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EFFICIENCY OF USING ORGANIC INHIBITORS FOR CORROSION PROTECTION OF OIL AND GAS INDUSTRY EQUIPMENT

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Abstract. This article investigates corrosion protection methods for technological equipment in the oil and gas industry and primary oil refining units. The classification of liquid-phase and volatile inhibitors depending on environmental aggressiveness, along with their adsorption and action mechanisms on metal surfaces, is described. A comparative analysis of the protective properties of organic compounds containing heteroatoms (N, S, P), specifically amide- and imidazoline-based inhibitors, was conducted. Using the example of the ELOU-AT-6 unit at the "KINEF" refinery, the technological scheme for feeding inhibitors and neutralizers, as well as the optimal dosing regime, is outlined.
Keywords: corrosion, inhibitor, oil refining, amides, imidazolines, adsorption, neutralizer, ELOU-AT-6, overhead line, protective layer, heteroatoms.

Introduction. Corrosion of equipment and pipelines caused by aggressive environments in the oil and gas industry remains a critical economic and environmental challenge. To prevent these adverse processes, reducing environmental aggressiveness, isolating metal surfaces, and introducing specific chemical agents—corrosion inhibitors—are considered the most effective methods. In particular, hydrocarbon-soluble organic inhibitors form a robust molecular protective film on the metal surface, ensuring the safety and integrity of the equipment. This article analyzes the effectiveness of amide- and imidazoline-based inhibitors, as well as the technology of their industrial application.

Main Part. Depending on the corrosion type and process characteristics, there are four fundamental principles of corrosion protection: increasing the chemical resistance of metals, reducing environmental aggressiveness, forming a protective layer on the metal surface, and controlling the electrical potential. Along with technological measures, non-metallic materials, specialized alloys, and electrochemical methods, the use of corrosion inhibitors demonstrates high efficiency in protecting oil and gas equipment.

Inhibitors are organic or inorganic chemical compounds that significantly reduce the corrosion rate when added to an aggressive medium in small quantities. Based on application conditions, they are classified into liquid-phase and volatile (gas-phase) types, while liquid-phase inhibitors are further subdivided into acid, alkaline, and neutral medium inhibitors.

Acid medium inhibitors. These are primarily used during the acid treatments of wells or equipment chemical cleaning. Their mechanism of action is based on the principle of adsorption (adhering to the metal surface). Composed mainly of nitrogen-containing (amines, imidazolines) or sulfur-containing organic compounds, they form a molecular barrier on the metal surface, effectively isolating it from the acid without altering the bulk aggressiveness of the medium.

Alkaline medium inhibitors ($pH > 7$). These agents enhance the transition of the metal into a passive state (passivation) and stabilize the surface protective layer. Consisting of silicates, phosphates, or organic complexes, they form insoluble, durable protective films on the metal surface within alkaline solutions.

Neutral and weakly acidic medium inhibitors (pH 5.5–6.5). These are predominantly applied in the condensation and cooling systems of primary oil refining (atmospheric distillation - AD) units. Characterized by excellent solubility in the hydrocarbon phase (gasoline, kerosene), these inhibitors (mainly amides, dioleates, and imidazoline bases) exhibit their protective performance after the environmental pH is stabilized by pre-injected neutralizers. Neutral medium inhibitors

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rapidly adsorb onto the metal surface, forming a highly hydrophobic (water-repellent) molecular film that prevents contact with water and residual micro-acids.

When protecting the condensation and cooling systems of primary oil refining units, the following fundamental requirements are imposed on corrosion inhibitors: they must be economically viable, structurally stable under operating conditions (not decompose), exert no adverse effects on the quality and physicochemical properties of petroleum products (especially aviation fuels) or the performance of catalysts used in secondary processes, and be environmentally safe.

Globally, hydrocarbon-soluble inhibitors account for approximately 30% of total corrosion inhibitor production, with the largest share (~70%) utilized specifically in petroleum refining. Thousands of inhibitors effectively used in industry belong to the class of organic compounds containing heteroatoms such as nitrogen, sulfur, oxygen, and phosphorus [1]. Their primary types include the following:

Amines and heterocyclic compounds. Amines and their derivatives, heterocyclic systems containing pyridine nitrogen, imines, imidazoles, and imidazolines.

Amides. Amides of dicarboxylic and other acids, as well as cyclic amidines.

