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PREPARATION OF OLEIC ACID–BASED CORROSION INHIBITOR REAGENTS FOR APPLICATION IN VARIOUS AGGRESSIVE ENVIRONMENTS OF THE OIL AND GAS INDUSTRY

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ABSTRACT

In the present study, the protective efficacy of conservation fluids formulated from bisimidazoline derivatives synthesized via the reaction of oleic acid with polyethylenepolyamine and triethylenetetramine in a 2:1 molar ratio was systematically investigated under various corrosive conditions, including hydrochamber exposure, seawater immersion, and in a 0.001% sulfuric acid solution. The resulting formulations were prepared at 5 and 10 % concentrations in a T-30 oil distillate matrix and applied for temporary corrosion protection of metallic surfaces. Experimental results showed that the T-30 oil distillate alone, in the absence of any corrosion inhibitor, exhibited minimal protective capability, providing surface protection for only 9–34 days. In contrast, formulations incorporating bisimidazoline derivatives particularly those containing 10% concentrations of polyethylenepolyamine- and triethylenetetramine-based compounds achieved continuous protective performance exceeding 300–400 days across all tested environments. The relative extension of the protection period was estimated to be approximately 10- to 23-fold. Furthermore, imidazolines synthesized using polyethylenepolyamine exhibited superior corrosion inhibition performance compared to those derived from triethylenetetramine, which can be attributed to their higher density of functional groups and enhanced coordination capability with metal surfaces. Consequently, these imidazoline-based formulations represent effective and practical candidates for temporary corrosion protection in atmospheric and aqueous environments.

Keywords: atmospheric corrosion; conservation fluids; bisimidazoline; polyethylenepolyamine; triethylenetetramine; conservation time; inhibitor effectiveness.

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1. Introduction

Since the corrosion process reduces the durability of industrial equipment, leading to economic losses and safety issues, its prevention is of great importance in modern technologies [1].

Rapid technological advancements in developed nations, coupled with the extensive deployment of diverse technical equipment, necessitate their effective protection against atmospheric corrosion during both operational service and periods of inactivity. In particular, the prolonged storage of agricultural and military equipment under conservation conditions throughout the year makes the implementation of corrosion mitigation strategies critically importance.

Atmospheric corrosion is recognized as the most prevalent form of electrochemical corrosion. It primarily occurs under humid atmospheric conditions at ambient temperatures, and exhibits several distinct characteristics [1].

The atmospheric environment typically contains oxygen, carbon dioxide (CO_2), water vapor, and various aggressive ions. The synergistic action of these constituents facilitates chemical and electrochemical reactions on metal surfaces, thereby promoting rust formation and accelerating corrosion. Notably, the thin moisture film formed on metallic surfaces is a critical factor that enhances the severity of this phenomenon.

The oxide layer and other corrosion products formed during atmospheric corrosion generally possess a more compact structure and exhibit stronger adhesion to the substrate than analogous layers formed in soil or bulk electrolyte environments. This behavior is primarily attributed to the presence of only a thin electrolyte film under atmospheric conditions, which promotes localized corrosion processes [2].

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carbon dioxide (CO_2), water vapor, and various aggressive ionic species. The combined action of these constituents induces chemical and electrochemical reactions on metal surface, thereby facilitating rust formation and accelerating corrosion. In particular, the presence of a thin moisture film on the metal surface is a critical factor that significantly intensifies these reactions [3].

The oxide layer and other corrosion products formed during atmospheric corrosion generally exhibit a denser structure and superior adhesion to the substrate than analogous layers formed in soil or bulk electrolyte environments. This phenomenon is primarily attributed to the fact that, under atmospheric conditions, the metal surface is covered only by a thin electrolyte film, which promotes localized and heterogeneous corrosion processes [2].

In this form of corrosion, the absence of a continuously replenished bulk electrolyte – meaning that the metal is exposed to natural atmospheric conditions without complete immersion – results in a relatively slower and more controlled progression of corrosion reactions. Consequently, the corrosion products formed tend to exhibit a more compact morphology and stronger adherence to the underlying metal surface.

The primary objective of mitigating atmospheric corrosion is to protect metallic surfaces from aggressive environmental factors and thereby extending the service life of technical equipment by suppressing corrosion processes [3, 4].

