

Article

Nitrile-Functional Organosilicon Coating on Steel: Formation, Surface Properties and Corrosion Protection

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Abstract

Organosilane interlayers are widely used to improve the adhesion and corrosion resistance of multilayer protective coating systems. In this work, a nitrile-functional organosilane, 3-[(3-(triethoxysilyl)propyl)amino]propanenitrile (AN), was investigated as a precursor for thin protective coatings on St20 steel and as an adhesion-promoting interlayer for acrylic paint coatings. The coating formation process was optimized, and the structure, morphology, surface properties, adhesion performance, and corrosion resistance of the resulting coatings were comprehensively characterized using spectroscopic, microscopic, and electrochemical techniques. The results demonstrated the formation of a continuous and homogeneous organosiloxane coating with an average thickness of 84 ± 5 nm. Pull-off adhesion tests showed that the AN interlayer provided the highest adhesion strength (0.85 MPa) among the investigated coating systems. Electrochemical impedance spectroscopy and potentiodynamic polarization measurements confirmed a significant improvement in the barrier properties and corrosion resistance of the coated steel in both model and formation water electrolytes. Salt spray testing further demonstrated a more than fivefold reduction in metal mass loss and a substantial decrease in corrosion propagation from an artificial defect compared with the paint-only system. These findings demonstrate that the AN coating is a promising adhesion-promoting organosilane interlayer capable of enhancing both the adhesion and corrosion protection of multilayer coating systems.

Keywords: nitrile functionalization; organic thin films; organosilane coating; thin film deposition; corrosion protection; adhesion promotion

1. Introduction

Ensuring the long-term corrosion protection of metallic materials and industrial equipment remains a major challenge in the petrochemical, mechanical engineering, and precision manufacturing industries. Corrosion not only causes premature equipment failure but also significantly increases maintenance and repair costs [1–3]. Consequently, the development of advanced protective coatings that combine high performance, ease of application, and environmental sustainability has become an important research priority [3]. The long-term durability of metallic structures and the performance of organic coating systems largely depend on the properties of the interfacial layer formed at the metal/coating interface [4–6]. The structure, chemical composition, and physicochemical characteristics of this interfacial region govern coating adhesion, resistance to aggressive service environments, and the initiation and propagation of corrosion processes [4–6].



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Surface pretreatment prior to the application of organic coatings has traditionally relied on conversion coatings based on chromates, phosphates, and other inorganic compounds [7–10]. Although these technologies provide excellent corrosion protection, they typically involve multistep processing, high energy consumption, and the generation of wastewater containing phosphates, nitrates, and heavy-metal ions. These environmental concerns, together with increasingly stringent environmental regulations, have stimulated the search for safer and more sustainable alternatives [7–10].

In recent decades, environmentally benign organosilicon-based coatings have attracted increasing attention as promising alternatives to conventional conversion coatings [8–10]. Among these materials, functional organoalkoxysilanes with the general formula $R_nSi(OR')_{4-n}$, where R denotes an organofunctional substituent and OR' is a hydrolyzable alkoxy group, are of particular interest [11–13]. One of the most important characteristics of organoalkoxysilanes is their ability to spontaneously assemble on metallic surfaces, forming thin siloxane films [12,14–19]. Under aqueous or aqueous-alcoholic conditions, the alkoxy groups undergo hydrolysis to generate silanol groups, which subsequently condense both with one another and with hydroxyl groups present on the metal oxide surface [13,14]. As a result, a three-dimensional cross-linked siloxane network is formed and becomes covalently anchored to the substrate through Me–O–Si metallosiloxane bonds [15,16].

Although organosilane films can provide a certain degree of corrosion protection on their own, they are primarily regarded as functional primers that enhance adhesion rather than as standalone barrier coatings [19]. Their principal role is to establish a chemically bonded interfacial layer between the metal substrate and subsequently applied organic coatings, thereby improving adhesion, suppressing underfilm corrosion, and enhancing the durability of the entire coating system. Consequently, the effectiveness of organosilane pretreatments is determined not only by their intrinsic barrier properties but also by their ability to modify the metal/coating interface and improve the overall performance of multi-layer protective systems [20]. The resulting interfacial layer also acts as an effective barrier against the penetration of water and aggressive ions while simultaneously promoting the adhesion of subsequently applied organic coatings [8,15–22].

The outstanding performance of organoalkoxysilanes is further attributed to their bifunctional molecular architecture and the broad opportunities they offer for chemical modification [11,12,17,21,23–25]. Tailoring the structure of the organofunctional substituent enables precise control over the composition and properties of the resulting coatings, whereas the ability of these molecules to interact with both the inorganic substrate and organic coating components makes them highly effective adhesion promoters [11,12,24,25]. Among the various classes of organosilanes, aminofunctional silanes are of particular practical interest because of their high reactivity during hydrolysis and condensation, as well as their ability to form stable solutions in water and other polar solvents through hydrogen-bonding interactions [23–25]. Among them, 3-aminopropyltriethoxysilane (APTES) is by far the most extensively investigated and widely used compound [25,26].

The presence of a primary amino group enables APTES to serve not only as an effective surface modifier but also as a versatile platform for the synthesis of functional derivatives with tailored properties. Chemical modification of organofunctional silanes represents one of the most effective strategies for tailoring the properties of organosilicon primers, as the nature of the non-hydrolyzable organic substituent largely determines the physico-chemical characteristics of the interfacial layer, its interaction with subsequently applied organic coatings, and ultimately the durability of the entire coating system. Therefore, the targeted modification of APTES provides an opportunity to develop novel organosilicon precursors with enhanced functional performance while preserving the ability of the tri-

ethoxysilyl moiety to undergo hydrolysis, condensation, and the formation of protective siloxane coatings [13,17,25].

