THE MAIN TYPES OF COMPOUNDS USED AS CORROSION INHIBITORS

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Introduction

Protection of metals against corrosion in different corrosive environments can be achieved using corrosion inhibitors, which are compounds added in small quantities to a corrosive solution to reduce or minimize the corrosion rate [1,2]. The economic impact of corrosion is substantial; for instance, according to international research by NACE (IMPACT 2016), the annual global economic damage due to corrosion amounts to approximately 2.5 trillion US dollars [3]. This represents about 3.4% of the average gross domestic product (GDP) of each country [4-6].

As shown [7], to reduce and even completely stop the destructive effects of corrosion, researchers are considering the synthesis of triethylenetetramine (TETA) derivatives with organochlorine compounds, in particular with 1,2-dichloroethane (DCE). The presence of two chlorine atoms in the EDC molecule leads to the formation of cyclic condensation products, which have high anti-corrosion activity [8]. One of the main reaction products is 1,4-bis-(2-aminoethyl) piperazine. The reaction takes place in an aqueous medium with short heating. It has been proven that the presence of cyclic nitrogen-containing components enhances the effectiveness of the inhibitory composition due to better adsorption of the reagent on the metal surface. The tests carried out showed the high activity of the inhibitor in drilling fluids[9,10].

The work [11] proposes a technology for the synthesis of a corrosion inhibitor by condensation of polyethene polyamine (PEPA) with 1,2-dichloroethane with the formation of high-molecular compounds of a cyclic structure. During the work, optimal conditions for the synthesis of the corrosion inhibitor were selected, the physicochemical properties were studied, and the structure of the compound was confirmed (1H NMR spectrum was obtained on a Bruker Avance 400 spectrometer), with an operating frequency of 400 MHz, internal standard TMS.

Inhibitor molecules have both hydrophilic and hydrophobic parts; they accumulate on the metal surface in the form of a protective film, oriented in space with the hydrophobic part towards the metal. This ensures the surface is shielded from the effects of dissolved oxygen and other oxidizing agents. The resulting inhibitor monolayer has a pronounced dendrite-like structure and consists of two layers - adsorbed and micellar. The authors of [12] propose an anti-corrosion additive, which is a mixture of orthophosphoric acid, water and a tertiary amine. During the research, optimal synthesis conditions were selected, physicochemical properties were determined, and the structure of the synthesized compound was confirmed. It has been shown that a new synthesized anti-corrosion composition based on nitrogen- and phosphorus-containing organic compounds provides a high protective effect under conditions of hydrogen sulfide and carbon dioxide corrosion of steel, amounting to Z = 53.0-80.9% at low dosages.

The authors [13] conducted research on the development of the synthesis of new corrosion inhibitors based on nitrogen-containing compounds. Divinyl hydrochloride and various amines were used as starting reagents. To expand the range of corrosion inhibitors used, the authors of propose compounds obtained from diethylenetriamine and a halogen derivative of an aromatic hydrocarbon in a molar ratio of 1:1, 1:2 and 1:3. As well as quaternary ammonium salts based on triethylenetetramine and benzyl chloride. To determine the optimal conditions for the production of ammonium salts, syntheses were carried out in the temperature range 303 – 333 K, at different molar ratios of the reacting substances, with a reaction duration of 1 to 4 hours. It was found that the highest yield is achieved in 4 hours at a temperature of 60ºC.

Evaluation of the inhibitory properties of the obtained compounds by the gravimetric method showed that the protective effect for mono-N-benzyldi-ethylene triammonium chloride is 79.2%; for di-NN'-benzyldiethylenetriammonium dichloride – 83.1%; for tri-NN’N’’-benzyldiethylenetriammonium trichloride – 88.6%. The inhibitory properties of the resulting quaternary ammonium salt based on triethylenetetramine and benzyl chloride showed that the protective effect for mono-N-benzyltriethylenetetramine chloride was 79.6%; for di-NN'-benzyltriethylenetetrammonia dichloride – 93.9%; for tri-NN' N''-benzyltriethylenetetrammonia trichloride – 94.5%; for tetra-NN'N''N'''-benzyltriethylenetetrammonia tetrachloride – 97.9%[14].

In [15], the technology for the synthesis of N-alkenyl-substituted salts based on pyridine and alkenyl chlorides, which can be used as metal corrosion inhibitors and bactericidal preparations, is of practical interest.

