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MICROBIOLOGICAL CORROSION OF METALS AND METHODS OF PROTECTION FROM IT

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ABSTRACT

The problems of microbiological corrosion of metals and ways of protection against it are considered. Methods for protecting metals from bio corrosion are based on the use of chemical biocides, as well as on the rational selection and use of acetylene compounds.

INTRODUCTION

Every year, about a quarter of the iron produced on Earth is lost due to corrosion. The cost of metals increases many times due to their consumption in the replacement and repair of car parts, in various equipment and communications made of metals, in water pipes. Corrosion causes serious environmental consequences: for example, its products pollute the environment and have a negative impact on human health and life.

Long years of fighting corrosion in the oil and gas industry have shown that the most effective and cost-effective way to protect against corrosion is the use of inhibitors. The protective mechanism for the use of corrosion inhibitors is based on the formation of a protective film on the surface of metals, with the help of which a separation occurs between the aggressive environment and the metal. At present, inhibitors produced in Russia and Germany are imported into our republic, and the demand for them in the chemical, electrochemical, oil and gas industries, water supply and water circulation is quite high.

According to the modern classification of inhibitors, they are divided into oxidizing, adsorbing, complexing and oligomeric. In addition, it is natural to pay great attention to the corrosion damage of metals under the action of microbes. Based on this, the effect of chemicals, mainly alcohols containing an acetylene group, on microbiological corrosion was studied. As is known from the literature, acetylene compounds contain many metal corrosion inhibitors. KI-1 is one of the most popular inhibitors in the production of adsorption inhibitors of acid corrosion of metals [1, 2]. According to the modern classification of inhibitors, they are divided into oxidizing, adsorbing, complexing and oligomeric. In addition, it is natural to pay great attention to the corrosion damage of metals under the action of microbes.

Based on this, the effect of chemicals, mainly alcohols containing an acetylene group, on microbiological corrosion was studied. As is known from the literature, acetylene compounds contain many metal corrosion inhibitors. KI-1 is one of the most popular inhibitors in the production of adsorption inhibitors of acid corrosion of metals [1, 2].

For acidizing deep wells, it is recommended to use a 4-component mixture for protecting equipment, which includes quaternary ammonium compounds and acetylene alcohol [5], which provide at least 99% protection of steel at 100°C in 14% HCl. Summing up the above, it seems relevant to comprehensively study the penetration of acetylenic alcohols into various structures in the protective properties of the KI-1 inhibitor. For this, a preparative form of an inhibitor was used, to which a 1% solution of such an alcohol and the anticorrosion properties of inhibitors were added as additives, and the modified samples were evaluated by the effect on corrosion in a hydrochloric acid medium. and sulfuric acid, the corrosion rate K and the drag coefficient γ were determined.

Corrosion study was carried out by mass spectroscopy in 20% HCl solution at 60°C and 20% H_2SO_4 solution. The control time was 24 hours, the working surface of steel samples was $7.2 \cdot 10^{-4}$ m^2, 5 $g \cdot l^{-1}$ inhibitor KI-1(1-9) prepared by adding 1% acetylene alcohol was used for inhibition. To compare the effect of inhibitors on corrosion under these conditions, the formulation of KI-1 inhibitors (st. 10) without alcohol additives was used as a reference.

The first guesses about the impact on the process of corrosion destruction of biological organisms appeared only at the end of the 19th century.

To protect metals from biocorrosion, the same biocides are used as for the protection of non-metallic materials. An essential requirement for such biocides is that they should not be aggressive to metals and not cause their corrosion, since some biocides are corrosive in this respect [6–7].

In this article, we tried to reveal the main points of identifying the characteristics of new inhibitors of biocorrosion of oilfield equipment and oil storage facilities based on acetylene alcohols, diols and establishing their minimum concentrations that ensure the maximum death of biocorrosion agent bacteria. The problem was solved by synthesizing acetylenic compounds [8]: acetylenic alcohols and diols, as well as by studying their effect on the vital activity of microorganisms - the main pathogens of biocorrosion of oilfield equipment, pipelines and oil storage facilities.

