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Composite Corrosion Inhibitors for the Protection of Oil and Gas Equipment

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ABSTRACT: The article presents the results of gravimetric and electrochemical tests of various ratios of a nitrogen-containing compound, a nonionic surfactant and a sulfur-containing component in laboratory conditions, as close as possible to factory conditions. As a result of the research, a multicomponent composition was obtained that showed high efficiency under corrosion conditions for the protection of oil and gas equipment.

KEY WORDS: corrosion, inhibitor, gravimetric method, protective effect, electrochemical method, reagent.

I. INTRODUCTION

Gas is a valuable hydrocarbon raw material intended for industrial and municipal purposes, but its intended use is often complicated by corrosion processes occurring inside installations. Violation of the operating conditions of the installations can lead to an immediate deterioration in the quality of commercial gas and even to an emergency shutdown of the installations. Since in the gas industry there is practically no possibility of reserving raw materials in the event of failure of process units, during shutdowns sulfur dioxide gases are burned in flares. This leads to losses of valuable raw materials and poisons the environment. Therefore, ensuring the reliability of operations of acid gas processing plants is of paramount importance [1].
These processes are caused by the presence of aggressive components in the gas composition of oil and gas, gas and gas condensate fields: hydrogen sulfide, oxygen, carbon dioxide. The problem of carbon dioxide corrosion is encountered at many gas processing complexes in Uzbekistan. When plants for processing wet gas, which contains carbon dioxide, operate, the gas-liquid mixture gradually cools and liquid condensate, consisting of aqueous and hydrocarbon phases, is released. The presence of water and carbon dioxide dissolved in it leads to corrosion according to the following mechanism [2]:

$$CO^2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-} \quad (1)$$

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3, \quad (2)$$

$$Fe^{2+} + HCO_3^- \rightarrow FeCO_3 + H^+, \quad (3)$$

$$Fe^{2+} + H_2CO_3 \rightarrow FeCO_3 + 2H^+ \quad (4)$$

A generalization of the operating experience of gas purification plants using amine solutions shows that the reliability of their operation decreases under the following conditions: destruction of amines due to side reactions and thermal decomposition; tarring; corrosion of equipment and product pipelines; foaming ethanolamine solutions in a gas purification system; deposition of solid impurities on the surfaces of pipes and equipment.

II. SIGNIFICANCE OF THE SYSTEM

This article reviews results of the research, a multicomponent composition was obtained that showed high efficiency under corrosion conditions for the protection of oil and gas equipment. The Methodology and Discussion is presented in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

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III. METHODOLOGY AND DISCUSSION

When operating amine desulphurization plants, the primary task is to maintain the ethanolamine solution in an active working condition for a long time. This is especially important due to the increasing use and cost of sorbents [3]. Over time, the solutions become contaminated with impurities introduced with gas, water and reagents that came with gas from the well that did not undergo separation before being supplied to the absorber. Amine solutions can also degrade in reactions with CO_2, O_2, and organic sulfur compounds, as a result of which they are no longer able to interact with H_2S and CO_2. However, not all decomposition leads to a loss of the solution's ability to capture CO_2 and H_2S. The absorption capacity of a solution can decrease without decomposition, for example, as a result of the formation of heat-resistant amine salts, from which the amine is not regenerated in the desorber. The concentration of these salts and the type of acid anion are determined by ion chromatography. Thus, in amine salts of nitric, nitrous, formic, oxalic, acetic, thiosulfuric, thiocyanic and other acids were found in solutions.

For each specific installation, it is very important to select the type of amine and regeneration parameters. For example, MEA systems typically require thermal regeneration with boiling of the amine and distillation, the salts are concentrated in the residue and removed from the system. Since DEA and MDEA are mines with high boiling points, with complete thermal regeneration (even using a vacuum) the degradation process cannot be avoided. Thermally stable salts are most effectively removed from MDEA solutions using ion exchange resins, electrochemically (electrodialysis) and in vacuum distillation units.

Returning to measures that prevent the degradation and formation of thermostable salts, in addition to gas separation and washing systems, the use of filtration is very effective: mechanical and through activated carbon. Coal adsorbs almost all foam-forming substances: condensate, degradation products and organic acids. During the filtration process, small particles of coal enter the circulation system. To capture these particles, a mechanical filter is usually installed after the carbon filter. Mechanical filtration is used to remove fine particles from the system. These particles are not foaming agents, but they do stabilize foam if it forms. High particle content in the system can cause erosive destruction of equipment where circulation rates are high.

One of the most accessible and effective methods of protecting equipment from gas corrosion is inhibitor protection [4]. Today, the market offers a wide range of corrosion inhibitors designed to protect oil and gas equipment. However, they are not universal, since each object is characterized by certain operating conditions and the composition of the liquid and gas phases. Therefore, the selection of corrosion inhibitors for each installation is made individually.

In order to develop an effective reagent for corrosion protection for the installations of the Mubarek Oil and Gas Processing Plant, studies were carried out to assess the protective ability of a number of components of corrosion inhibitors. The most common methods for determining the effectiveness of corrosion inhibitors were used in the work: gravimetric and electrochemical.

