EFFECT OF MECHANOACTIVATION ON THE CORROSION INHIBITOR EFFICIENCY OF 1-PHENYL – 1 - CYCLOHEXYLMETHYL – BENZOTRIAZOLE

Reshetnikov S.M[1]., Lubnin A.N[2]., Kanunnikova O.M.[*2], Aksenova V.V.[2], Muhgalin V.V[2]., Solovyev A.A.[3], Altsybeeva A.I.[4], Ladyanov V.I.[2]

[1]Department of fundamental and applied chemistry, Udmurt State University, Izhevsk, 426000, Russia

[2]Department of structure and phase transformations, Physico-technical institute UB RAS, Izhevsk, 426000, Russia

[3] Department of gystology. embryology and cytology, Izhevsk State Medical Academy, Izhevsk, 426000, Russia

[4]Scientific Production Association «Neftechim», St-Petersburg, 190000, Russia

*Corresponding author Email: olam313597@gmail.com/ Tel: +79226814451

ABSTRACT

During ball milling, a decrease in the number of unsaturated bonds and the destruction of the heterocyclic molecule structure of 1-phenyl – 1 - cyclohexylmethyl – benzotriazole are observed. Degradation products are less toxic and exhibit increased inhibitory properties compared to the original inhibit-ROM. In borate buffer the inhibitory properties of the initial and mechano-activated inhibitor appear directly after adding to the corrosive solution. In chloride-sulphate solution inhibitory properties appear a few hours after adding to the solution.

KEY WORDS: inhibitory properties, ball milling, cells, microelectrophoretic mobility, IR - spectra

1. INTRODUCTION

The relevance of the problem of corrosion of metal structures is known and requires no further argumentation. The usage of inhibitors in comparison with other methods of corrosion protection has a number of advantages, chief among which are the following: does not require changes in existing technological processes, it is possible to replace scarce, expensive steels of ordinary carbon. Currently, the inhibitors used practically in all industries: oil and gas, metallurgical, engineering, food, pharmaceutical etc. The operating conditions of pipelines and steel structures are becoming more stringent (conditions of the Far North, the development of offshore oil and gas fields, deep strip, maintenance of structures and pipelines at temperatures above 100°C, in conditions of high pressure and deformations effects). In addition, the important point is the environmental safety of inhibitors and products of their degradation during exploit.

The main problem of most of the corrosion tests is the remoteness of the obtained results from the real performance. Basically, this is due to the fact that are not modeled technical conditions close to practical ones.

In this paper, we have study the stability of the inhibitor on the basis of cyclohexylamine – benzotriazole in conditions close to real operating conditions. To simulate operating conditions, the inhibitor was subjected to mechanical activation in a planetary ball mill. During mechanoactivation the sample is exposed to deformation and thermal effects, which may change the crystal structure and chemical composition of the sample. You need to find out firstly, how these impacts will affect the inhibitory properties, and, secondly, whether there will be toxic substances.

2. EXPERIMENTAL

The object of the study was 1 - phenyl – 1 - cyclohexylmethyl – benzotriazole, which was synthesized in SPA “Neftechim”.

Mechanoactivation was carried out in a ball planetary mill AGO-2. The speed of rotation of the drum of the mill was 600 rpm, the power density of the mill was 2 kJ/g. During ball milling, the sample is subjected to deformation effects, which are accompanied by heating.

The structure of the samples of the inhibitors was investigated by x-ray diffraction on a D8 Advance spectrometer (Bruker AXS) the geometry of the parallel beam of the CuKα. Mirror Goebel 2nd generation (PGM2) in the primary beam, horizontal Soller slit of 0.12 deg and Si(Li) detector in the secondary one. The survey was conducted by the method of variable scanning speeds (VCT) in the embodiment Shankland: the exposure time was increased with increasing angle 2θ. The chemical state of the samples was analyzed by optical spectroscopy (IR and UV range). IR spectra were obtained on IR Fourier spectrometer FSM 1202 (St-Petersburg) with a resolution of 1 cm^{-1} and averaged over 16 scans. Aqueous solutions were investigated by attachment of multiple frustrated total internal reflection (multiple ATR unit). To obtain IR transmission spectra of the powders were compacted with KBr in the ratio 1:250. UV spectra were obtained on a dual beam spectrophotometer Lambda 650 (Perkin Elmer). Electronic spectra of aqueous solutions were recorded in a quartz cell with a thickness of 10 mm at room temperature. The measurements were performed relative to distilled water.