One particularly attractive approach involves the reaction of the primary amino group of APTES with acrylonitrile via an aza-Michael addition. This reaction introduces a nitrile functional group into the organic moiety of the molecule while preserving the hydrolyzable triethoxysilyl group responsible for hydrolysis, condensation, and the formation of the siloxane network on the metal surface [25].

The nitrile functional group is characterized by high polarity, excellent chemical stability under the hydrolysis and polycondensation conditions of organoalkoxysilanes, and the presence of a nitrogen atom bearing a lone electron pair. Unlike hydrolyzable alkoxy groups, the nitrile functionality does not participate in the formation of the siloxane network and is therefore expected to remain incorporated within the resulting organosilicon coating. Owing to its high dipole moment, the nitrile group can strengthen intermolecular dipole-dipole interactions between adjacent organosilane molecules, thereby promoting a more ordered organization of the organic component of the coating and potentially enhancing its barrier performance. Furthermore, the retention of the polar nitrile functionality may strengthen the interactions between the organosilane primer and subsequently applied organic coatings, thereby improving interfacial adhesion [23,24].

Despite the widespread use of APTES for the modification of metallic surfaces, reports on the use of its nitrile-containing derivatives as precursors for organosilicon coatings remain scarce. To date, the mechanisms governing the formation of siloxane layers on steel from solutions of such compounds have not been systematically investigated. In particular, the influence of nitrile functionality on the structure, morphology, and properties of the resulting coatings, as well as its role in determining their corrosion-protective and adhesion performance, remains poorly understood. Previous studies on nitrile-containing organosilanes have focused primarily on surface modification and self-assembled silane layers, demonstrating that the introduction of nitrile functionality can alter surface wettability, interfacial interactions, and the characteristics of the resulting films [27–29]. However, the influence of nitrile functionality on the formation and corrosion-protective performance of organosilane coatings on steel has received little attention. Furthermore, no systematic studies have established the relationship between the chemical structure of nitrile-containing APTES derivatives, the mechanisms of surface layer formation, and the resulting functional properties of the coatings. These knowledge gaps motivated the present study, which aims to investigate the formation mechanisms, structure, and corrosion-protective performance of organosilane coatings derived from a nitrile-containing APTES derivative.

Accordingly, the aim of this work was to synthesize a nitrile-functionalized organosilicon precursor based on 3-aminopropyltriethoxysilane and acrylonitrile, fabricate organosilicon coatings on steel from this precursor, investigate the mechanisms of surface layer formation, and evaluate the structure, physicochemical characteristics, and corrosion-protective performance of the resulting coatings.

2. Materials and Methods

2.1. Reagents and Materials

The following chemicals were used in this study: 3-aminopropyltriethoxysilane (APTES, $\geq 98\%$, CAS No. 919-30-2, Sigma-Aldrich, St. Louis, MO, USA), acrylonitrile (99%, Sigma-Aldrich, St. Louis, MO, USA), methanol ($\geq 99.8\%$, Sigma-Aldrich, St. Louis, MO, USA), diethyl ether (analytical grade, AppliChem GmbH, Darmstadt, Germany), acetic acid (chemically pure grade, Sigma-Aldrich, St. Louis, MO, USA), citric acid monohydrate (chemically pure grade, Sigma-Aldrich, St. Louis, MO, USA). All reagents were used as received without further purification.

St20 steel samples with a thickness of 2 mm were used as the metal substrate.

2.2. Synthesis of the Nitrile-Containing APTES Derivative

The nitrile-containing derivative of 3-aminopropyltriethoxysilane was synthesized via the addition reaction of acrylonitrile to the amino group of APTES according to the procedure described in [18].

A mixture of APTES (1 mmol) and acrylonitrile (1 mmol) was dissolved in 10 mL of methanol and stirred at 50 °C for 2 h under an inert atmosphere. After completion of the reaction, the solvent was removed under reduced pressure. The resulting product was repeatedly washed with diethyl ether and dried under vacuum. The product yield was 99%–100%. The synthesized compound was obtained as a colorless oily liquid.

2.3. Preparation of Solutions and Coating Formation

To prepare the modifying solutions, the synthesized APTES derivative was dissolved in distilled water pre-acidified with acetic acid or citric acid to a pH of 3–6. The organosilane concentration in the solution ranged from 1 to 15 wt.%. To ensure uniform wetting of the steel surface and the formation of a continuous coating, sodium dodecyl sulfate (SDS) was additionally added to the composition at a concentration of 0.01–0.03 wt.%. The resulting solutions were stirred for 5–10 min and then aged for 12 h to complete the hydrolysis of alkoxy groups.

Prior to coating deposition, the surface of the steel samples was sequentially ground with abrasive papers of grit sizes ranging from P80 to P600 and then degreased with White spirit. To remove residual contaminants and grinding debris, the samples were additionally treated in an ultrasonic bath containing an ethanol-water solution (1:1 by volume) for 15 min. After treatment, the samples were dried in air at room temperature.

Silane coatings were formed by immersing samples in the hydrolyzed organosilane solution. The treatment time ranged from 1 to 30 min. After withdrawal from the solution, the samples were kept at room temperature for 5 min and then subjected to heat treatment at a temperature of 80–140 °C for a specified time.

