



CORROSION INHIBITORS CLASSIFICATION. A REVIEW

Quvonchbek Haydarov

Faculty of Industrial Viticulture and Food Production Technology,
Shahrisabz branch of Tashkent Institute of Chemical Technology,
Shahrisabz 181306, Uzbekistan
e-mail address: haydarovquvonchbek7@gmail.com

Tilavov Husan Shomurodovich

Faculty of Industrial Viticulture and Food Production Technology,
Shahrisabz branch of Tashkent Institute of Chemical Technology,
Shahrisabz 181306, Uzbekistan
e-mail address: husan.tilavov86@gmail.com
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ABSTRACT

Corrosion inhibitors are essential chemical substances used to prevent or reduce the corrosion of metals and alloys in various environments. This review categorizes corrosion inhibitors based on their chemical composition, mechanism of action, and application areas. The primary classifications include anodic, cathodic, and mixed inhibitors, each serving different functions in mitigating corrosion processes. Additionally, the review highlights the importance of environmentally friendly inhibitors, addressing the growing concern over the ecological impact of traditional methods. By examining recent advancements and trends in corrosion inhibitor research, this paper aims to provide a comprehensive understanding of their effectiveness, selection criteria, and future prospects in industrial applications. This review serves as a valuable resource for researchers and practitioners seeking to enhance the durability and longevity of metallic materials through effective corrosion management strategies.

Introduction Corrosion processes are mainly problem in the chemical industries such as gas and oil pipelines, petrochemical processes, water cycling systems and so on. Corrosion is responsible for destruction of metal constructors which are the significant part of chemical industries so it is the danger as an economically and natural also hazardously. For example, according to world corrosion organization said that the annual cost of corrosion worldwide is over 3% of world's GDP, approximately US\$2.2 trillion. In order to stop or lessen the corrosion of metals and alloys in a variety of settings, corrosion inhibitors are necessary chemicals. The chemical makeup, mode of action, and application domains of corrosion inhibitors are the basis for this review's classification. The three main categories—anodic, cathodic, and mixed inhibitors—each have distinct roles in reducing corrosion processes. In response to the growing concern over the ecological impact of conventional procedures, the review also emphasizes the significance of environmentally friendly inhibitors. Through an analysis of

current developments and patterns in corrosion inhibitor research, this paper seeks to offer a thorough grasp of corrosion inhibitors' efficacy, selection standards, and potential future uses in industrial settings. This review is an invaluable tool for scientists and professionals looking to improve the robustness and longevity of metallic materials by. However many governments and companies pay little attention to corrosion high risk-areas like aircraft and pipelines. Toxic chemicals from corrosion processes damage the air and water; as a result they kill many species and impact poison point on human body [1].

At the modern times metallic materials have biggest role as a great part of construction material elements in the chemical industries, agricultural equipment, oil, gas and petrochemical factories, medical services, metallurgy and machinery industries and civil services. In these industries, the metallic material's corrosion problems cause their environment loses its integrity over a period of time. Some of these environments are atmosphere, aqueous solution, solids, acids and bases, inorganic solvents, molten salts, liquid metals, human body etc. At times, the effect of the loss in integrity may be very severe as to result in loss of valuable production time, accident and in the extreme death. The cost associated with the problem is enormous and its influence in the economy life of a nation is significant [2].

Many scientists suggest many combating ways that are effective, economically beneficial, non-toxic and environmentally friendly. Around the world many companies suggest their products as an anti-corrosion inhibitors because the using inhibitors are the best ways in fight with corrosion. The chemical inhibitors decrease the degree of corrosion processes by many ways. The corrosion inhibitor is the chemical compound that, at addition in corrosion system at it's small concentration has absorbed on surface of metal and has connected with metal ions. Afterwards they decrease the corrosion rate. Inhibitors can react with a metallic surface or the environment, gives protection film which are metallic oxide, anodic film, thin film, chemical complex with metal ions, supramolecular substance or absorbs ion film on metal surface due to there several reasons, firstly if inhibitor has electron donor groups then chemical bonds is reason for adsorption, secondly if inhibitor has plus or minus charge then it connected with metal surface by an electrostatic impact, thirdly if it is no organic the protective metal oxide is essential role on anti-corrosion cycles [4].