Study of corrosion rate was carried out by indirect measurement of the corrosion resistance using the corrosion MONICOR-1. As corrosive of the material of the selected iron-armco, steel 20 (C 0.17-0.24 %, Si 0.17-0.37%, Mn 0.35-0.65 %; Cu and Ni is not more than 0.25%, As not more than 0.08%, S not more than 0.04%, P 0.035%) and steel 40 (C 0.37-0.45 %, Si 0.17-0.37%, Mn 0.5-0.8 %; Cu and Ni is not more than 0.3%, As not more than 0.08%, S not more than 0.04%, P not more than 0.035%, Cr 0.25%). The corrosion rate in borate buffer solution (17 g $Na_2B_4O_7$ + 75 g H_3BO_3 in 1 liter of water, pH 6.6) and in solution simulating atmospheric corrosion (30 mg NaCl+ 70 mg Na_2SO_4 per liter, pH = 6.0). The corrosion rate of metal specimens in corrosive environments without inhibitor taken as 1.

Potentiometric polarization curves were obtained in potentiostat "PI-50-1.1" with a numeric prefix "E14-140 Lcard". Before recording the electrode was polarized for 500 s at -0.7 V. the scanning Speed of the potential of 1mV/c.

The degree of inhibitory protection was calculated for the potential of -0.45 mV according to the formula:

$$Z = (i_f - i_{ing}) / i_f$$

where i_f the corrosion current in a corrosive medium without inhibitor; i_{ing} – current corrosion in a corrosive environment with the addition of the inhibitor (0.4 g/l in the ethanol-butanol mixture).

The efficiency of inhibitor was calculated for the potential of -0.45 mV according to the formula:

$$\gamma = i_f / i_{ing}.$$

The toxicity of samples of inhibitor was studied by microelectrophoresis in vivo study of the interaction of solutions of substances with buccal cells (epithelial cells). The essence of the method of microelectrophoresis is to measure the amplitude of the oscillations of cells in field of view of the microscope. In the electrophoretic cell, the cells are forced to commit reciprocating motion while changing the sign of the voltage on the electrodes (10 V, with a frequency of 0.1 Hz). The oscillation frequency of the cells is equal to the frequency of changing the signs on the electrodes, but the amplitude may be different depending on charge of the cell surface, which is an indicator of the physiological state of the cell. The study was conducted by using a complex "Citoexpert".

3. RESULTS AND DISCUSSION

3.1. The structure of ball milling inhibitor

Main physico-chemical and adsorption properties of the inhibitor are examined in detail in earlier works (Altsybeeva et al., 2006; Altsybeeva et al., 2011). The melting point of the inhibitor 144ºC, water solubility 0.5 g/100 g H_2O. The pH of a 0.3% aqueous-alcoholic solution of 9.05. The degree of protonation (ratio of the concentrations of [RNH_3^+/ RNH_2]) is equal to -3.9, i.e. the responsible form for the adsorption and inhibition in aqueous solution is not protonated form, but the original molecule. Adsorption centers are heteroatoms (nitrogen and oxygen).

The activation does not change the type of crystalline lattice of the inhibitor, as evidenced by the preservation of the set of diffraction peaks. Changes on x-ray diffraction patterns are associated with a decrease in the size of crystallites and growth of microscopic strains.

Ball milled powder inhibitor 1-phenyl – 1 - cyclohexylmethyl – benzotriazole does not change the structure of chemical bonds up to 18h of treatment, as evidenced by the IR spectra of powders of the inhibitor (Fig.1).