The influence of organosilane concentration, temperature, and duration of heat treatment on the protective properties of the coatings was evaluated using the Akimov test method. Based on the optimization results, coatings obtained from a 5 wt.% organosilane solution followed by heat treatment at a temperature of 130 °C for 20 min was selected for further research.

2.4. Characterization Methods for the Synthesized Compound

FTIR spectra were recorded using Varian 3100 (Varian, Inc., Palo Alto, CA, USA) and Nicolet iS5 (Thermo Scientific, Madison, WI, USA) spectrometers in the range of 4000–400 cm^{−1}.

The ¹H, ¹³C and ¹⁵N NMR spectra were acquired in CDCl₃ at room temperature using Bruker DPX-400 and AV-400 spectrometers (Bruker BioSpin, Kalsruhe, Germany) (400.13, 100.61, and 40.56 MHz, respectively). Chemical shifts were referenced to tetramethylsilane (TMS).

Elemental analysis of the synthesized compound was performed using a Flash 2000 elemental analyzer (Thermo Fisher Scientific Inc., Milan, Italy).

The hydrolysis of the organosilane was monitored by thin-layer chromatography (TLC) using Silufol UV-254 plates (Kavalier, Sazava, Czech Republic).

2.5. Surface Characterization of the Coatings

The surface morphology of the coatings was examined by optical microscopy using a DM 6000 microscope (Leica Microsystems GmbH, Wetzlar, Germany). Dark-field images were acquired using the focus stacking technique.

Surface topography and microrelief parameters were studied by atomic force microscopy (AFM) using a Solver Spectrum instrument (NT-MDT Spectrum Instruments, Moscow, Russia). Measurements were performed in semi-contact mode using a standard silicon NSG01 probe with a tip radius of approximately 10 nm. Topographic images were recorded over scan areas of 50×50 and 10×10 μm .

The surface morphology, local elemental composition, and element distribution were investigated by scanning electron microscopy (SEM) using a JSM-6610LV microscope (JEOL, Tokyo, Japan). For SEM analysis, St20 steel specimens with dimensions of 10×10 mm were prepared prior to coating deposition. The AN coating was then applied according to the procedure described in Section 2.3. Before SEM-EDS analysis, a thin conductive carbon layer was deposited on the specimen surface. The coating thickness was estimated using the ThinFilmID software package, version 1.3.0 (Oxford Instruments Analytical Ltd., High Wycombe, UK), which calculates thin-film thickness based on SEM-EDS analysis. Thickness calculations were performed at three different surface locations, yielding estimated thickness values of 79, 85, and 88 nm, with an average estimated coating thickness of 84 ± 5 nm (mean $\pm$ standard deviation, $n = 3$).

The surface chemical composition and the chemical state of the elements in the coatings were analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo Fisher Scientific Nexsa XPS system (Waltham, MA, USA). Photoelectrons were excited using Al K α radiation ($h\nu = 1486.6$ eV). The binding energy scale was calibrated against the C1s carbon peak at 284.8 eV.

The structural features of the coatings were investigated by Raman spectroscopy using a Solver Spectrum spectrometer (NT-MDT Spectrum Instruments, Moscow, Russia). The spectra were recorded using a 473 nm excitation laser and a $100\times$ objective lens. A diffraction grating with 600 grooves/mm was employed for signal acquisitions, providing a spectral resolution of 4 cm^{-1} . To assess coating homogeneity, spectra were collected from at least three randomly selected locations on the surface. The signal acquisition time was 100 s for each measurement.

2.6. Evaluation of the Protective Properties of the Coatings (Akimov Test)

During the optimization stage, the protective properties of the coatings were evaluated using the Akimov drop test. A drop of the test solution containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (82 g/L), NaCl (33 g/L), and HCl (0.1 N, 13 mL/L) was placed on the coated surface. The protective ability was expressed as the time (s) required for the color of the test solution to change from blue to red-brown, indicating the onset of corrosion processes on the metal surface. Thus, higher protective ability values correspond to better barrier properties of the coating. For each sample, at least five parallel measurements were performed, and the average value was calculated.

2.7. Electrochemical Characterization

To provide a quantitative assessment of the corrosion protection performance of the optimized organosilicon coating, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements (Tafel analysis) were performed.

Electrochemical measurements were carried out using a GillAC potentiostat/galvanostat (ACM Instruments, Cumbria, UK) in a conventional three-electrode glass electrochemical cell (500 mL). St20 carbon steel specimens ($50 \times 25 \times 2$ mm) with an exposed working area of 0.785 cm^2 were used as the working electrode. A saturated Ag/AgCl electrode served as the reference electrode, while a platinum electrode was used as the counter electrode. Electrochemical measurements were performed for both uncoated steel and steel coated with the organosilicon coating.

The electrochemical characterization was carried out in a model electrolyte (MS1) prepared according to GOST 9.502, containing NaCl (0.243 g/L), MgSO₄ (0.025 g/L), CaCl₂ (0.005 g/L), Na₂SO₄ (0.192 g/L), and NaHCO₃ (0.008 g/L). Before each experiment, the specimens were immersed in the electrolyte for 10 min to stabilize the open-circuit potential (OCP). All measurements were performed at $(25 \pm 2)^\circ\text{C}$.