The reaction was carried out at atmospheric pressure in the temperature range from 313 to 373 K, with the molar ratio of pyridine: alkenyl chloride (AC) from 1:1 to 1:2 in chloroform and an aqueous medium. The duration of the reaction varied from 2 to 9 hours. As a result of research, it was established that the optimal technology conditions for the synthesis of N-alkenylpyridinium salts in chloroform solution are: temperature 338 K, reaction duration 8 hours, molar ratio pyridine: AX = 1:1.05. The maximum yield is 97%, and salt precipitates. In an aqueous solution at a temperature of 353 K, reaction duration 4 hours, molar ratio of pyridine: AX = 1:1.05 - the yield is 98%.

When 2-methylpyridine, acetone and bromine or iodine interact in a 2:1:1 ratio, inhibitory mixtures are obtained that reduce the rate of sulfuric acid corrosion of steel 20 at 293 K by 23 and 26 times, respectively, and at 333 K by 300 and 600 once. The presence of iodide ions in the mixture doubles the effectiveness of its protective effect at 333 K, compared to a mixture containing bromide ions, which is due to the higher synergistic effect of iodide ions [16]. The reaction of pyridine or 2-methylpyridine and the above reagents in a ratio of 4:1:2 leads to the formation of double salts that exhibit a high inhibitory effect, especially at elevated temperatures of the corrosive solution. Thus, for iodine-containing mixtures with and without methyl substituents, the inhibition coefficients of sulfuric acid corrosion of steel 20 at 333 K are 870 and 500, respectively.

The works [17] present the results of studying the reactions of aminoguanidine and hydrazine hydrate with carboxylic acid derivatives, leading to 1,2,4-triazines with an amino group in different positions. The conditions (molar ratio of reagents, solvent, temperature) for the maximum yield of target products have been established. When chloroacetyl chloride reacts with unsubstituted aminoguanidine, 3-amino-1,2,5,6-tetrahydro-1,2,4-triazin-6-one is formed. The reaction of monochloroacetic acid with hydrazine hydrate produces 4-amino-1,4,5,6-tetrahydro-1,2,4-triazin-5-one. 4-Amino-1,4,5,6-tetrahydro-1,2,4-triazine-5,6-dione is obtained from diethyl oxalate, hydrazine hydrate and formic acid. The corresponding amides were obtained based on the synthesized amino triazines and isobutyric acid chloride.

To expand the raw material base of new corrosion inhibitors, technologies for the production of imidazoline derivatives were developed; distilled naphthenic acid (DNA) was used as the starting acid, which was introduced into a condensation reaction with diethylenetriamine (DEET) at different ratios of reagents [18]. The compounds 1-aminoethyl- and 1-amido-2-substituted imidazoline were obtained in yields of more than 95%.

The work [19] presents studies on the development of high-molecular amines by the condensation reaction of the simplest amines with aldehydes, as well as N-substituted and ring-substituted alkenyl arylamines using derivatives of aniline, allyl chloride - intermediate products of petrochemical industries and piperylene - a waste product from the production of synthetic rubber. Utilization of piperylene is carried out both directly by reaction with arylamines and through the stage of obtaining chloropentene. Using chloropentene and various aniline derivatives, a wide class of surfactants - potential corrosion inhibitors and bactericides - has been developed. The preparation of surfactants is as follows. In the first stage, using chloropentene and various anilines in the presence of triethylamine at a temperature of 363 K, N-pentenyl aniline is synthesized. Next, N-pentenylaniline is reacted with allyl chloride in the presence of triethylamine at a temperature of 363 K to form N-allyl-N-pentenylaniline. When the resulting product interacts with acids (HC1, H_2SO_4 and H_3PO_4), ammonium salts are formed, which have high bactericidal and inhibitory properties.

Studies have shown that in a 15% solution of hydrochloric acid at temperatures (298-363 K), pentenyl arylamines substituted into the core at dosages of 0.5 - 5.0% wt. have a degree of protection of 97 – 99%. Ammonium salts of nitrogen-substituted anilines have high bactericidal and inhibitory activity in mineralized environments containing hydrogen sulfide. At dosages of 25-100 mg/l, these compounds completely suppress sulfate-reducing bacteria and have a fairly high inhibitory efficiency (95-98%) in hydrogen sulfide-containing mineralized environments.