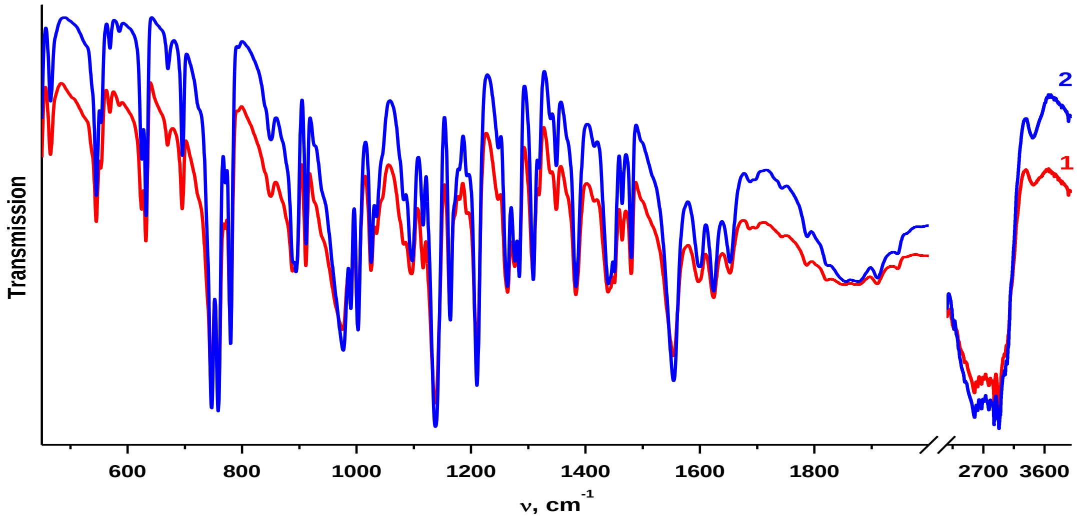


Fig.1: IR spectra of initial (1) and ball milled (18h) 1 - phenyl – 1 - cyclohexylmethyl – benzotriazole powders (2).

If 1 - phenyl – 1 - cyclohexylmethyl – benzotriazole aqueous solutions are exposed to ball milling the connection structure changes after 15 min of mechanoactivation (Fig.2). The absorption at ~190-200 nm refers to the n→π* transitions in the limiting cyclic and acyclic heterocycles. Containing one or more heteroatoms with unshared electron pairs. Unsaturated five-membered heterocycles have two absorption bands, intense in the visible region (200-210 nm) and low-intensity in the longer-wavelength region. Compounds containing a benzene ring conjugated with five-membered heterocyclic rings, also have in the spectrum two absorption bands with vibrational structure. In addition, the spectral range 240-300 nm transitions in monogamistic benzenes are possible π→π*in the spectral range. Batochromic shift of the absorption is associated not only with substitution on the benzene ring, but with the use of polar solvent (water).

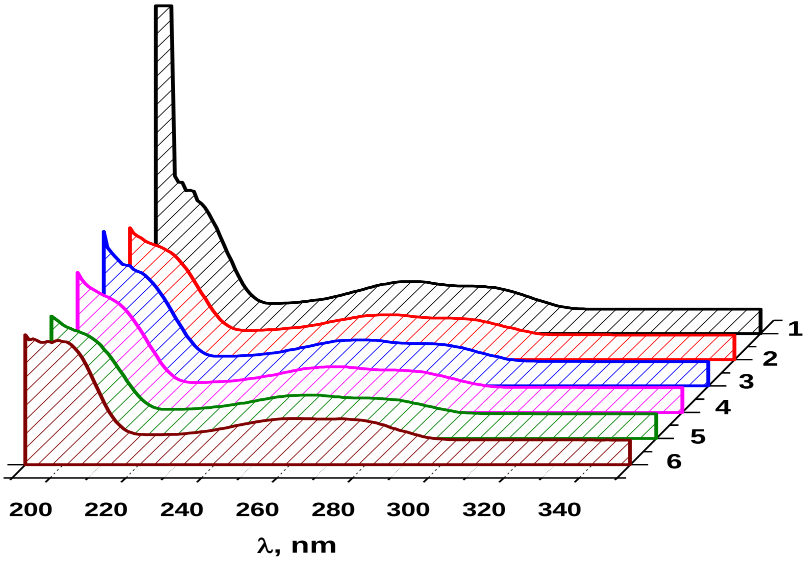


Fig.2: UV spectra of ball milled water solutions (0.5%) of initial inhibitor (1) and after ball milling during 15 min (2), 30 min (3); 1h (4); 1.5h (5) and water solution of inhibitor after 18 h ball milling.