The principal environmental factors influencing the initiation and progression of atmospheric corrosion include relative humidity, temperature fluctuations, and the presence of various aggressive chemical species in the atmosphere. Significant variations in these parameters across different geographical regions considerably complicate the monitoring and prevention of corrosion on metallic surfaces [5].

Accordingly, the allocation of substantial financial resources for the protection of metal structures and technical systems underscores the critical importance of corrosion control and its strategic significance in scientific and technological development.

The widespread use of conservation materials helps mitigate both direct and indirect economic losses caused by atmospheric corrosion. Consequently, the development of next-generation corrosion inhibitors that are cost-effective and environmentally benign is regarded as a priority research direction in contemporary materials science and corrosion engineering [6-15].

In this context, significant research efforts in Azerbaijan have focused on the development and application of highly effective corrosion inhibitors for the temporary protection of metallic equipment and industrial infrastructure.

In study [16], the co-authors synthesized the amidoamine of soybean oil acid with 1.6-diaminohexane at a 1:1 molar ratio and prepared its compositions with various fatty acids (cottonseed, soybean, sunflower, corn). These compositions were incorporated into a T-30 oil distillate and evaluated as conservation fluids. The results showed that the composition based on soybean oil acid amidoamine and sunflower oil acid at 10% concentration provided protection periods of 291, 112, and 107 days for Steel-3 panels in a Q-4 thermo-humidity chamber, seawater, and 0.001% H_2SO_4 solution, respectively.

V. M. Abbasov and co-authors [17] investigated nitrocompounds obtained via the nitration of mineral oil, both individually and in combination with cobalt, nickel, and magnesium salts of petroleum acids, as corrosion inhibitors in conservation fluids. A composition of the nitrocompound synthesized from α-olefin ($C_{14}H_{28}$) and an amide in T-30 oil distillate was evaluated as a conservation fluid, and it was established that the mixture containing 3.5% nitrocompound and 3.5% amidoamine exhibited a synergistic effect in various media (hydraulic chamber, seawater, sulfuric acid solution).

In the work of U. B. Abbasova [18], amidoamine was synthesized from natural petroleum acids with ethylenediamine, and alkylamides were synthesized with propylamine, dipentylamine, octylamine, and nonylamine. Conservation fluids were prepared by incorporating 5–20 % of these compounds into T-46 oil distillate. The study showed that 2.5% amidoamine and 2.5% nonylamide demonstrated the best protection, while higher concentrations (10%) ensured even longer protection times: 223 days in the hydraulic chamber, 115 days in seawater, and 110 days in 0.001% H_2SO_4 solution.

In the study by Y. J. Aghazada [19, 20], compositions of oxidized liquid rubber, polyethylene polyamine complexes with petroleum acids, and nitrocompounds derived from α-olefins were prepared in T-30 turbine oil and tested as conservation fluids. By adding 10% paraffin (by weight), conservation lubricants were obtained. The results showed that the composition of the inhibitor with nitrocompound and oxidized liquid rubber provided higher protection (up to 476 days) compared to their individual use.

In the work of N. S. Rzayeva [21], amides based on sunflower oil acids and PEPA, as well as nitrocompounds based on C_{16}–C_{18} α-olefins, were synthesized. Their compositions with T-30 oil were tested as conservation fluids, and the results showed that the protective effect was enhanced when the amide and nitrocompound were used in combination. For example, the amide synthesized at a 2:1 molar ratio, when added at 10% concentration into T-30 oil distillate, provided protection for 57 days in a 0.001% H_2SO_4. However, when the same amide (5%) and nitrocompound (5%) were used together, the protection period increased to 91 days.

As evidenced by the foregoing, the most appropriate strategy for the temporary conservation of metal equipment against atmospheric corrosion involves the use of conservation fluids.

In the present study, nitrogen-containing organic derivatives of oleic acid were synthesized to mitigate atmospheric corrosion. These compounds were formulated in T-30 oil and evaluated as conservation fluids under controlled conditions in a «G-4» hydrochamber, in seawater, and in a 0.001% H_2SO_4 solution.

2. Materials and methods

The reagents employed in the synthesis of the conservation fluids were procured from Sigma-Aldrich.

