QO‘QON DAVLAT PEDAGOGIKA INSTITUTI ILMIY XABARLARI
(2025-yil 1-son)

TABIIY FANLAR

NATURAL SCIENCES

APPLICATION OF ACETYLENE ALCOHOL BASED CORROSION INHIBITORS IN THE OIL AND GAS INDUSTRY

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ABSTRACT In this study, the use of acetylenic alcohols synthesized from benzaldehyde derivatives in the EtMgBr/Ti(OiPr)4/PhMe catalytic system as inhibitors in the oil and gas industry was investigated. It was analyzed that the synthesized inhibitors retain layer-forming ions in wastewater from the oil and gas industry. It was found that the use of acetylenic alcohols as inhibitors reduces the formation of scale-forming salts of calcium carbonate, calcium sulfate, calcium bicarbonate and calcium phosphates in equipment by up to 74%.

Keywords: acetylene alcohol, biological activity, oil, gas, waste water, inhibitors, salts.

INTRODUCTION

Technological devices, equipment and metal structures used in the extraction, transportation, storage and processing of oil and oil products are subject to biocorrosion under the influence of various microorganisms [1, 2].

Biocorrosion is the destruction of corrosion-resistant surfaces of metal and steel structures and materials under the influence of microorganisms (bacteria, fungi, lichens, algae). As a result of the combined action of all microorganisms in the process of biocorrosion, they are divided into aerobic and anaerobic types [3, 4, 5].

Identification of microorganisms found in oil and oil products, their types and composition, and the study of the causes of biocorrosion are important scientific and practical problems awaiting solution [6, 7].

Biocorrosion of metals is a process that can be caused by the action of various bacteria. These bacteria significantly increase the corrosion of metals in oil production and in seawater. The bacteria replace hydrogen, creating a pit of damage with increased metal corrosion at the anode location.

Microorganisms in jet fuel cause severe corrosion of aluminum fuel tanks. In most cases, they are present in a passive state in steel, aluminum, zinc, magnesium, and chrome-plated nickel. They are not found in metals such as stainless steel, copper, nickel, and lead.

Iron, zinc, copper, cadmium, and aluminum can be affected by rubber and Teflon, polyamide and polystyrene, paint and epoxy coatings, and oak as inhibitors. Other products have little effect on these metals. Zinc impregnated with phenol-formaldehyde mass or binder causes corrosion at a rate of ~3.7 mkm/(ms), copper at 0.3 mkm/(m s) (relative humidity 100%, temperature 35 °C).

The corrosive effect of plastics on metals is especially strong in places where the gap between the plastic and metal does not exceed 5-10 mm. In this case, steel corrodes at a rate of 0.5-1 mkm per month, zinc at a rate of 0.5-20 mkm, copper at a rate of 0.1-1.5 mkm, and aluminum at a rate of 0.05-0.2 mkm per month.

One of the main reasons for premature failure of pipes is the high aggressiveness of well products. The most aggressive source of water is wastewater used in pressure maintenance systems in oil and reservoir tanks. The service life of wastewater injection pipes in some cases is only 1.5–2 years instead of the designed 10–15 years [8]. In addition, acid treatment of well bottomhole zones is currently one of the most common methods for enhancing oil recovery from low-permeability carbonate and mixed formations [9, 10]. However, this leads to intense corrosion of metal equipment. The use of inhibitors is one of the most effective methods for combating metal corrosion in various aggressive environments [11]. Pyrans, pyrenes, dioxanes, phenols, cyclic and linear ethers, allyl alcohols, benzaldehydes and benzoic acid esters, alcohols, furans, dioxolanes, acetals, dioxocyclanes, etc. cannot be used as inhibitors, since they do not have a sufficient protective effect. Even in the conditions of an oil and gas production department or field, when using inhibitors, this indicator can vary significantly in different areas [12, 13, 14].