When assessing the effectiveness by the gravimetric method, tests were carried out in cells with a volume of 600 ml with constant stirring of the aggressive environment. Metal plates of size 20x25x2 mm, made of steel grade St.20 prepared in accordance with GOST 9.506-87 [5], were used as control samples.

The electrochemical method consists of obtaining polarization curves that convey the relationship between the potential of the electrode under study and the current density during polarization from an external source of direct electric current, followed by assessment of the protective ability of the inhibitor based on the current density in inhibited and uninhibited environments.

These methods are used in laboratory testing of corrosion inhibitors and allow for a comparative assessment of their effectiveness.

Despite the fact that during the experiment, conditions are created as close as possible to real factory ones, the actual corrosion rates will differ from the laboratory ones. In this regard, in this work, a comparative assessment of the effectiveness of corrosion inhibitors was carried out at a dosage of 20 grams per ton.

The development of a corrosion inhibitor began with the selection of the most effective active base. The following reagents were chosen as active bases: a mixture of amidoimidazolines, a mixture of alkylimidazolines, ethoxylated imidazolines, methyldiethanolamine ether, mixture of azole compounds. All of the listed reagents are various nitrogen-containing compounds that work according to a film protection mechanism. Polymer macromolecules, due to the presence of many amino groups, interact with adsorption centers on the metal surface, forming a film that prevents corrosion processes.

The results of gravimetric and electrochemical tests of these reagents are presented in Table 1.

As a result, it was determined that the best results were demonstrated by a mixture of amidoimidazolines and a mixture of alkylimidazolines, which, as a result of gravimetric tests, showed a protective effect of about 60%, and in

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electrochemical tests the effect was more than 90%. These reagents were selected as active bases for the further formation of a multicomponent corrosion inhibitor.

Table 1.
Results of electrochemical and gravimetric tests of active bases of corrosion inhibitors

No	Reagent	Gravimetric method			Electrochemical method		
		Average corrosion rate, mm per year		Protective effect	Average corrosion rate, mm per year		Protective effect
1.	ethoxylated imidazolines	0.808	0.397	50.9	1.217	0.164	86.5
2.	mixture of azole compounds	0.775	0.386	50.2	1.08	0.198	81.7
3.	amidoimidazoline mixture	0.821	0.339	58.7	1.12	0.096	91.4
4.	methyldiethanolamine ether	0.717	0.352	50.9	0.995	0.167	83.2
5.	mixture of alkylimidazolines	0.751	0.307	59.1	0.986	0.091	90.8

IV. EXPERIMENTAL RESULTS

At the next stage, the formation of the composition was carried out by mixing selected nitrogen-containing compounds with various additives, which were used as a nonionic surfactant (oxyethylated fatty acid) and sulfur-containing compounds CC-1 and CC-2. The choice of additives is determined by the presence of hydrophilic and sulfur-containing functional groups that strengthen the protective film.
In the composition, the amount of the sulfur-containing component was constant and amounted to 5% by weight; methanol was used as a solvent in an amount of 65% by weight, the remaining part (45% by weight) was a nonionic surfactant and a nitrogen-containing compound in various proportions. As a result of mixing, the following compositions were obtained:
Composition No. 1-3: nitrogen-containing component, nonionic surfactants, CC-1;
Composition No. 4: nonionic surfactants, sulfur-containing compound CC-1;
Composition No. 5-7: nitrogen-containing component, nonionic surfactant, sulfur-containing compound CC-2;
Composition No. 8: nonionic surfactants, sulfur-containing compound CC-2.
Table 2 presents the results of assessing the effectiveness of composite compositions.

Table 2.
Gravimetric and electrochemical tests of compositions with various nonionic surfactant contents

No	Ratio of nonionic surfactants: nitrogen-containing compound	Gravimetric method		Electrochemical	
		Protective effect mixtures of amidoimidazolines	Protective effect mixtures of alkylimidazolines	Protective effect mixtures of amidoimidazolines	Protective effect mixtures of alkylimidazolines
1	0 : 1	59.1	59.6	94.2	91.1
2	1 : 2	64.2	60.1	95.8	93.1
3	2 : 3	52.2	50.9	94.8	91.2
4	1 : 0	26.5	26.5	43.8	43.8
5	0 : 1	58.9	59.3	92.6	90.9
6	1 : 2	61.9	58.2	93.4	91.6
7	3 : 2	49.8	47.2	84.3	81.1
8	1 : 0	24.3	24.3	40.2	40.2

From Table 2 it can be seen that compositions No. 4 and No. 8 without a nitrogen-containing component do not show high results when testing protective properties, however, when mixed with nitrogen-containing compounds, a synergistic effect appears and the protective effect of the composite compositions increases. This is explained by an increase in adsorption on the metal surface. Molecules of a nonionic surfactant, interacting with free amino groups of adsorbed

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molecules of the active base located on the surface, form an additional layer, thus increasing the strength of the resulting protective film. Sulfur-containing compounds are chemisorbed due to the sulfur atom on the surface of the steel.

V. CONCLUSION AND FUTURE WORK

Thus, based on the results of both electrochemical and gravimetric tests, it was determined that the optimal concentration in the composition of nonionic surfactants is 9% by weight, and a mixture of amidoimidazolines is 21%. At the same time, the greatest protective effect is observed in formulations containing a mixture of amidoiidazolines and the sulfur-containing additive CC-1.

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