1. Infrared (IR) spectra were recorded in the range 400–4000 cm^{-1} on an ALPHA FT-IR spectrometer (Bruker, Germany); the spectrum is shown in figure 1.
2. ^1H NMR spectra were acquired on a Bruker Fourier 300 spectrometer operating at 300.18 MHz (^1H) at ambient temperature using $CDCl_3$ as solvent; chemical shifts (δ) are reported in ppm relative to the residual $CHCl_3$ signal (δ=7.26 ppm). The spectrum is presented in figure 2.

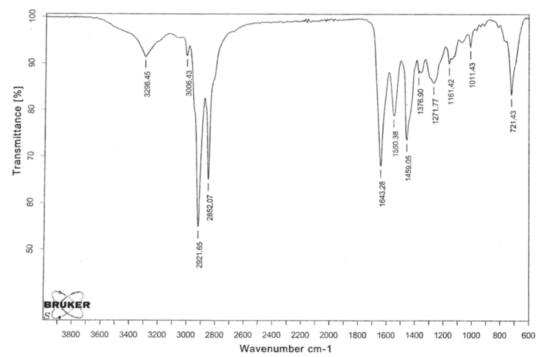


Fig. 1. Graphical representation of the IR spectrum of bisimidazoline synthesized from PEPA and oleic acid

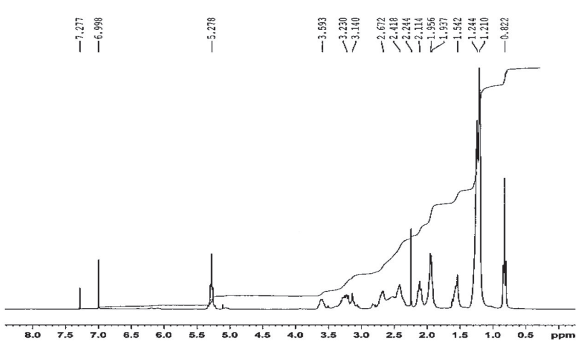


Fig. 2. ^{1}H NMR spectrum of the bis-imidazoline obtained from PEPA and oleic acid

3. High-resolutionmass spectra were acquired using the Agilent 6224 LC/MS spectrometer, operating in both positive and negative modes.
4. The corrosion protection properties of the conservation fluids were evaluated in accordance with the requirements of GOST 9054-75. The experiments were conducted in a «Q-4» hydrochamber under conditions of high relative humidity (98–100 %) and a temperature of 40±1 °C, with periodic condensation of moisture on the protected metal surfaces.

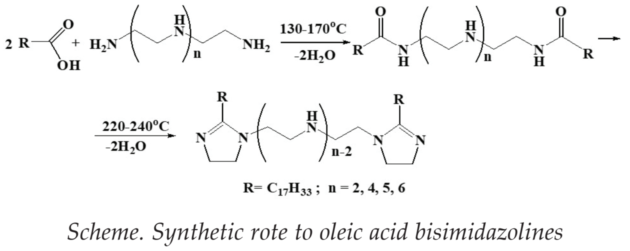
In accordance with this standard, additional tests were performed in seawater (Caspian Sea water) and in a 0.001% H_2SO_4 solution. Steel-3 samples with dimensions of 40×5×0.3 mm were used for the evaluations. Prior to testing, the surfaces of the steel specimens were mechanically polished using a polishing machine, subsequently degreased with absolute ethanol, and immersed in the conservation fluid for 1 hour. Thereafter, the specimens were removed, air-dried for 24 hours, and subsequently exposed to a hydrochamber, seawater, and 0.001% H_2SO_4 solution. The exposure was continued until the initial manifestation of corrosion was observed.

In parallel, control tests were conducted using T-30 mineral oil distillate without the addition of inhibitors (i.e., without the synthesized compounds and their respective formulations).

3. Experimental part

In the initial stage of the study, bisimidazoline derivatives were synthesized via condensation reactions of oleic acid with polyethylenepolyamine (PEPA) and triethylenetetramine (TETA). The imidazolines were synthesized at a temperature of 220–240 °C over a period of 5–7 hours. The yield of the synthesized bisimidazolines was found to be 90–91 %.

The condensation reaction of oleic acid with polyamines proceeds according to scheme.