Best inhibitors required several parameters such as (a) can be easily synthesized from cheap, commercially available materials, (b) exhibit high inhibition efficiency even at very low concentrations, (c) are highly soluble in acid medium, (d) non-toxic and biodegradable corrosion inhibitors, and (f) have donor groups such as nitrogen and oxygen, that they have more p-delocalization electrons which improve their chemical and physical adsorption on metals. In addition to polar functional groups (such as CO, NH, OH), multiple bonds (double bonds) and extensive conjugation in the form of no-aromatic rings can promote absorption of these inhibitors on metal surfaces.

Practically the mechanism of inhibition is is consisted from following stages:

- a) the inhibitor chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film or by combination between inhibitor ions and metallic surface; the inhibitor leads a formation of a film by oxide protection of the base metal;
- b) the inhibitor reacts with a potential corrosive components present in aqueous media with formation of complexes.

Methods. Corrosion inhibitors are classified with the depending on the metal construction and the environment type. On the fig.1. classification of inhibitors are presented. They divided on the environmental conditioners and interface inhibitors [5].

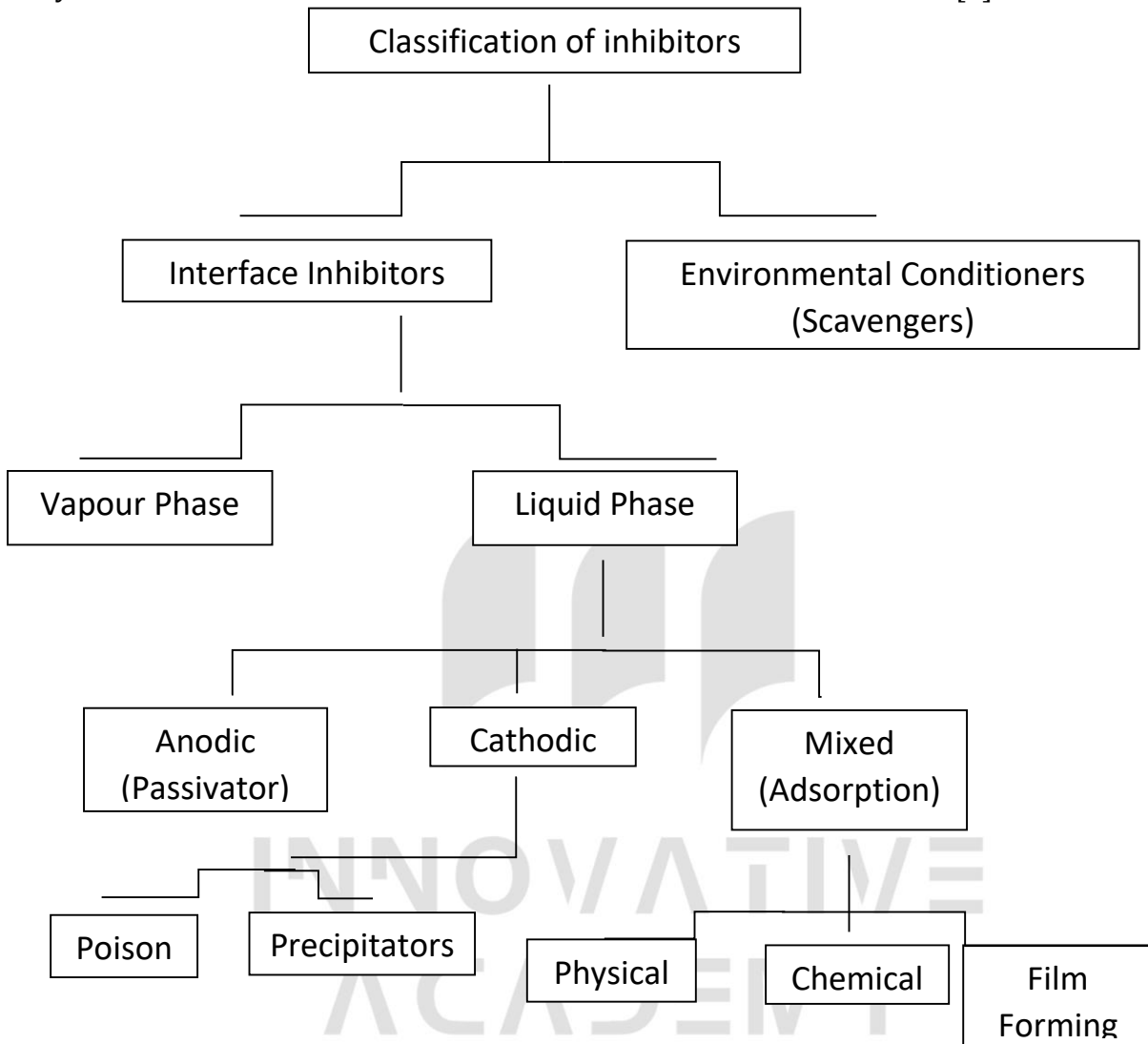
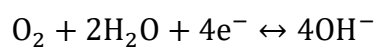