Salts and acids. Phosphate salts of amino-containing copolymers, calcium and sodium salts of alkylarylsulfonic acids, and liquid dicarboxylic acids.

Sulfur-containing compounds. Sulfonic acids, sulfonates, thiophenol derivatives, and sulfamides.

Esters occupy a special place among corrosion inhibitors. In industrial applications, esters of oleic, naphthenic, acrylic, carbamic, nicotinic, and phosphoric acids synthesized with various aliphatic alcohols, alkylene glycols, and amino alcohols are widely recommended.

Globally, hydrocarbon-soluble inhibitors predominantly consist of amides (diamides), imidazoline bases, and their formulations, serving as the fundamental cornerstone of modern industrial inhibitors. The inhibition efficiency of organic compounds increases based on the electronegativity and polarizability of their heteroatoms in the following sequence:

$O \rightarrow N \rightarrow S \rightarrow P$

However, since the toxicity of these substances rises proportionally along this series, nitrogen-containing compounds are preferentially selected for industrial applications due to environmental and safety constraints [2,3].

Specific inhibitors that ensure the process safety of technological systems in the petroleum refining industry are primarily the condensation products of polyamines with carboxylic acids. These chemical processes yield highly effective amide and imidazoline derivatives, as well as their respective salts. These surfactants form a robust chemisorption protective layer on the metal surface of primary and secondary refining equipment, significantly mitigating the impact of aggressive media.

The protective efficiency of inhibitors directly depends on their chemical structure and the molar ratio of their components [4-7]:

Amidoamine systems. Certain studies indicate that amide groups exhibit higher efficiency compared to imidazolines. Specifically, for the "Neftexim-1" inhibitor, the ratios of amidoamines based on oleic acid, diethylenetriamine, and amine salts investigated by the method of isomolar series demonstrate that maximum protective effect is achieved at an amidoamine-to-amine salt molar ratio of 3:7 → 5:5.

Amido-imidazoline formulations. Carboxylic acids (oleic, lauric, stearic, palmitic, naphthenic, tall oil fatty acids, dimer, and trimer acids) and polyamines (aminoethylethanolamine, diethylenetriamine, triethylenetetramine, dipro-pylenetriamine) are utilized in the synthesis of this type of inhibitor. The combination of imidazolines with alkaline agents or their salts formulated with long-chain hydrocarbon radical carboxylic acids yields a high synergistic effect.

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International experience (Nalco patents). A 20% solution in kerosene of the condensation product synthesized from dipropylenetriamine and naphthenic acid (molecular weight 300–415, acid number = 120–180 mg KOH/g) exhibits high technological performance. This inhibitor, synthesized at an amine-to-acid ratio of 1:2, provided a 97% protection rate when injected into the overhead lines of refinery columns at a concentration of 12 ppm (with a recommended continuous working dose of 2–5 ppm).

Regional practice (Olazol, Vikazol, Kastazol, Naftazol, Priazol). These inhibitors represent modified amphiphilic imidazoline bases. For instance, the "Olazol" inhibitor consists of a blend of 1-diethyldiamino-2-heptadecenyl-2-imidazoline (90% wt.) and oleic acid monoamide (10% wt.). It provides a protective efficiency exceeding 90% for St10 steel in aggressive hydrogen sulfide environments (0.1M HCl + 0.2 g/dm^3 H_2S) at a temperature of 25 ^{0}C and a concentration of 50 ppm. It has been established that the adsorption capacity and overall efficiency of this inhibitor increase further with rising system temperatures.

Preparation and Feeding of Corrosion Inhibitors in Primary Oil Refining. According to the modern "traditional" scheme of inhibitor protection for primary oil refining units, the injection of inhibitors is carried out into the overhead lines of the evaporator, atmospheric, and stabilizing columns. As a practical example, Figure 1 illustrates the operational feeding scheme for the inhibitor and neutralizer implemented at the ELOU-AT-6 unit of the "KINEF" production association. The corrosion inhibitor is utilized in a diluted state within the unit. Stable gasoline is used as the solvent. The concentration of the inhibitor working solution is maintained at 7.0–7.5% by weight [8-14].