Scheme. Synthetic rote to oleic acid bisimidazolines

Synthesis of N1,N2-bis(2-(2-((Z)-heptadec-8-enyl)-4,5-dihydroimidazol-1-yl)ethyl)ethane-1,2-diamine (Bisimidazoline-PEPA-6)

Synthesis of oleic acid bisimidazolines involved a two - step reaction, including amidation and followed by cyclization to form bisimidazoline rings, as illustrated in scheme. The oleic acid (20 mmol) was added to a three-necked round-bottomed flask equipped with of a Dean–Stark trap. The pentaethylenehexamine (10 mmol) was added dropwise and mixture was stirred for 4 h with continuous reflux at 130-170 °C. The mixture's color slightly changed to dark yellow. Then temperature increased to 240 °C for 5 h. Finally, the bisimidazoline product was obtained as a dark yellow wax in 90 % yield.

Figures 1 and 2 present the IR and ^{1}H NMR spectra, respectively, of the bisimidazoline synthesized from oleic acid (OA) and PEPA. The IR spectrum exhibits the characteristic absorption bands, while the ^{1}H NMR spectrum displays the corresponding proton signals.

IR, The absorption bands observed in the spectrum at 1545 and 3286 cm^{-1} are attributed to the deformation and stretching vibrations of N–H bonds, respectively. The band at 1646 cm^{-1} corresponds to C=N bonds. The band at 1129 cm^{-1} corresponds to $C_{(aliphatic)}$–N bonds. N bonds, while the band at 1297 cm^{-1} is attributed to the stretching vibrations of $C_{(cyclic)}$–N bonds. The bands at 1371 and 1453 cm^{-1} correspond to the deformation vibrations, while those at 2815, 2857, and 2873 cm^{-1} correspond to the stretching vibrations of C–H bonds in CH_2 groups. Thus, FTIR spectroscopy confirms the formation of C=N bonds, indicating the formation of an imidazoline ring.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.36−5.22 (m, 4H, −CH=CH−), 3.69−3.50 (br, 4H, =N−CH_2−), 3.40−3.20 (br, 4H), 3.14 (br, 4H), 2.72−2.69 (m, 4H), 2.60−2.35 (m, 6H), 2.11 (t, J = 7.5 Hz, 4H), 1.95−1.90 (br, 8H), 1.56−1.50 (m, 4H), 1.30−1.20 (m, 40H), 0.822 (t, J = 4.7 Hz, 6H); HRMS (ESI) m/z: (M)+ Calculated for $C_{46}H_{88}N_6$, 724.7077; found 7024.7053.

4. Discussion of the results obtained

The most practical and effective approach for the temporary protection of metallic equipment against atmospheric corrosion is the application of conservation fluids. The protective performance of conservation fluids depends on both the type of oil medium utilized and the specific corrosion inhibitor incorporated; however, the inhibitor plays a predominant role in determining the overall efficacy.

Table 1

Results of corrosion resistance tests (days) of 5 and 10 % solutions in T-30 oil distillate used as conservation fluid

Sample code	«G-4» in hydrochamber	In seawater	In 0.001% H_2SO_4 solution
T-30 oil distillate	34	15	9
No 1	>347	151	147
No 2	340	135	127
No 3	>397	215	211
No 4	>397	192	190

Table 2

Relative increase in conservation time of various compositions in the hydrochamber, seawater, and weakly acidic environment (in times)

Samples	«G-4» in hydro-chamber	Increase in conservation time in seawater	Increase in conservation time in acidic environments
No 1	10.2	10.1 times	16.3 times
No 2	10	9.0 times	14.1 times
No 3	11.7	14.3 times	23.4 times
No 4	11.7	12.8 times	21.1 times

In this study, a series of formulations were prepared based on nitrogen-containing derivatives of oleic acid and T-30 oil distillate as follows:

- Sample No. 1: 5.0% solution of bisimidazoline synthesized from oleic acid and polyethylenepolyamine (PEPA) in a 2:1 molar ratio, formulated in T-30 oil distillate.
- Sample No. 2: 5.0% solution of bisimidazoline synthesized from oleic acid and triethylenetetramine (TETA) in a 2:1 molar ratio, formulated in T-30 oil distillate.
- Sample No. 4: 10.0% solution of bisimidazoline synthesized from oleic acid and PEPA in a 2:1 molar ratio, formulated in T-30 oil distillate.
- Sample No. 5: 10.0% solution of bisimidazoline synthesized from oleic acid and TETA in a 2:1 molar ratio, formulated in T-30 oil distillate.