Molecule 1 - phenyl – 1 - cyclohexylmethyl – benzotriazole consists of cyclohexylamine and of benzotriazole, so that the UV-absorption spectrum of the initial sample has two absorption maximum: at 200-220 nm and 240-300 nm typical for aromatic compounds. The wide peak at 240 to 300 nm without distinct extrema may indicate the presence of a number of substances with conjugated aromatic structures. As the result of ball milling transitions in the aromatic structures are stored, and the electronic transition at ~190 nm is the only feature of the original sample. The UV-spectrum of the solution of 18 h ball milled powder (Fig.2, spectrum 6), similar to the spectra of the ball milled solutions (Fig.2, spectra 1-5).

Fig.3 shows the IR spectra of aqueous solutions of corrosion inhibitor after subtraction of the spectrum of distilled water and smoothing using a Gaussian for 25 points.

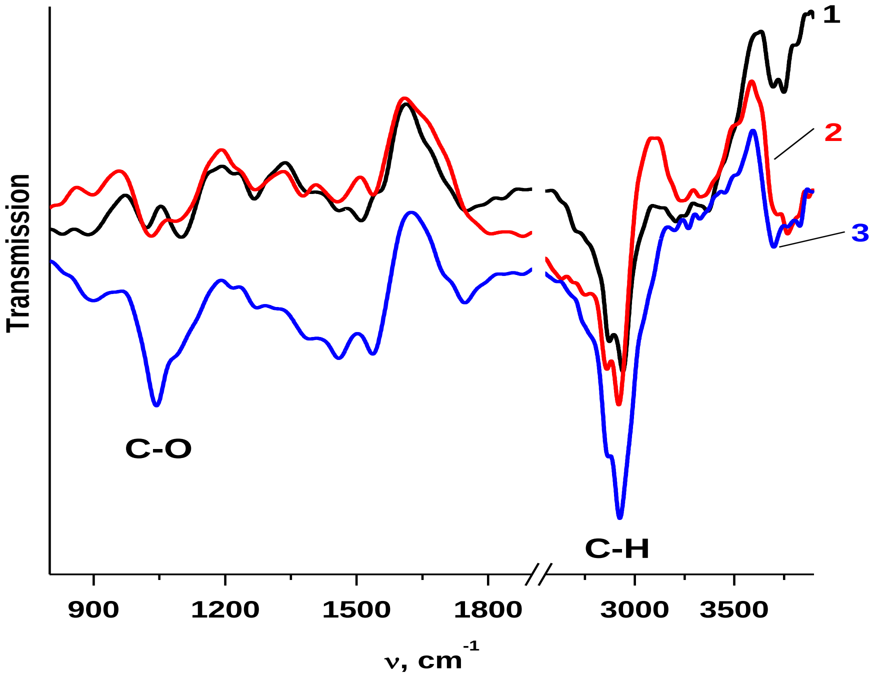


Fig.3: IR spectra of water solutions (0.5%) of inhibitor (1- initial, 2 – 30 min of ball milling, 3 – 1h of ball milling)

Changes in the absorption region of 1000-1100 cm^{-1} corresponding to vibrations of single bond C-O, are observed already after 30 min ball milling. For a more detailed study of inhibitor structural transformations character during ball milling further investigations are necessary.

In the XPS C1s spectrum of the source model contains components from carbon in the composition of the adsorbed layer ($(CH_2)_n$ E_b = 285.0 eV) and carbon associated with oxygen and nitrogen (C-O and C =N groups with the E_b = 286.0 eV and E_b =287.0 eV, respectively). Low-intensity C1s peak in the region 291.0 – 292.0 eV indicates the presence of aromatic ring in the molecule of the inhibitor. Component of the O1s spectrum with a binding energy 535.5 eV correspond to the oxygen atoms in the composition of the adsorbed layer, the component with a binding energy of 533.5 eV – to oxygen atoms in the C-O groups. In the N1s spectrum there are components from the nitrogen atoms of an aromatic heterocycle (399.0 eV), in groups of N-N=C and CH_2-N=CH_2 (400.5 eV) and adsorbed layer (402.0 eV). After ball milling the number of nitrogen atoms in the heterocycle decrease in 2 times and the number of nitrogen atoms in the group N-N=C and CH_2-N=CH_2 increases.