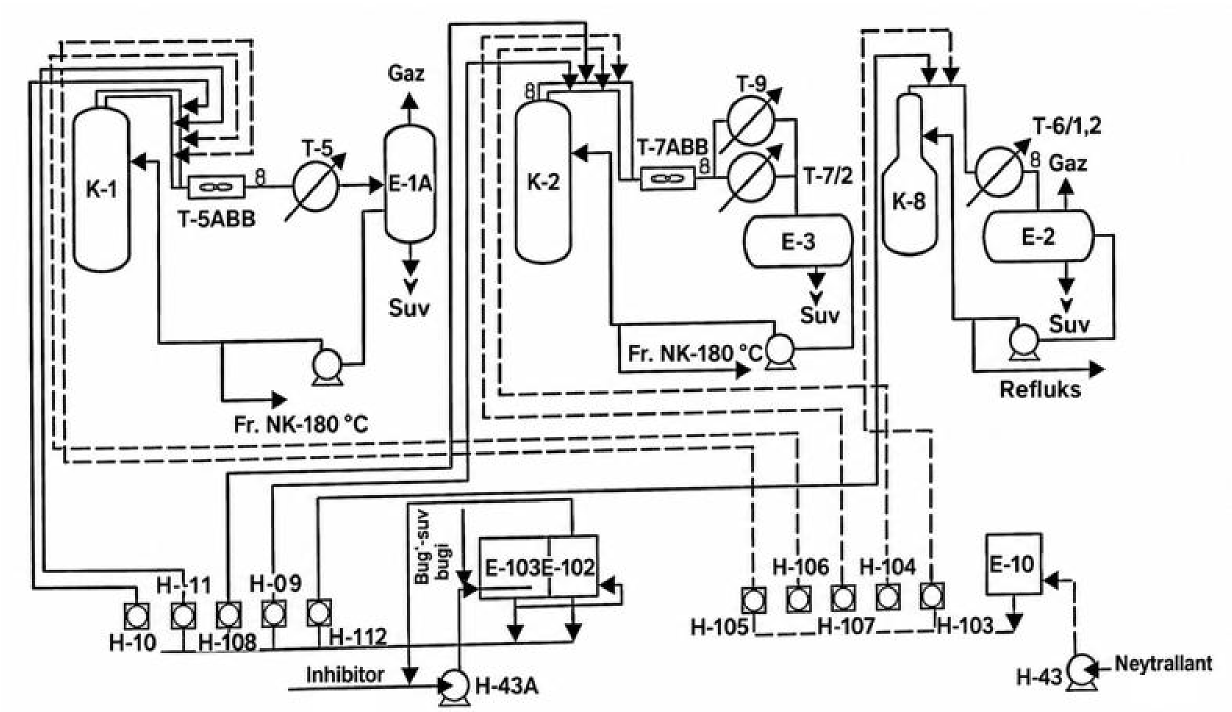

Figure 1. Operational feeding scheme for the inhibitor and neutralizer implemented at the ELOU-AT-6 unit of the "KINEF" production association.

After the pipelines are filled, the inhibitor injection is carried out using a "shock" dose for the initial three days: to effectively clean the metal surface from contaminants and ensure the rapid formation of the protective barrier, it is administered at a rate of 20 ppm on the first day, and 10 ppm for the subsequent two days. Treatment with a "shock dose" is also performed periodically during the startup of the unit following maintenance or repairs. After the "shock dose" treatment, the inhibitor dosage is reduced to optimal values.

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The neutralizer is introduced in its commercial (undiluted) form using metering pumps through injection nozzles into the column's overhead lines, at a distance of ~5–7 meters from the inhibitor injection points. The neutralizer consumption is adjusted based on the pH values of the drainage water leaving the respective reflux drums, and these indicators must be maintained within the range of 5.5–6.5.

Conclusion. In conclusion, nitrogen-containing organic compounds (amides and imidazolines) represent the optimal solution for protecting the condensation and cooling systems of primary oil refining units due to their low toxicity and high chemisorption capacity. Operational experience from the "KINEF" AT-6 unit demonstrates that initial "shock" dosing (10 → 20 ppm) combined with amine neutralizers ensures rapid formation of a durable protective barrier on the metal surface, increasing the overall protection efficiency up to 97%. Systematic regulation of reagent dosage and continuous monitoring of the drainage water pH within the stable range of 5.5 → 6.5 serve as the primary criteria for ensuring the operational reliability and process safety of refinery equipment.

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