The results of corrosion resistance tests for these conservation fluid formulations, conducted in the hydrochamber, in seawater, and in a 0.001% H_2SO_4 solution, are presented in table 1.

As evident from table 1, pure T-30 oil distillate was employed as a conventional reference standard for comparative purposes.

The test durations for the unmodified T-30 oil distillate were 34, 15, and 9 days, respectively, under hydrochamber, 0.001% H_2SO_4 solution, and seawater conditions. These results clearly demonstrate that the conservation properties of the pure oil distillate are inadequate, leading to rapid corrosion of metal surfaces in the absence of an inhibitor.

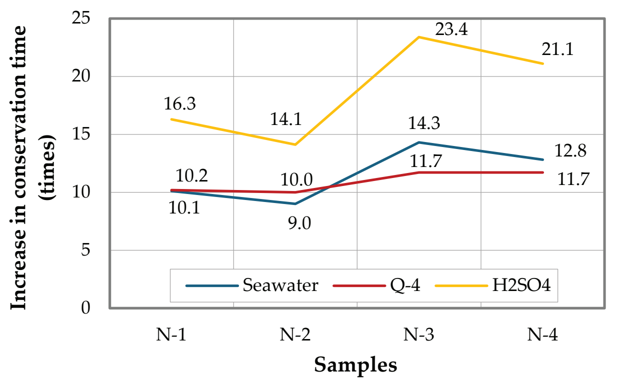


Fig. 3. Relative increase in conservation time (in times) of bisimidazoline-based compositions in various environments

In contrast, formulations containing bisimidazoline-based inhibitors exhibited markedly superior corrosion protection compared to the pure T-30 oil distillate (table 2).

The results presented in table 2 indicate the following:

- An increase in inhibitor concentration leads to a corresponding enhancement in conservation time.
- Compositions based on PEPA (Samples No. 1 and 3) demonstrated higher efficiency compared to those based on TETA (Samples No. 2 and 4) at equivalent concentrations.
- The maximum protective effect was observed for the bisimidazoline composition synthesized with 10% PEPA.

The performance results of the prepared compositions evaluated as conservation fluids in various environments are depicted in figure 3.

The high efficiency of PEPA-based bisimidazolines is attributed to their unique structural and chemical characteristics. PEPA (polyethylenepolyamine)-derived bisimidazolines are structurally multifunctional nitrogen-containing compounds.

Their molecular structure incorporates multiple amine groups, which facilitate strong interactions with the metal surface via donor–acceptor (coordination) bonds, thereby promoting effective adsorption. As a result, PEPA-based bisimidazolines form a dense, uniform, and durable protective film on the metal surface.

Through strong chemisorption, multiple donor nitrogen atoms within the PEPA-based molecules coordinate with the vacant d-orbitals of the metal substrate, resulting in the formation of highly stable coordination complexes. This interaction yields a robust and resilient protective layer that is resistant to degradation.

Moreover, PEPA-based molecules effectively block active corrosion sites on the metal surface, thereby inhibiting both anodic and cathodic electrochemical reactions. This dual inhibition mechanism restricts electron transfer and ion exchange, significantly decelerating the overall corrosion process.

The hydrophobic segment of the bisimidazoline molecule, consisting of the long aliphatic chain derived from oleic acid, imparts water-repellent properties to the surface, reducing interactions between water molecules and the metal. In contrast, the hydrophilic functional groups anchor firmly to the metal substrate, ensuring the stability and integrity of the protective coating.

Conclusion

1. Additionally, PEPA-based molecules possess longer molecular chains and a greater number of functional groups compared to their TETA-derived counterparts. This structural advantage enables them to cover a larger surface area and form a thicker, more coherent molecular barrier.
2. The incorporation of a 10% concentration of inhibitor in the composition facilitates the formation of a denser and more continuous molecular film on the metal surface. This high surface coverage ensures a stable and persistent protective effect, even under highly aggressive conditions such as elevated humidity, saline environments, and acidic media.
3. Accordingly, the 10% PEPA-based bisimidazolines composition (Sample No. 3) exhibited optimal adsorption and passivation behavior on the metal substrate. Owing to its favorable chemical structure and appropriately selected concentration, this formulation achieved maximum protective efficacy across all test environments, including the hydrochamber, seawater, and the weakly acidic solution.

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