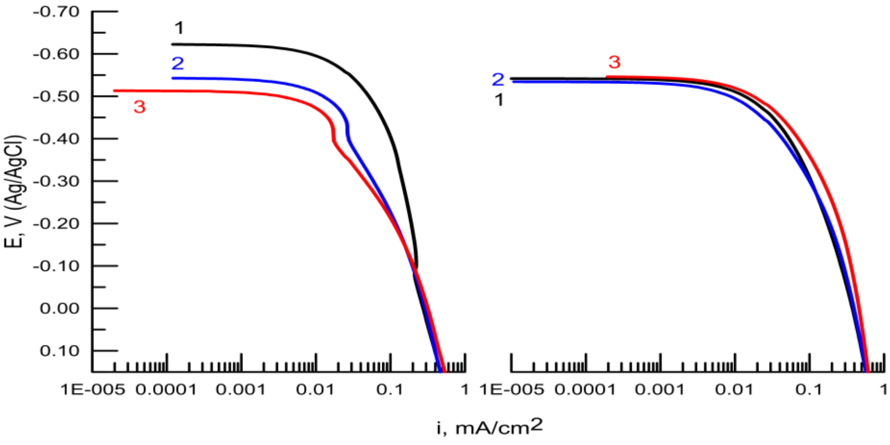
Thus, we can conclude that ball milling leads to a decrease in the number of heterocycles from unsaturated bonds.

The observed transformations take place, apparently in the thin surface layers of powder particles of the inhibitor. Therefore, they are observed only in XPS spectra, which give contribution in thin surface layers and not observed in the IR spectra and x-ray diffraction pattern.

3.2. Corrosion tests

Potentiometric curves obtained in borate buffer are shown in fig.4. The effectiveness of the inhibitor in borate buffer (at -0.45 mV) are 64% and 81% for the source and ball milled inhibitor, respectively. Inhibitor protection degrees are 2.8 and 5.1 for the initial and ball milled inhibitor, respectively.

In Fig.4 shows potentiometric curves obtained in chloride-sulphate solution with pH=5.8. It is seen that in the solution of 1 - phenyl – 1 - cyclohexylmethyl – benzotriazole, and products of its destruction do not have inhibitory activities in electrochemical corrosion.



a **b**

Fig.4: Potentiometric polarization curve of iron in borate buffer solution (a) and chloride sulfate solution (b): 1 – initial inhibitor, 2 – 1h of ball milling; 3 – 18h of ball milling).

The introduction of inhibitor to corrosive medium reduces the corrosion rate of metals in 2 times. The greatest effect was observed for corrosion of pure iron in borate buffer. Local corrosion damages on the surface of iron and steel were observed.

TABLE 1: The corrosion rate of iron (Fe), steel 20 (St20) and 40 steel (St40) in borate buffer and chloride sulfate solutions measured on a MONICOR

Corrosion solution		Corrosion rate		
		Fe	St 20	St 40
borate buffer solution	without inhibitor	1	1	1
	with initial inhibitor (0.5%)	0.52	0.52	0.52
	ball milled (18h) inhibitor (0.5%)	0.32	0.42	0.40
chloride sulfate solution	without inhibitor	1	1	1
	with initial inhibitor (0.5%)	0.54	0.54	0.54
	ball milled (18h) inhibitor (0.5%)	0.44	0.44	0.40

Different effect of an inhibitor in chloride-sulphate solution in the electrochemical studies and from studies on a MONICOR due to the different duration of the experiment: 0.5 h during the electrochemical measurements and 3 h during measurements on a MONICOR. During the electrochemical tests, the adsorption of Cl^- ions and SO_4^{2-} , which activate the process of corrosion of metals, prevails over the processes of inhibition of corrosion in presence of inhibitor. The reason, apparently, is the different rate of adsorption of ions and molecules of the inhibitor. During long trials the action of the inhibitor is manifested. Apparently, the binding energy of adsorbed molecules of the inhibitor is large enough to form a stable protective layer on the surface of metals.

3.3. Microelectrophoretic mobility of epithelial cells

The solution of the original inhibitor led to a complete blocking of the bioelectrical activity of living cells, and leukocytes. In the solution of the ball milled samples (if the ratio "blood : concentrated solution of the substance" is equal to 1:1) bioelectrical activity of erythrocytes and leukocytes remained.

