weak acid and in solution it practically completely hydrolyses to give the acid and base. Therefore, the polarization curves were measured in a 0.1 M NaCl solution containing ammonia and hydrogen sulfide in concentrations allowing formally to obtain 50 mg/L  $(\text{NH}_4)_2\text{S}$ . To evaluate the action of the inhibitor, it was also injected into a similar solution at the given concentration.

As an example, Figure 2 shows the data obtained in a solution containing 50 mg/L  $(\text{NH}_4)_2\text{S}$  (conditional) and 100 mg/L IFKhAN-114. The presence of  $(\text{NH}_4)_2\text{S}$  in the uninhibited solution decreases the corrosion potential by 0.090 V immediately after immersing the electrode into the liquid phase due to inhibition of the cathodic reaction. At the same time, the corrosion current decreases relatively weakly.



**Figure 2.** Potentiodynamic polarization curves of St3 steel in a 0.1 M NaCl solution in the absence of (1) and in the presence of ammonium sulfide 50 mg/L (2, 3) and 100 mg/L IFKhAN-114 (3).

Addition of IFKhAN-114 inhibitor slows down the anodic reaction Figure 2, curves 2 and 3) and, as a result, increases  $E_{\text{cor}}$  by 0.070 V.

The protective effect of the inhibitor calculated from the data of potentiodynamic polarization measurements immediately after immersing the electrode into the corrosive medium is near 50%. This is noticeably less than the results obtained by gravimetry (Table 3). The difference is due to the fact that the latter data were obtained from 10-day corrosion tests.

## Conclusion

In the presence of  $\text{CO}_2$  at a concentration 6.7 times greater than the background value, the inhibitors studied inhibit the corrosion of carbon steel almost completely.

The presence of  $10 \text{ mg/m}^3$  hydrogen sulfide instead of  $\text{CO}_2$  reduces the protective effect to 93–97%, and it is as low as 21–74% when  $20 \text{ mg/m}^3$  of ammonia is added to the gas phase.

In atmospheres containing simultaneously two corrosion stimulators ( $\text{CO}_2 + \text{NH}_3$  or  $\text{CO}_2 + \text{H}_2\text{S}$ ) at concentrations three times higher than the maximum permissible one for livestock buildings, the values of  $Z$  are 96 and 94% respectively, and it decreases to 83% in the presence of  $\text{H}_2\text{S}$  and  $\text{NH}_3$  simultaneously.

Reducing the concentration of CS under similar conditions three-fold has almost no effect on the protective efficacy of inhibitors, among which IFKhAN-114 possesses the maximum protective ability. Its protective effect in the presence of all three CS is 95% and is due to inhibition of the cathodic reaction rate.

The experimental results were obtained using the equipment of the Center for Collective Use of Scientific Equipment of TSU named after G.R. Derzhavin.

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