Potentiodynamic polarization curves were recorded within the potential range from -100 to $+100$ mV versus OCP at a scan rate of 0.1 mV s^{-1} . Corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined by Tafel extrapolation. Electrochemical impedance spectra were recorded over the frequency range from 10^{-2} to 10^2 Hz using a sinusoidal perturbation amplitude of 10 mV. The impedance spectra were fitted using an equivalent electrical circuit to determine the charge-transfer resistance (R_{ct}). Corrosion rate (CR) and protection efficiency (PE) were subsequently calculated from the electrochemical parameters.

Electrochemical measurements were performed for coatings prepared from a 5 wt.% solution of the nitrile-functionalized APTES derivative and cured at 130°C for 20 min, corresponding to the optimum coating preparation conditions established in this work.

2.8. Salt Spray Test

Anti-corrosion tests were carried out in a salt spray chamber (Dongguan Tianshuo Testing Equipment, Dongguan, China) in accordance with GOST 9.308–85 (35°C , 5 wt.% NaCl solution).

After completion of the salt spray test, corrosion propagation from the artificial scribe was evaluated visually using a graduated ruler and a magnifying glass. Measurements were performed at three to four representative locations along each scribe, including areas with the largest and smallest corrosion propagation, and the average value was calculated and reported. Three independent specimens were tested for each coating system. The mass loss and corrosion propagation values reported in this study represent the average values obtained from the three specimens.

After exposure, the specimens were rinsed with distilled water, corrosion products were removed, and the mass loss of the steel substrate was determined.

2.9. Pull-Off Adhesion Test

The adhesion-promoting performance of the organosilane coatings was evaluated using a pull-off adhesion test. St20 steel panels ($50 \times 50 \times 2$ mm) were used as substrates. The organosilane coatings were deposited according to the procedure described in Section 2.3 (Preparation of Solutions and Coating Formation). After complete curing of the organosilane layer, a commercial acrylic paint was applied by spray coating in a single layer to obtain a multilayer coating system representative of the intended application of the organosilane coating as an adhesion-promoting interlayer. Pull-off adhesion measurements were performed using a PosiTest AT digital adhesion tester (DeFelsko Corporation, Ogdenburg, NY, USA) in accordance with ISO 4624. Aluminum dollies were bonded to the painted surface using a two-component epoxy adhesive. Prior to bonding, the paint surface was lightly abraded with fine sandpaper to improve adhesion between the adhesive and the paint coating. The adhesive was applied according to the manufacturer's instructions, after which the dollies were carefully aligned to ensure axial loading during the test. Following complete curing of the adhesive, the paint coating around each dolly was cut through to the steel substrate using a circular cutting tool. The specimens were then subjected to tensile loading perpendicular to the surface at a loading rate not exceeding 1 MPa s^{-1} until failure occurred. The pull-off adhesion strength was recorded in MPa, and the fracture surfaces were visually examined to determine the failure mode.

3. Results and Discussion

3.1. Synthesis and Characterization of the Nitrile-Containing APTES Derivative

A nitrile-containing derivative of 3-aminopropyltriethoxysilane (APTES) was synthesized via the aza-Michael reaction, the addition of acrylonitrile to the amino group of the initial silane (Figure 1). The reaction was carried out in methanol at 50 °C and resulted in the formation of the target product with a quantitative yield.

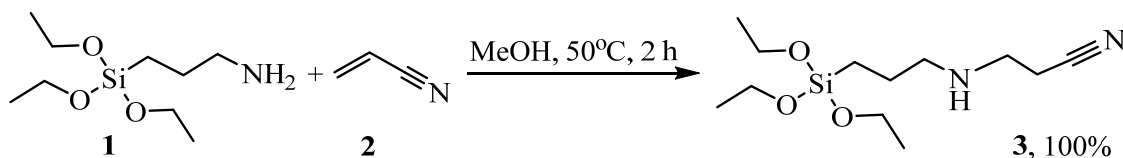


Figure 1. Reaction of 3-aminopropyltriethoxysilane with acrylonitrile.

The obtained compound combines in its structure a triethoxysilyl fragment, which enables the formation of organosilicon layers on the metal surface, with a nitrile-containing organic substituent capable of influencing intermolecular interactions and the structure of the resulting coating. For convenience, the synthesized nitrile-containing derivative, 3-[(3-(triethoxysilyl)propyl)]-amino]propanenitrile, is hereafter referred to as AN.

3.2. Spectral Characterization of AN

The structure and composition of the compound were characterized by FTIR and NMR spectroscopy and were found to be consistent with the literature data [18]. The results of the elemental analysis were in good agreement with the calculated composition of the target compound, providing additional confirmation of its proposed structure.

In the FTIR spectrum of the synthesized AN compound (Figure 2), broad absorption bands were observed in the range 3376–3179 cm^{-1} , corresponding to stretching vibrations of the N-H bond of the secondary amino group. The bands at 2980, 2936, and 2889 cm^{-1} are attributed to stretching vibrations of aliphatic C-H bonds in methylene and methyl groups. A characteristic feature conforming the formation of a nitrile-containing derivative is the intense absorption band at 2252 cm^{-1} , assigned to the stretching vibrations of the nitrile group ($\text{C}\equiv\text{N}$). The band at 1600 cm^{-1} can be attributed to N-H bending vibrations and C-N bond vibrations (Figure 2). The intense absorption bands at 1172, 1092, and 1018 cm^{-1} correspond to the stretching vibrations of Si-O-C bonds in the ethoxysilyl fragment, whereas the signals at 798 and 682 cm^{-1} are characteristic of organosilicon compounds and are associated with Si-C and Si-O vibrations, respectively.