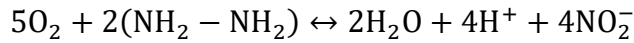
Fig. 1. Classification of corrosion inhibitors.

Environmental conditioners (Scavengers). Corrosion can be controlled by removing the corrosive species in the medium. Inhibitors that decrease corrosiveness of the medium by scavenging the aggressive substances are called environmental conditioners or scavengers. In such situations corrosion can be controlled by decreasing the oxygen content using scavengers (e.g., hydrazine) [10].

The mechanism of environmental conditioners (Scavengers) inhibition. In a near-neutral medium oxygen has absorbed on the metal surface and the cathodic reaction has carried out:



Environmental conditioners (Scavengers) can reduce the amount of oxygen by it is chemical bonding, for example hydrazine containing NH_2 functional groups can connect oxygen molecules according to following equation:



Interface inhibitors. Interface inhibitors control corrosion by forming a films on the metal/environment interface. Interface inhibitors can be classified into liquid- and vapor-phase inhibitors.

Liquid-phase inhibitors. Liquid-phase inhibitors are classified as anodic, cathodic or mixed inhibitors depending on whether they inhibit the anodic, cathodic, or both electrochemical reactions.

Anodic inhibitors. Chemical industries use anodic type inhibitors in near-neutral medium because there are small quantities of corrosion products: oxides, hydroxides or salts. The anodic type inhibitors can impact on a metal surface by passivating films so they called passivators. This forming passivating films can inhibit the anodic metal dissolution reaction in corrosion medium. Anodic type inhibitors connect with metal ions and metal ionic complex thus they passivate anodic reaction in corrosion medium. The inhibition processes depend on an anodic inhibitor concentration, if it is not sufficient they can not protect metal from corrosion, corrosion may be increased. If anodic inhibitor's concentration is above the critical concentration then they are effective and their effectiveness depends on the nature and concentration of the aggressive ions [6].

The mechanism of anodic inhibition. On fig. 2 in presented the polarization diagram of anodic inhibition mechanism. In the absence of inhibitors, the metal corrodes in active state, the amount of corrosion products amount growth, the potential amount goes down to the negative area, also the corrosion current increase, this information is illustrated by on area on this figure. As the concentration of inhibitor is increased, the corrosion rate increased until a critical concentration (point B, Fig. 2). At the critical concentration of inhibitor, there is a rapid transition from the metal to the passive state and the corrosion rate is decreased to minimum (point C).

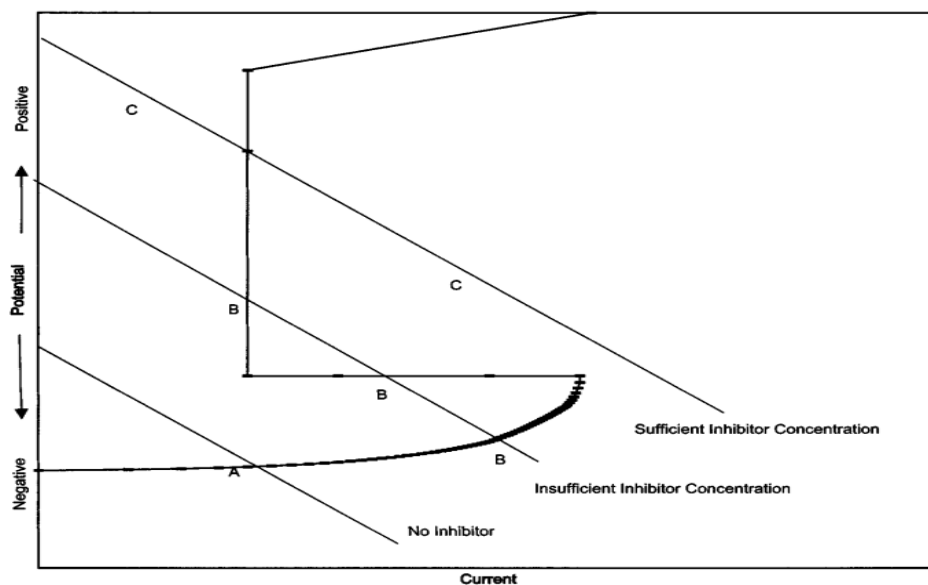


Fig. 2. Polarization diagram of an active-passive metal showing the dependence of the current on concentration of passivation-type inhibitor