MATERIALS AND METHODS

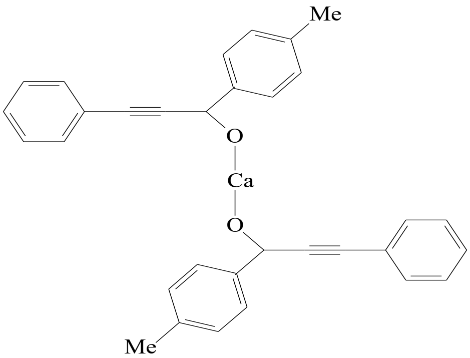
Synthesis of acetylenic alcohols: 200 ml in a five-necked flask (reactor) with a total capacity of 2500 ml. Two TS24/40 dropping funnels, a Dimrota cooler with a cooling surface of 0.084 m^2, a 2-Channel thermometer and a stirrer (Eurostar 20/PTFE70.15.600/5000) were installed. Initially, 0.025 mol (7.6 ml) of $Ti(O^iPr)_4$ and 0.15 mol (16.0 ml) of PhMe were added to the reactor through the first dropping funnel, and a solution of $Ti(O^iPr)^4$ in toluene was prepared over 30 minutes. To the prepared solution 0.3 mol (38.7 ml) of EtMgBr and 0.3 mol (33.0 ml) of phenylacetylene were added in an equimolar ratio over 30 minutes. Then the catalyst in the reactor, namely FA, $Ti(O^iPr)_4$, PhMe and EtMgBr, was continuously stirred for 30 minutes at a temperature of -10 °C. To the obtained catalyst 0.1 mol (10.6 ml) of benzaldehyde was added dropwise over 30 minutes using a second dropping funnel. After complete addition of benzaldehyde, the entire system in the reactor was stirred for 60 minutes. The temperature was maintained at -10 °C using liquid nitrogen, and hydroquinone was added to prevent polymerization. Then the reaction was stopped by adding 5% HCl solution to the system and leaving it for 18 hours at a temperature of 0 °C. After separating the organic portion of the settled mixture in a flask, the aqueous portion was extracted with DEA (3x50 ml). The organic layer was washed with a weak solution of sodium chloride and dried over MgSO4 for

360 min. The organic portion of the resulting system was separated into individual fractions by vacuum distillation. As a result, 18.9 g of 1,3-diphenylpropyn-2-ol-1 were synthesized with a yield of 91% [15, 16]. Four types of acetylenic alcohols used as objects of study (inhibitors) by this method include 1-(4-methylphenyl)-3-phenylpropyn-2-ol-1, 1-(4-chlorophenyl)-3-phenylpropyn-2-ol-1, 1-(3-methoxyphenylheptynyl)-3-phenylpropyn-2-ol-1 and 1-(4-fluorophenyl)-3-phenylpropyn-2-ol-1 were synthesized.

Application of synthesized acetylenic alcohols as inhibitors: in this work, the following acetylenic alcohols were synthesized in the EtMgBr/Ti(OiPr)4/PhMe catalytic system: 1-(4-methylphenyl)-3-phenylpropyn-2-ol-1, 1-(4-chlorophenyl)-3-phenylpropyn-2-ol-1, 1-(3-methoxyphenylheptynyl)-3-phenylpropyn-2-ol-1 and 1-(4-fluorophenyl)-3-phenylpropyn-2-ol-1 were used as inhibitors against scale-forming components in wastewater generated in the oil and gas industry. The object of the study was wastewater generated in metal structures and pipelines of “Gissarneftegaz” JV LLC. Pilot industrial tests of a fire-regenerating device against salt deposits formed under the influence of wastewater on metal equipment and pipelines of the “Gissarneftegaz” were conducted.

RESULTS AND DISCUSSION

The obtained results show that the proposed inhibitors bind metals, forming phosphates, carbonates, hydrocarbons and sulfates, forming chelates. It was noted that acetylene alcohols, selected as inhibitors, bind calcium ions and form water-soluble chelates (**1-4**). It was found that these compounds reduce scale formation in devices by up to 74%, which leads to the formation of calcium carbonate, calcium sulfate, calcium bicarbonate and calcium phosphates.



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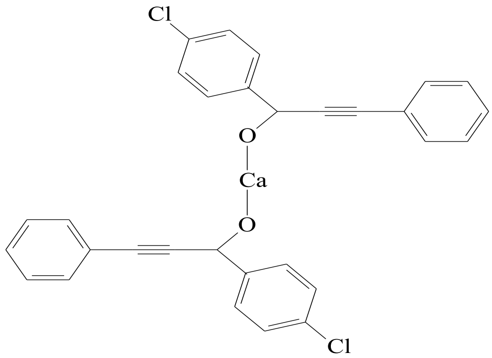

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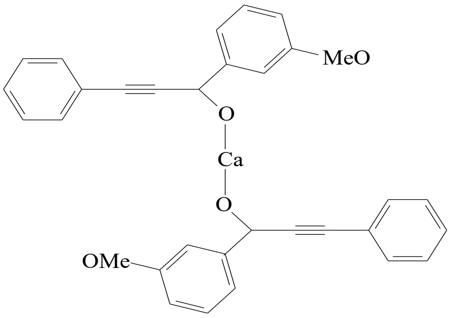