Among the studied compounds, 1-phenyl-3-methylpentyn-1-ol-3 is synthesized conveniently, in a single step, based on phenylacetylene and methyl ethyl ketone and was used as an inhibitor of the vital activity of microorganisms that cause biocorrosion of oilfield equipment, which causes their 100% death.

It has been established that the main causative agents of aerobic corrosion in air are iron bacteria, and in anaerobic (in an airless environment) corrosion - sulfate-reducing bacteria assigned to the genera Desulfovibrio and Desulfotmaculum.

A thorough study of the quantitative and qualitative composition of the microflora isolated from scrapings showed that the largest number of participants in the process of oil destructurization and biocorrosion of metal surfaces are bacterial families: Pseudomonaceae, Micrococcaceae, Rhodococcaceae, Vibrionaceae, Desulfovibrioceae.

Based on the study of cultural and morphological and physiological characteristics, the identified pure cultures of bacteria were assigned to the genera: Pseudomonas, Arthrobacter, Micrococcus, Acinetobacter, Rhodococcus, Desulfovibrio.

Bacteria of the Pseudomonas family were isolated from all scraping samples taken from the Kokdumalak and Northern Urtabulak deposits. Most strains of these families belong to the genus Pseudomonas, species Ps.aeruginosa. Grayish-white colonies of bacteria of the genus Desulfovibrio were most often isolated from water-oil emulsions of the Kokdumalak field. From scrapings taken from the internal surfaces of oilfield equipment, bacteria of the genera Arthrobacter, Acinetobacter, Micrococcus, etc. were isolated in a smaller amount. Microscopic fungi and actinomycetes were isolated in mass quantities.

The following is a taxonomic description of bacteria found in water-oil emulsions and scrapings (adhesive forms) from metal equipment.

The bacterial species Pseudomonas putida was isolated from the Kokdumalak oilfield equipment. Colonies coral pink, oily, mucilaginous and pasty. Cells of cultures 16-20 hours old are long (0.8-13 x 16-35 μm), profusely branching, often with vacuolated protoplasm. Fast By 24-30 hours of growth, the filaments are fragmented; colonies 3-8 days old consist of coccoid oval cells, non-acid-resistant. Glucose, sucrose, lactose, arabinose, galactose, sorbitol are acidified, mannitol and inositol are not acidified. Assimilate sodium salts of citric, acetic and succinic acids, identified as Rhodococcus sp.

The belonging of this isolate to the genus Rhodococcus was confirmed experimentally.

Bacterial species Desulfovibrio vulgaris was isolated from scrapings of oilfield equipment "Kokdumalak". The colonies are orange-yellow on peptone agar and wort agar. The cells are rod-shaped, V-shaped and palisade-shaped. By 19 o'clock, they already break up into short rods and cocci, form acid from glucose, arabinose, galactose, mannitol, sorbitol, sucrose, but do not form from lactose. Assimilate sodium salts of citric, acetic and succinic acids except tartaric.

All of the above isolates actively degrade oil. The oil film is destroyed, and at the same time, turbidity and flakes appear. Oil on the walls disappears and culture liquids without hydrocarbons are formed in the liquid.

The study of the morphological, cultural, and physiological-biochemical properties of bacteria and their relationship to oil hydrocarbons showed that all isolates assimilate crude oil well as the only source of carbon nutrition.

Rhodococcus eruthropolis bacterial species was isolated from Severny Urtabulak oilfield equipment. Bacteria grow well on oil and oil products, being their active destructors. The oil-oxidizing microorganisms of the genera Pseudomonas, Rhodococus, and Arthrobacter isolated by us can be used in the development of domestic oil-oxidizing biological preparations. Local strains of bacteria are most suitable for introduction into the external environment compared to imported ones, since they are well adapted to local climatic conditions: high temperatures, drying, ultraviolet radiation, high salinity, etc. Rhodococcus dominated with pinkish colonies, similar in many ways to Rhodococcus erythropolis.