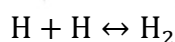
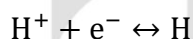
Cathodic inhibitors. Cathodic inhibitors divided into two type: cathodic poisons and cathodic precipitators. The first type inhibitors has decreased the reduction rate of corrosion

processes; the second type precipitate the cathodic areas on the metal surface. Sulfides and selenites are adsorbed on the metal surface, that is they are cathodic poisons. However, arsenic, antimony and bismuth can reduce the cathode production on metal surface and form a metallic layer on the metal surface. This type of inhibitors impacts cathodic cycles on corrosion processes. In the corrosion mechanism the hydrogen release on the acid solution, cathodic inhibitors reduce it because they connect with it and form the film on the metal surface. In the neutral and alkaline mediums, they act on corrosion processes same condition. Metallic layers are very important for cathodic inhibitors protections because they reduce the amount of corrosion products and do not soluble in environment [7].

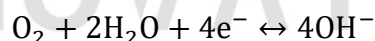
In neutral and low alkaline medium, inorganic anions such as phosphates, silicates, and borates form anticorrosion films that decrease the cathodic reaction through decrease the diffusion of oxygen to the metal surface. Some condition cathodic poisons have disadvantages which it cause hydrogen blisters and hydrogen embrittlement the reasons hydrogen absorb on metal surface under a low pressure and high temperature in acid solution.

Cathodic precipitators increase the alkalinity at cathodic sites and precipitate insoluble compounds on the metal surface. The most widely used cathodic precipitators are the carbonates of calcium and magnesium [8].

The mechanism of cathodic inhibition. Cathodic inhibition is available in acid solution because in this environment hydrogen ions change to hydrogen atoms, finally it converts to hydrogen molecules:



In alkaline solution the cathodic reaction is oxygen reduction:



Cathodic inhibitors impact all reduction reactions in acid and alkaline environment, they impede cathode products. Fig. 3 illustrates that evaluate hydrogen molecules in acid medium and release $4OH^-$, which have over potential, their cathodic and anodic curves locate a high potential area on this figure with high corrosion current. With cathodic inhibitor medium this trend changed: potential reduced and corrosion current also decreased respectively. There is a significant pattern is that cathodic curve dramatically changed with went down to negative potential area with contrast to anodic slope remained stable. So cathodic inhibitors can decrease corrosion current and corrosion rate but not change anodic slope.