TABLE 2: Microelectrophoretic mobility of epithelial cells in solutions of the inhibitor

Time of ball milling, h	Fraction of active cells, %	Oscillation amplitude of cells, μm	Oscillation amplitude of cells nuclei, μm
0	28.7 ± 1.1	1.3±0.2	0
1	37.7 ± 1.2	1.2 ± 0.2	0
2	62.0 ± 2.0	2.3± 0.5	0
18	72.5 ± 2.2	4.5 ± 0.7	2.6± 0.2

4. CONCLUSION

Ball milling of 1-phenyl – 1 - cyclohexylmethyl – benzotriazole powder, simulating conditions of operation of the inhibitor (deformation effects and high temperatures), leads to a decrease in the number of unsaturated bonds of nitrogen-containing heterocycle and the destruction of the heterocycle. Inhibitory properties of ball milled 1-phenyl – 1 - cyclohexylmethyl – benzotriazole are improved compared to the original substance. With the destruction of the inhibitor molecules probably "fragments" of a radical type possessing high reactivity are formed. According to (Reshetnikov, 1986; Pletnev et al., 1990; Reshetnikov et al., 1991; Pletnev, 1993; Shirobokov et al., 1994; Pletnev et al., 1995) such fragments are well adsorbed on the surface of metals and exhibit a higher inhibiting properties than the original molecule inhibitors. Upon dissolution of the inhibitor fragments interact with water to form groups C-O which also contribute to the inhibitory properties of the solution.

In borate buffer solution the inhibiting properties of 1-phenyl – 1 - cyclohexylmethyl – benzotriazole appear immediately after the introduction of the inhibitor in a corrosive environment. In chloride-sulfate environment, the corrosion inhibiting properties of 1-phenyl – 1 - cyclohexylmethyl – benzotriazole, and products of its destruction are manifested in some hours after making the solution.

The toxic properties of the original inhibitor are expressed to a greater degree than the mechanically activated samples. The decrease in the number of unsaturated bonds and the destruction of the heterocyclic structure of the molecule of inhibitor during mechanical activation lead to the fact that degradation products have a more beneficial effect on living cells than the original inhibitor.

This work was supported by RFBR p-a № 16-42-180814.

References

Altsybeeva A. I., Burlov V. V., Kosinova T. M., Palatic G. F., Reshetnikov S. M., 2006. *Behaviors aminoimidazole corrosion inhibitors in water-hydrocarbon environments*. Corrosion: materials, protection, №1, p.25 – 30 (in Russian).

Altsybeeva I. A., Burlov V. V., Fedorova N. S., Reshetnikov, S. M., 2011. *Volatile inhibitory of atmospheric corrosion of ferrous and nonferrous metals. Part 5. The study of adsorption inhibi-*

tion on steel in aqueous electrolyte solution. Corrosion: materials, protection, № 4, p.33 – 38 (in Russian).

Pletnev M. A., Reshetnikov S. M., Ternavtsev I. V. etc., 1990. *Peculiarity of inhibitory actions of quaternary ammonium salts, phosphonium and arsonia during corrosion of iron in sulfur acid*. Protection of metals, vol.26, № 1, p.144-147 (in Russian).

Pletnev M.A., Shirobokov I.B., Butorina O.V., Reshetnikov S.M., 1993. *Influence of tetraalkylammonievyh salts on the conductivity of acidic bromidic solutions*. Electrochemistry, vol.29, p.1137 (in Russian).

Pletnev M. A., Shirobokov I. B., Ovechkin O. E., Reshetnikov S. M., 1995. *Influence of salts tetraalkylammonium on the cathodic evolution of hydrogen in concentrated acidic bromiden solutions.* Protection of metals, vol.31, №4, p.351-355 (in Russian).

Reshetnikov S. M., 1986. *Inhibitors of acid corrosion of metals*. L.: Chemistry, 144 p. (in Russian).

Reshetnikov S. M., Pletnev M. A., Makarova L. L., 1991. *Peculiarities of the influence of quaternary ammonium salts on the anodic dissolution of iron in hydrochloric acid*. The double layer and adsorption on solid electrodes, Tartu, p.152-154 (in Russian).

Shirobokov I.B., T. A. Korepanova, Pletnev, M. A., Reshetnikov S. M., 1994. *Influence of inorganic and organic cations on the conductivity of acidic bromidic solutions*. Protection of metals, vol.30, № 6, p.620-623 (in Russian).