The NMR spectroscopy data are also consistent with the proposed structure of compound AN. In the ^1H NMR spectrum, characteristic signals of ethoxy groups are observed: a triplet at ~1.25 ppm, corresponding to methyl protons, and a quartet at ~3.7 ppm, related to the methylene protons of the OCH_2 fragment. The multiplet signals in the range of 0.6–3.0 ppm are attributed to the methylene groups of the $\text{Si}-(\text{CH}_2)_3\text{-NH-CH}_2\text{-CH}_2\text{-CN}$ chain. In the ^{13}C NMR spectrum, the signals at 17 and 63 ppm correspond to the CH_3 and CH_2 carbon atoms of the ethoxy groups, respectively, whereas the signal at 118 ppm is assigned to the carbon atom of the nitrile group. The obtained NMR spectroscopic characteristics are identical to those in the literature [18].

The combined FTIR and NMR spectroscopy data confirm the successful addition of acrylonitrile to the APTES molecule and the formation of the target nitrile-containing derivative, AN.

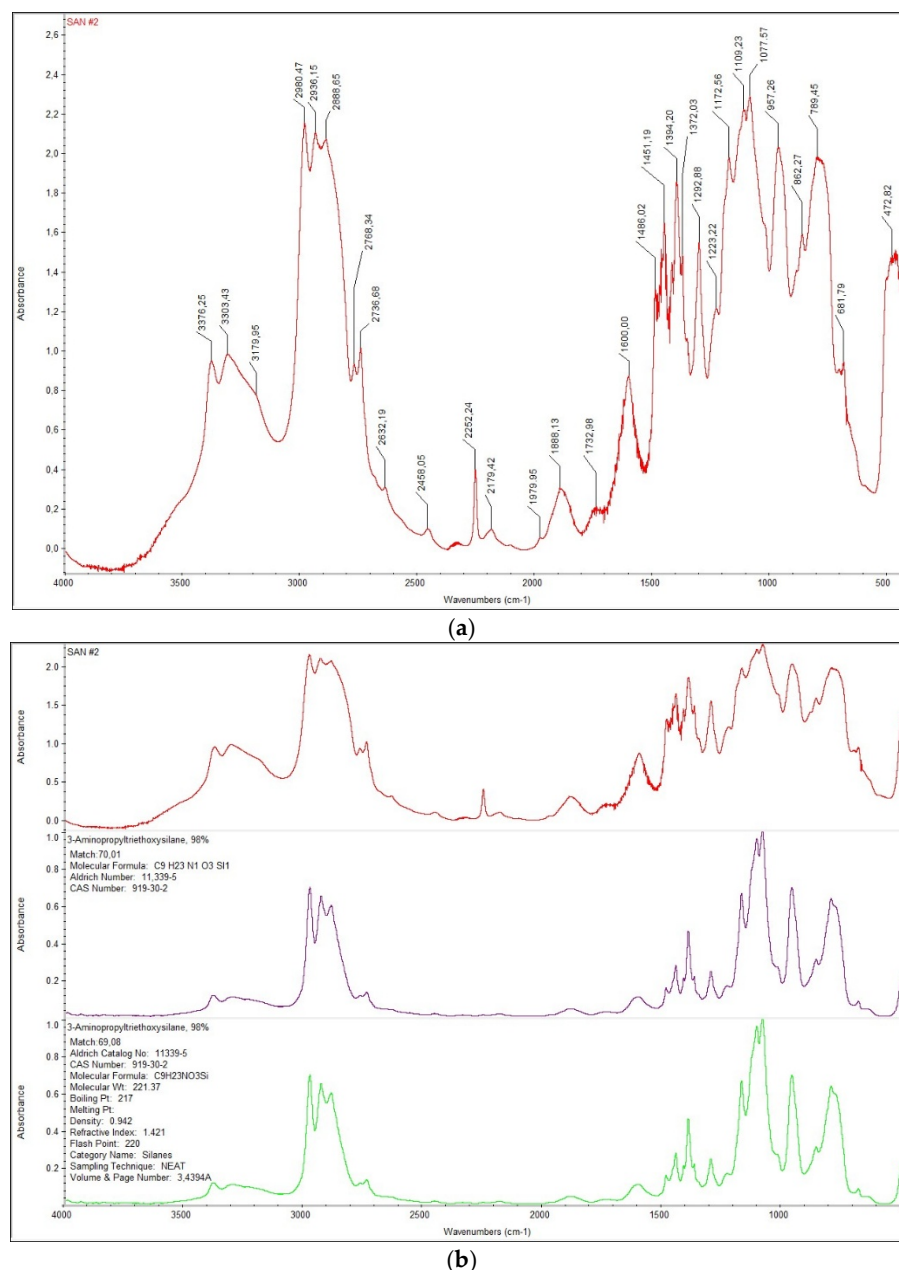


Figure 2. FTIR analysis of the AN: (a) FTIR spectrum of the AN; (b) comparison of the experimental FTIR spectrum with the reference spectrum of APTES.

3.3. Optimization of AN-Based Coating Formation Conditions

The formation of organosilicon coatings based on the nitrile-functional APTES derivative (AN) is expected to proceed through the hydrolysis of the alkoxy groups, followed by adsorption of the resulting silanol species on the hydroxylated steel surface and their subsequent condensation into a crosslinked siloxane network (through the formation of O-Si and Si-O-Me bonds) during thermal treatment. The proposed reaction pathway is schematically illustrated in Figures 3 and 4 and is based on the well-established hydrolysis–condensation mechanism of organofunctional alkoxy silanes reported in the literature [13,21,30].