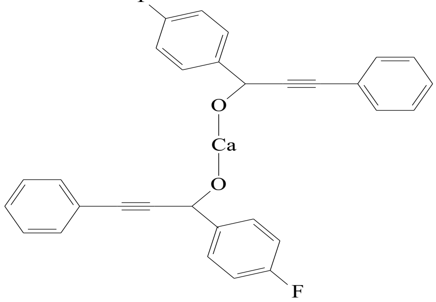

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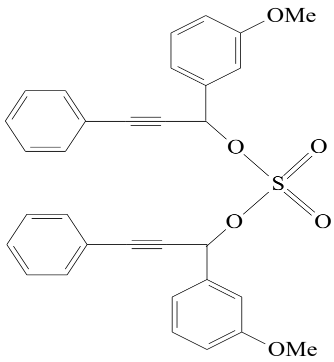
These acetylenic alcohols have also been found to combine with sulfate, carbonate, and phosphate ions in wastewater to form readily soluble esters (**5-7**), which reduce the amount of salt formation by up to 88%. An example is the esters of 1-(3-methoxyphenylheptynyl)-3-phenylpropyn-2-ol-1.



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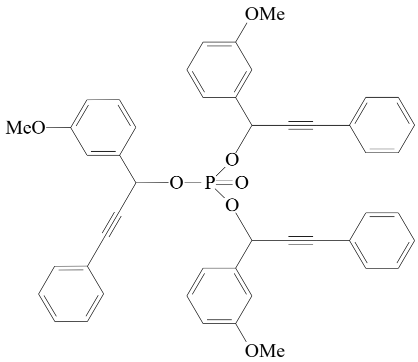

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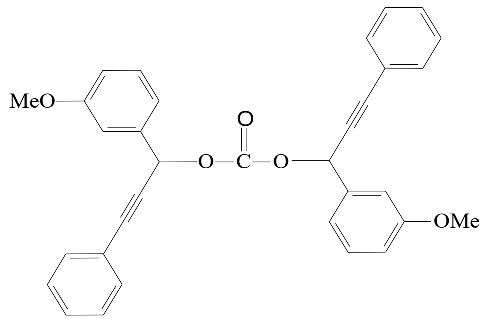

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Samples were taken from the recycled wastewater of “Gissarneftegaz” LLC taken as the object of study and their hardness was studied. The water hardness of the selected regions was determined. The studies were conducted using solutions of the selected inhibitors with a concentration of 25.0 mg/l (see table).

It was established that the proposed inhibitors have high selectivity in retaining layer-forming ions in wastewater due to the formation of complexones and esters with calcium, magnesium, barium and sodium cations, as well as sulfate, carbonate, phosphate, hydrophosphate and bicarbonate anions.

Salt-forming ions and their formation of chelates in the circulating wastewater of the “Gissarneftegaz” LLC*

Layer-forming ions	**1 liter. amount of ions in water, g**	**Amount of neutralized ions, g**	**Amount of ions forming a layer, g**	**Efficiency, %**
Calcium	26,2	19,39	6,81	74
Magnesium	6,3	3,91	2,39	62
Barium	17,2	12,04	5,16	70
Sodium	1,4	0,78	0,62	56
Sulfate	4,2	3,15	1,05	75
Carbonate	7,9	6,95	0,95	88
Phosphate	2,3	1,47	0,83	64
Hydrophosphate	1,2	0,96	0,24	80
Hydrocarbonate	0,86	0,46	0,40	54

**in the example of 1-(3-methoxyphenylheptynyl)-3-phenylpropyn-2-ol-1 (25,0 mg/l.)*

Based on the obtained results, the efficiency of the selected preparations against the formation of complex salts, layers and sediments in industrial wastewater was determined. The efficiency against the formation of layers and deposits is as follows: 1-(4-methylphenyl)-3-phenylpropyn-2-ol-1<1-(4-chlorophenyl)-3-phenylpropyn-2-ol-1<1-(4-fluorophenyl)-3-phenylpropyn-2-ol-1<1-(3-methoxyphenylheptynyl)-3-phenylpropyn-2-ol-1. In particular, it was found that 1-(3-methoxyphenylheptynyl)-3-phenylpropyn-2-ol-1 neutralizes on average 74% of layer-forming components by binding with metal ions and anions of acidic residues in wastewater, and is also used in the chemical industry.

Recommended for use as an inhibitor against components that form salt deposits in metal equipment of enterprises.

CONCLUSIONS

In this research work, relevant studies were conducted on the use of acetylene alcohols as inhibitors and active agents in the oil and gas industry. The research of domestic and foreign scientists on the use of acetylene alcohols as inhibitors is analyzed. For the synthesis of acetylene alcohols, R-substituted benzaldehyde derivatives were selected and their alkynylation reactions were carried out in the selected catalytic system. As a result, four types of acetylene alcohols were synthesized, each of which contains several active reaction centers in its molecule. The range of efficiency of the synthesized acetylene alcohols as inhibitors was determined. The synthesized acetylene alcohols found practical application as anti-ionites against scale-forming components in wastewater from oil and gas industry enterprises and are recommended for industrial production.

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