The authors of [20] have developed and proposed bactericides and acid corrosion inhibitors based on polyethene polyamines, heterocyclic amines and pentenyl chlorides. By hydrochlorination of isoprene and piperylene, chloropentenes were obtained, which were successfully used in the N-alkylation of hexamethylenetetramine, di- and trialkyl amines, polyalkanolamines and polyethene polyamines. It has been proven that in the concentration range of 20-100 mg/l, polyalkylated hexamethylenetetramine completely inhibits the growth of sulfate-reducing bacteria and reduces the rate of hydrogen sulfide corrosion by 80-95%[21,22].

The resulting inhibitor is low-toxic and effective in protecting the metal surface in a hydrochloric acid environment due to the following distinctive features:

1) increased solubility in hydrochloric acid due to the abundance of ammonium nitrogen;

2) cationic macromolecules of polyamines are easily adsorbed on the surface of metals, in particular iron, which is characterized by a negative value of zero surface

charge in a hydrochloric acid environment, and create a durable film that prevents the corrosion process.

The authors of [23] developed a technology for the synthesis of a composition based on boric acid, ethylenediamine and methenamine, taken in a molar ratio of 1:2:0.1, respectively, and dissolved in water. The technology for the synthesis of the composition was carried out in two stages: the first stage is the interaction of boric acid and ethylenediamine for 4 hours at a temperature of 353 K; the second stage is represented by dissolving the resulting compound in an aqueous solution of hexamine for 1-1.5 hours at a temperature of 313 K. The resulting composition is a viscous liquid of a reddish-orange color, soluble in hydrochloric acid.

It has been shown that the composition has an inhibitory effect with an average protective effect of 98.57% and an average inhibition coefficient of 70.29. This composition can also be used as an active base for an acid corrosion inhibitor.

Some features of the issue of protecting metals from corrosion inhibitors

The most accessible and widespread way to reduce the corrosive activity of circulating waters is their inhibition [24]. However, it has a number of significant disadvantages: the use of harmful chemicals and their release into water bodies with wastewater; contamination of circulating water with chemicals and intensive growth of microorganisms; local corrosion damage to the metal of equipment due to non-compliance with the dosage of inhibitors. In order to reduce the cost of corrosion protection, we investigated the possibility of forced regulation of the ionic composition of circulating water, which allows us to specifically influence their corrosive activity. To regulate the ionic composition of water, magnetohydrodynamic treatment (MHDT) [25], carried out using a specially designed

The authors of [27-30] studied the rheological properties of materials pigmented with core pigments. The influence of core pigments on the physical and mechanical properties of coatings obtained from aqueous dispersions of copolymers of various natures has been established. Visual corrosion and potentiodynamic studies have shown that the introduction of core pigments into a water-dispersed material, in contrast to strontium chromate, makes it possible to exclude an instant corrosion inhibitor from the formulation, which can lead to a decrease in aggregative stability.

In [31], the objects of study were metal corrosion inhibitors, including oligomeric inhibitors. Nitrogen and phosphorus-containing inhibitors were studied: hexamethylenediamine monophosphate (MFGDA), hexamethylenediamine formaldehyde oligomer (OHFO) and two-component inhibitor $(NaPO_3)n$+OHDA at different temperatures and concentrations. The corrosion behaviour of steel was studied on samples in the form of plates. The studies were carried out in background solutions of the composition 5% Na_2SO_4 + 3% H_2SO_4 (F-1), 3% NaCI + 5% Na_2CO_3 (F-3) and tap water (F-2) at different temperatures[32-35].

Conclusion

From the above literature review it is clear that today the problem of protecting oilfield equipment and pipelines from corrosion in mineralized environments containing hydrogen sulfide and carbon dioxide is very relevant. One of the most effective ways to combat corrosion in the oil industry is inhibitor protection. Despite the fact that a large number of corrosion inhibitors have been developed, the range of reagents that would effectively solve the problem of corrosion protection in environments containing both hydrogen sulfide and carbon dioxide, as well as those that suppress the activity of sulfate-reducing bacteria (SRB), is very limited. Reagents based on nitrogen and phosphorus-containing compounds are promising as corrosion inhibitors.

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