The proposed mechanism is also supported by the experimental observations obtained in the present work. FTIR spectroscopy confirmed the disappearance of ethoxy groups and the formation of Si–O–Si bonds, while XPS analysis verified the presence of silicon–oxygen bonds characteristic of an organosiloxane network. Furthermore, SEM, AFM, and elemental mapping demonstrated the formation of a continuous and homogeneous surface layer

on the steel substrate. Although these techniques do not directly monitor the individual reaction steps, the obtained results are fully consistent with the accepted hydrolysis and condensation mechanism of organofunctional silanes. Therefore, the reaction schemes presented in Figures 3 and 4 should be regarded as proposed mechanistic interpretations derived from both the experimental findings of this study and the established chemistry of organofunctional alkoxysilanes.

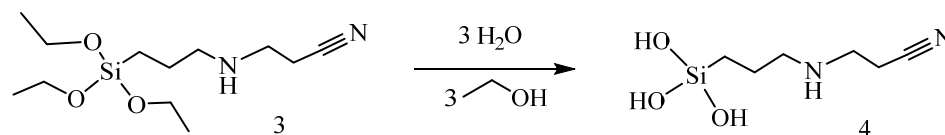


Figure 3. Schematic representation of AN hydrolysis.

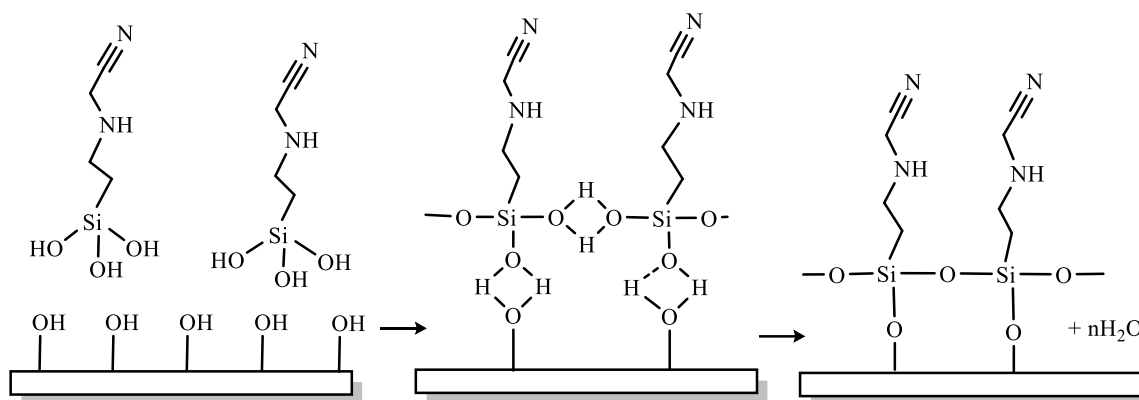


Figure 4. Schematic representation of the formation of AN-based coating on the steel surface.

The coating formation efficiency was evaluated using the protective ability determined by the Akimov drop test, where higher values indicate a longer time before the onset of corrosion and, consequently, better protective performance. Preliminary studies showed that the AN hydrolysis proceeds most effectively under acidic conditions. At pH 3, stable hydrolyzed solutions were obtained, providing the formation of uniform coatings with higher protective ability compared to those prepared at higher pH values. Therefore, an AN solution hydrolyzed at pH 3 for 12 h was used in subsequent experiments. The concentration of AN in solution was found to be an important factor affecting the coating formation. Increasing the AN concentration from 1 to 5 wt.% resulted in a significant improvement in the protective ability of the coating (Figure 3). A further increase in concentration did not lead to a substantial enhancement of the protective properties and, in some cases, even caused their deterioration. This behavior is likely associated with the acceleration of silanol group condensation reactions in the bulk solution and the formation of oligomeric structures, which reduce the number of reactive groups available for interaction with the metal surface. Based on these results, an AN concentration of 5 wt.% was selected as the optimal value.

Unlike the previously studied acrylate-functional APTES derivatives [31], AN exhibited insufficient wettability toward the steel surface. When aqueous solutions without a surfactant were applied, the composition tended to run off the surface, resulting in the formation of a discontinuous layer. To improve wettability and ensure uniform coating distribution, sodium dodecyl sulfate (SDS) was added to the solution. It was found that the addition of 0.01–0.03 wt.% SDS promoted the formation of more homogeneous coatings and increased their protective ability (Akimov drop test, expressed as the time before the onset of corrosion) (Figure 5). At higher concentrations of surfactants, a decrease in the protective performance was observed.