The proposed biocides are mainly synthesized on the basis of industrial products of the republic, they are cheaper, technologically convenient, at low concentrations (10-15 mg/l) they exhibit 100% bacteriostatic and bactericidal activity.

Mass sampling was carried out at an ambient temperature of 8-40 ^{0}C. Samples for the isolation of corrosion agents were taken from the surface (scrapings) of oil pipelines, pumps, operating wells, oil tanks and other equipment of oil fields. Microbiological seeding was carried out on liquid and solid Raymond mineral media of composition (g/l): KNO_3-1,0; Na_2HPO_4-0,8; K_3PO_4-0,14; $MgSO_4$-0,1; NaCl-1,0; distilled water - 1 part; sterile oil - 1-1.5%. Petri dishes with inoculation were inoculated in a thermostat at a temperature of 20-30 ^{0}C, then in a polythermostat.

More than ninety pure bacterial cultures were isolated from the selected samples. To do this, individual colonies grown on a solid nutrient medium were inoculated on slant agar in test tubes. If the growth along the stroke is homogeneous, then a suspension of microorganisms was prepared from this test tube and again inoculated on a solid medium in cups. The grown colonies were uniform in appearance. The purity of the culture was monitored under a light microscope. Cultural, morphological and physiological properties of bacteria isolated in pure culture were studied according to the guidelines of F.M. Gerhardt [9] and N.S. Egorov [10]. Identification of isolated and studied bacteria was carried out according to the determinant of D. Bergey [11].

Example-1. 1-phenyl-3-methylbutyn-1-ol-3 at a concentration of 40 mg/l was added to a sterile flask with Raymond's elective nutrient medium (control) from test tubes with a bacterial suspension: one drop (0.20 ml) was applied to the cup Petri with medium. The same flask with Raymond agar medium in an amount of 1 L was prepared with the addition of 1-phenyl-3-methyl-butyn-1-ol-3 at concentrations up to 100 mg/L. Next, the

agar medium with the inhibitor was poured into Petri dishes, on the surface of which one drop (0.20 ml) of the bacterial suspension prepared in sterile test tubes was applied. Petri dishes were placed in a thermostat at 26-28 0C, the growth of the colony was monitored for 7 days. As a result of the experiments, it was found that out of the tested concentrations at a concentration of 40 mg/l, the growth of bacterial colonies is absolutely absent, therefore, this concentration is a lethal concentration that ensures 100% death of bacteria that cause corrosion. Example-2. 1-Phenyl-3-methylpentyn-1-ol-3 was added to a sterile flask with Raymond's elective nutrient medium (control) at a concentration of 20 mg/l. One drop (0.20 ml) was applied from the test tubes with the bacterial suspension onto a Petri dish.

The same flask was prepared with 1 L of Raymond agar medium supplemented with 1-phenyl-3-methylpentyn-1-ol-3 at concentrations up to 60 mg/L. Next, the agar medium with the inhibitor was poured into Petri dishes, on the surface of which one drop (0.20 ml) of the bacterial suspension prepared in sterile test tubes was applied. Petri dishes were placed in a thermostat at 26-28 0C. Observations of the growth of colonies were carried out for 7 days. As a result of the experiments, it was found that out of the tested concentrations at a concentration of 20 mg/l, the growth of bacterial colonies is absolutely absent, therefore, this concentration is a lethal concentration that ensures 100% death of corrosion pathogen bacteria.

Example-3. Hexine-3-diol-2.5 at a concentration of 500 mg/l was added to a sterile flask with Raymond's elective nutrient medium (control). From test tubes with bacterial suspension, one drop (0.20 ml) was applied to a Petri dish.

The same flask was prepared with 1 L of Raymond agar medium supplemented with hexine-3-diol-2.5 at concentrations up to 20,000 mg/L. Next, the agar medium with the inhibitor was poured into Petri dishes, on the surface of which one drop (0.20 ml) of the bacterial suspension prepared in sterile test tubes was applied. Petri dishes were placed in a thermostat at 26-28 ^{0}C. Observations of the growth of the colony were carried out for 7 days.