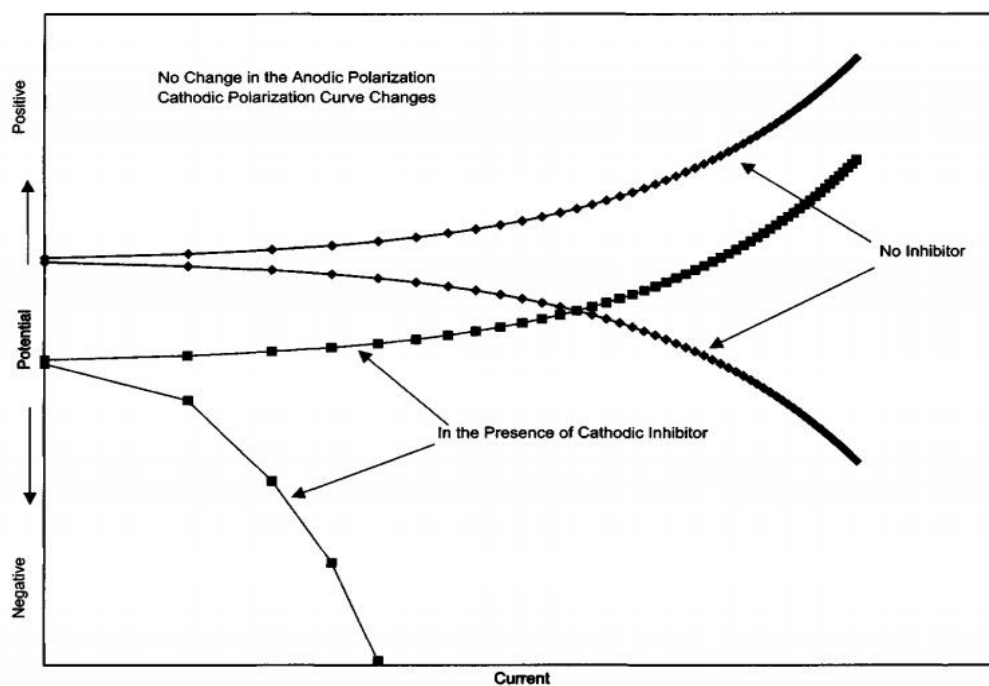


Fig. 3. Polarization curve in the presence of cathodic inhibitor

Mixed inhibitors. In corrosion science, nearly 75% of inhibitors are the mixed type that called adsorption inhibitors. They adsorb on the metal surface and cover the metal surface as results they can reduce the cathodic and anodic reactions. Their absorption properties depend on the structure of the inhibitor, presence of charge on the metal surface and the type of electrolyte.

Mixed inhibitors protect the metal by three possible ways: physical adsorption, chemisorption and film formation. Physical (or electrostatic) adsorption is a result of electrostatic attraction between the inhibitor and the metal surface [9]. When the metal surface is positively charged the adsorption of negatively charged (anionic) inhibitors has carried out.

Positively charged molecules acting in combination with a negatively charged intermediate can inhibit a positively charged metal. Anions, such as halide ions in solution have adsorbed on the positively charged metal surface, and organic cations subsequently adsorb on the dipole. Corrosion of iron in sulphuric acid containing chloride ions is inhibited by quaternary ammonium cations through their synergistic effect.

Physically adsorbed inhibitors interact rapidly, but they are also easily removed from the metal surface. Increasing in temperature generally facilitates desorption of physically adsorbed inhibitor molecules. The most effective inhibitors are those that chemically adsorb (chemisorb), a process that involves charge sharing or charge transfer between the inhibitor molecules and the metal surface [10].

Chemisorption processes on anti-corrosion mechanism are very slowly than physical adsorption but more strong. When temperature growths the adsorption and inhibition also increase. Chemisorption is complex processes and is very difficult for investigate. Adsorbed inhibitor molecules may undergo surface reactions, producing polymeric films. Corrosion protection increases markedly as the films grow from nearly two-dimensional adsorbed layers to three-dimension films up to several hundred angstroms thick. Inhibition is effective only when the films are adherent, are not soluble, and prevent access to the solution to the metal.

Protective films may be non-conducting (sometimes called ohmic inhibitors because they increase the resistance of the circuit, thereby inhibiting the corrosion process) or conducting (self-healing films) [11].

The inhibition mechanism of inhibitors of mixed type. The inhibition mechanism of action of inhibitors of mixed type was depended on the electrostatic forces between the electric charge on the surface of metal and ionic charges or dipoles of inhibitor molecules.

In table 1 zero-charge potentials (ZCP) of different metals are presented. The charge on metal surface calculated by corrosion potential (E_{CORR}) and ZCP. If the difference $E_{CORR} - ZCP$ is negative, the charge on the metal surface is negative and adsorption of cations is dominant.

Table 1.

Values of zero charge potentials.

Metal	Zero-charge potential, mV
Ag	-440
Al	-520
Au	+180
Bi	-390
Cd	-720
Co	-450
Cr	-450
Cu	-90
Fe	-350
Ga	-690
Hg	-190
In	-650
Ir	-40
Nb	-790
Ni	-300
Pd	0
Pt	+20
Rh	-20
Sb	-140
Tl	-750

The charge of inhibitor molecules depends on presence of pair electrons, π -electrons, aromatic rings and electro donor functional groups especially elements of 5 and 6 in periodical table. Nearly all organic inhibitor molecules contain at least one functional groups, which is reaction center or anchoring groups, they are hetero atom or group, for example, furan having oxygen atoms which is reaction center, second example: alcohols in molecules of which there is hydroxyl anchoring group. The force of adsorption depends on the charge on anchoring groups or the central hetero atom, like nitrogen, oxygen or phosphorus including aromatic rings, and space orientation of inhibitor molecules. The structure of molecules influences on the charge density of anchoring groups [12].