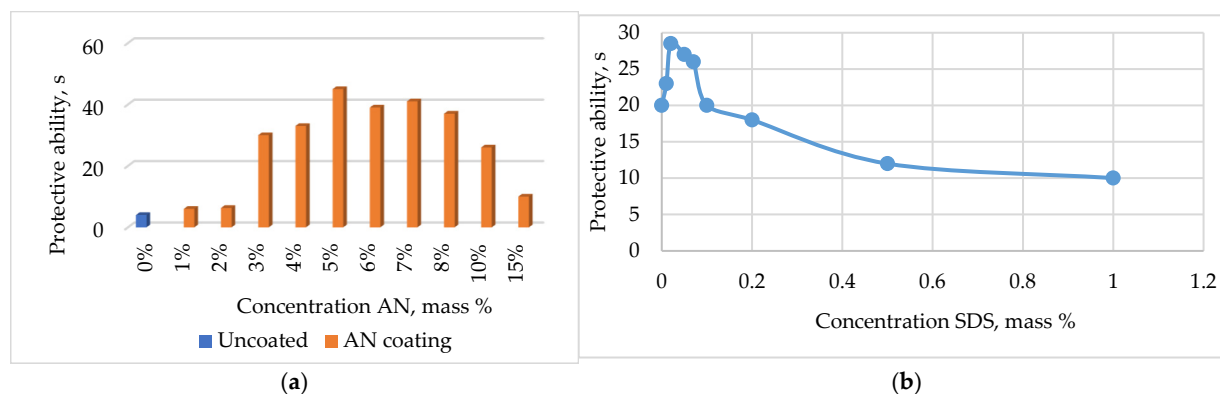


Figure 5. Effect of AN concentration on protective ability (a); Effect of SDS concentration on protective ability of AN-based coating (b).

The temperature of the coating solution during the deposition stage had a significant effect on the coating formation process. The highest values of the protective ability were obtained at a solution temperature of 25–35 °C (Figure 5). Increasing the temperature to 40–50 °C resulted in a decrease in the protective performance of the coating. This behavior is likely associated with the accelerated self-condensation process of hydrolyzed forms of organosilane, which reduces the number of silanol groups available for the formation of a surface-bound organosilicon layer.

The duration of contact of the metal surface with the hydrolyzed solution had a less pronounced effect on the coating properties. After 5 min of immersion, further increase in the deposition time resulted in little or no improvement in the protective ability of the coating. Considering the technological advantages of shorter processing times, a deposition time of 5 min was selected for subsequent experiments.

Thermal treatment is a critical stage in the formation of organosilicon coating. During this step, a strong siloxane network covalently bonded to the metal surface is formed (Figure 4). The study of the effects of heat-treatment temperature and duration showed that heating above 80 °C significantly accelerates the formation of organosilicon coatings. The optimal heat-treatment temperature was found to be in the range of 120–140 °C (Table 1), and the optimal heat-treatment time at this temperature was 20 min. The optimal duration of heat treatment was defined as the minimum time required to obtain a coating with the highest protective ability (PAA) at a given temperature.

Table 1. Minimum curing time required to achieve the maximum protective ability of the AN coating at different heat-treatment temperatures (Akimov test).

Heat-treatment temperature (°C)	25	40	60	80	100	120	130	150	160
Minimum curing time required to achieve maximum protective ability (min)	1440	1440	180	60	40	30	20	20	20

3.4. Raman Spectroscopic Characterization of AN Coating

Raman spectroscopy was employed to confirm the formation of an organosilicon coating on the steel surface and to verify the retention of functional groups of nitrile-containing silane after hydrolysis and condensation processes. Spectra were recorded at three selected locations on the sample surface. In all cases, a similar set of characteristic bands was observed, indicating the homogeneity of the formed coating. The coating spectra exhibited intense bands in the range of 377–531, 734–827, and about 1012 cm^{-1} , which are assigned to Si-O-Si vibrations and are characteristic of the siloxane network. In addition, bands in the range of 2832–2933 cm^{-1} were observed and attributed to the stretching

vibrations of C-H bonds in the organic fragment of the AN molecule. Of particular interest is the band at 2246 cm^{-1} , corresponding to the stretching vibration of the nitrile group ($\text{C}\equiv\text{N}$). The presence of this signal confirms the preservation of the nitrile functionality in the coating structure after hydrolysis and application to a metal surface. These results are in good agreement with the FTIR spectroscopy data obtained for the synthesized compound (Figure 6).

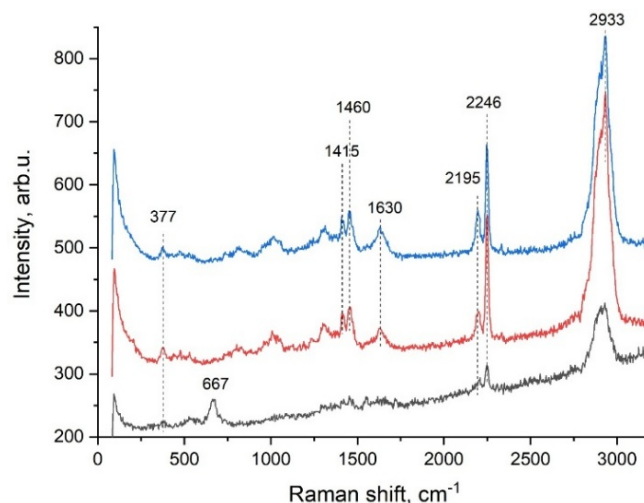


Figure 6. Raman spectra of the AN coating were recorded at three randomly selected locations on the coated steel surface to evaluate the coating homogeneity.

Thus, the Raman spectroscopy results confirm the formation of an organosilicon coating consisting of a siloxane network and the retention of nitrile-containing substituents within its structure.

3.5. Surface Morphology and Elemental Composition of AN-Based Coating

SEM analysis of the surface of St20 steel coated with AN revealed the formation of a continuous layer uniformly distributed over the metal surface. No signs of cracking, delamination, or other pronounced coating defects were observed in the examined areas. The formed coating follows the microrelief of the substrate, preserving the characteristic features and grooves resulting from the mechanical surface preparation of the steel.