As a result of the experiments, it was found that from the tested concentrations at a concentration of 500 mg/l, the growth of bacterial colonies decreases, therefore, this concentration is a lethal concentration that provides 25% death of bacteria that cause corrosion.

Example-4. Butin-3-ol-2 at a concentration of 400 mg/l was added to a sterile flask with Raymond's elective nutrient medium (control), and one drop (0.20 ml) from test tubes with a bacterial suspension was applied to a Petri dish.

The same flask was prepared with 1 L of Raymond's agar medium supplemented with butyn-3-ol-2 at concentrations up to 4000 mg/L. Next, the agar medium with the inhibitor was poured into Petri dishes, on the surface of which one drop (0.20 ml) of the bacterial suspension prepared in sterile test tubes was applied. Petri dishes were placed in a thermostat at 26-28 ^{0}C. Observations of the growth of the colony were carried out for 7 days.

As a result of the experiments, it was found that from the tested concentrations at a concentration of 400 mg/l, the growth of bacterial colonies decreases, therefore, this concentration is a lethal concentration that provides 20% death of bacteria that cause corrosion.

Example-5. Butyne-2-diol-1,4 was added at concentrations up to 1000 mg/l to a sterile flask with Raymond's elective nutrient medium (control), and one drop (0.20 ml) from test tubes with a bacterial suspension was applied to a Petri dish.

The same flask was prepared with 1 L of Raymond agar medium supplemented with butyn-2-diol-1,4 at concentrations up to 5000 mg/L. Next, the agar medium with the inhibitor was poured into Petri dishes, on the surface of which one drop (0.20 ml) of the bacterial suspension prepared in sterile test tubes was applied. Petri dishes were placed in a thermostat at 26-28 0C. Observations of the growth of colonies were carried out for 7 days.

As a result of the experiments, it was found that out of the tested concentrations at a concentration of 1000 mg/l, the growth of bacterial colonies decreases, therefore, this concentration is a lethal concentration that ensures 10% death of bacteria that cause corrosion.

Based on the studied acetylenic compounds, the following biocorrosion inhibitors have been developed: 1-phenyl-3-methylbutyn-1-ol-3; hexine-3-diol-2.5; butin-3-ol-2; butin-2-diol-1.4; 1-phenyl-3-methylpentyn-1-ol-3. Their action on sulfate-reducing bacteria, the main causative agents of biocorrosion of oilfield pipelines, has been established. The results obtained are presented in table.1.

In the studies, nutrient media of Raymond and Muntz were used with the addition of the above-synthesized preparations at concentrations from 1 mg/l to 1000 mg/l with an interval of 20 mg/l. The same nutrient media, but without the addition of biocides, served as the control.

Because of studying the effect of anti-corrosion preparations on the vital activity of sulfate-reducing bacteria, their bacteriostatic and bactericidal activities were determined. Among the studied biocides, 1-phenyl-3-methylpentyn-1-ol-3 proved to be the most effective and promising in combating microbial corrosion of oilfield equipment.

In this direction - on the synthesis and study of the properties of acetylene compounds, work continues [12-15] and we will report on the results obtained in the following works.

Table 1.

Bactericidal and bacteriostatic activities of new inhibitors biological corrosion of metals

№	New inhibitors	Bacteriostatic activity			Bactericidal activity		
		Concentra-tion, mg/l	bacterial cells, %		concentration, mg/l	bacterial cells, %	
			alive	dead		alive	dead
1	1-phenyl-3-methylbutyn-1-ol-3	40	0	100	100	0	99,9
2	1-phenyl-3-methylpentyn-1-ol-3	20	0	100	60	0	100
3	hexine-3-diol-2,5	500	75	25	20000	90	10
4	butin-3-ol-2	400	80	20	4000	93	7
5	butin-2-diol-1,4	1000	90	10	5000	88	12

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