Water molecules adsorbed on the metal surface, when the inhibitor goes into this medium it water particularize substituted by its molecules. This action depends on the electrostatic interaction between the metal and the inhibitor; second factor is the size and orientation of inhibitor molecules. So the first interaction between the metal surface and the inhibitor is physical adsorption which is not specific, rapidly and reversible involves low energy.

On the other hand, the inhibitor molecules chemically interacted with metal surface owing to formatting of chemical bonds and this action is called chemisorption. It is specific, not reversible, involve all thermodynamics. Chemisorption has carried out owing to forms the electron transfer from inhibitor to metal's transition vacant electron box and low electron orbitals. The inhibitor efficiency of the homologs of organic substances different only by heteroatom is usually increased in following sequence: $P > S > N > O$. The table 2 are presented that the anchoring groups of organic compounds, which are the high quality inhibitors. The active ingredients of organic inhibitors invariably contain one or more functional groups containing one or more hetero atoms, such as N, O, S, P, or Se (selenium), through which the inhibitors anchor has adsorbed on the metal surface [13].

References:

1. Wang W., Peter E.J., Zhiyong R., Electrochemical corrosion of carbon steel exposed to biodiesel/simulated seawater mixture // Corros. Sci. - UK, 2012, -Vol. 215, -pp. 57-61
2. Холиков А.Ж., Акбаров Х.И. Влияние двухкомпонентных ингибиторов на коррозию стали в различных пластовых водах // Химическая промышленность. -Санкт-Петербург, 2014. -Т.91. -№6. -С. 37-43. (02.00.00, №21);
3. Bentiss F., Lebrini M., Lagrenee M., Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2,5-bis(n-thienyl)-1,3,4-thiadiazoles/hydrochloric acid system // Corros. Sci. -UK, 2005, -Vol. 2915, -pp. 47-52
4. Bentiss F., Traisnel M., Gengembre L., Lagrenee M., Inhibition of acidic corrosion of mild steel by 3,5-diphenyl-4H-1,2,4-triazole // Appl. Surf. Sci. -USA, 2000, -Vol. 161, -pp. 194-201.
5. Bouayed M., Rabaa H., Srhiri A., Saillard J.Y., Ben Bachir A., Le Beuze A., Experimental and theoretical study of organic corrosion inhibitors on iron in acidic medium // Corros. Sci. - UK, 1999, -Vol. 41 -pp. 501-509.
6. Kholikov A.J., Phisico-chemical properties alkilaminomethylen-fosfonovyh inhibitors // Austrian Journal of Technical and Natural Sciences. -Vienna (Austria), 2015, № 11-12. -pp. 68-71. (02.00.00, №2);
7. Collins W.D., Weyers R.E., Al-Qadi I.L., Chemical treatment of corroding steel reinforcement after removal of chloride contaminated concrete // Corrosion, -USA, 1993, -Vol. 49, -pp.74-79

8. Холиков А.Ж., Акбаров Х.И., Новые аминокислотосодержащие ингибиторы коррозии стали для пластовых вод // Коррозия: материалы, защита. -Москва, 2014. -№10. -С.30-34. (№11, Springer. IF=0,740);
9. Prabhu R.A., Shhanbhag A.V., Venkatesha T.V., Temperature effect on mild steel corrosion in acid media in presence of azoles // Corros. Sci. – UK, 2007, -Vol.49, -pp. 2144-2155.
10. Plotnikov M.D., Shein A.B., Inhibition of corrosion mild steel in acidic and neutral media // Proceedings of the universities. Chemistry and chemical technology. –France, 2013. T. 56. № 3. -pp. 35-40.
11. Vigdorovich V.I., Strelnikova K.O., Criteria for assessing the effectiveness of corrosion inhibitors protective // Condensed substance and phase boundary. –Germany, 2011. T. 13. № 1. -pp. 24-28.
12. Kim Y.R, Tsygankov L.E, Kichigin V.I, Inhibition of corrosion and hydrogenation of steel in model formation waters // Corrosion: materials protection. –Russia, 2005. № 8. -pp. 30-37.
13. Kholikov A.J., Akbarov Kh.I., Elaboration of anticorrosion compositions based on local raw materials // European Conference on innovations in Technical and Natural Sciences. 4th International scientific conference 10th October 2014 East West Assjciation for Advanced Studies and Higher Education GmbH. -Vienna, (Austria), 2014. -№ 4. -pp. 194-198.

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