For the uncoated St20 substrate, the EDS spectrum is dominated by signals corresponding to iron and manganese (Figure 7a). After coating deposition, the appearance of nitrogen together with an increase in the intensities of silicon and oxygen signals is observed (Figure 7b), indicating the formation of an organosilicon layer on the surface.

SEM observations of the AN-coated St20 steel surface at different magnifications (Figure 8) revealed the formation of a continuous and uniform organosilicon layer. At low magnifications (Figure 8c,d), the coating uniformly covers the steel surface and follows the substrate microrelief without visible cracks, delamination, or other large-scale defects. Higher-magnification images (Figure 8a,b) show a compact surface morphology with no evidence of discontinuities or localized coating failure. The observed linear features correspond to the grinding marks remaining after the mechanical preparation of the steel substrate and indicate that the thin AN coating conforms to the underlying surface topography rather than masking it. Surface morphology of the coatings formed at pH 3–6 was also examined during the optimization stage and showed no significant differences within this pH range. Therefore, the superior protective performance observed at pH 3 is attributed primarily to more favorable hydrolysis kinetics under acidic conditions, which promote efficient formation of reactive silanol groups prior to condensation and subsequent

coating deposition. As demonstrated in our previous study [31] on acrylate-functional APTES derivatives, the morphology of organosilicon coatings is influenced more strongly by the organosilane concentration and the composition of the hydrolysis medium than by relatively small variations in pH within the acidic region.

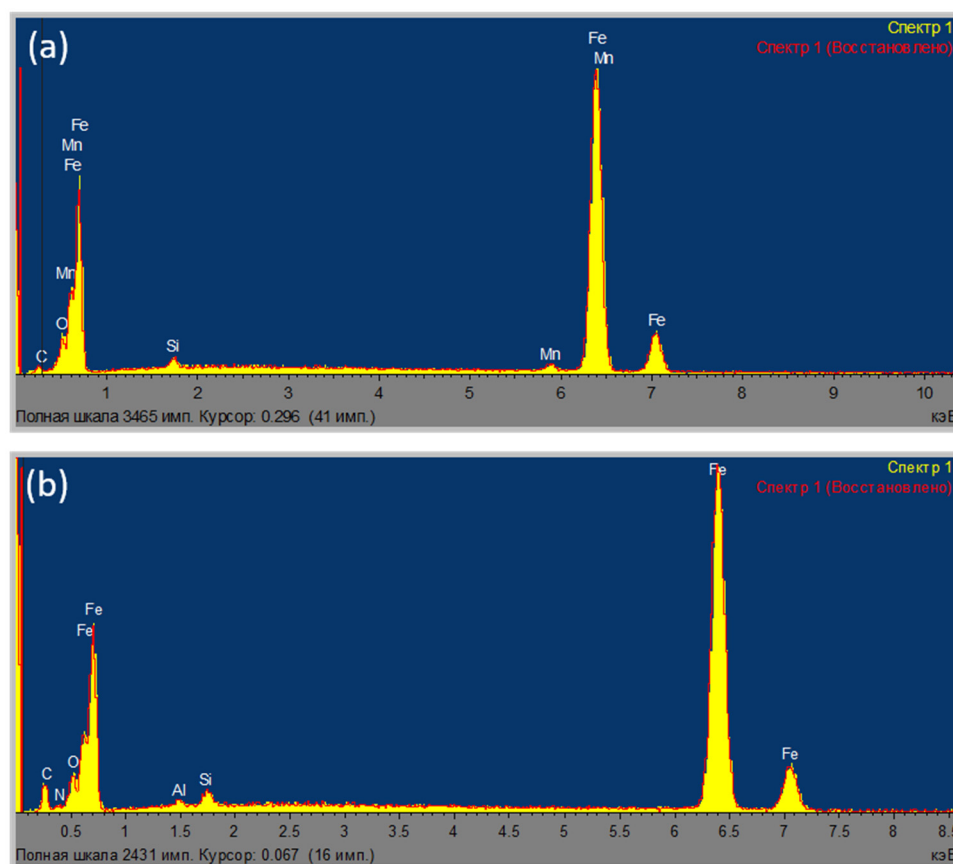


Figure 7. EDS spectra and SEM images of: (a) uncoated St20; (b) St20 coated with AN-based coating.

The average elemental composition of the coated surface was 7.48 wt.% C, 1.28 wt.% N, 4.50 wt.% O, 1.40 wt.% Si and 94.73 wt.% Fe (Table 2). Despite the presence of the coating, intense iron signals remained visible in the spectra. The average estimated coating thickness was 84 ± 5 nm, as determined using the ThinFilmID software based on SEM–EDS analysis at three different surface locations. Such a small thickness is considerably lower than the characteristic X-ray generation depth under the applied SEM–EDS conditions. Therefore, the detected EDS signal is dominated by the steel substrate despite the formation of a continuous organosilicon coating. Therefore, a significant portion of the detected signal originates from the metal substrate. Compared with the uncoated steel, the carbon content increased from 2.02 to 7.48 wt.%. However, this increase may be associated not only with the organic component of the coating but also with the conductive carbon layer deposited prior to SEM analysis. In this regard, the carbon content was not considered a primary indicator of coating formation. More reliable evidence for the presence of the AN layer is provided by increased silicon and oxygen contents relative to the uncoated steel surface, as well as by the detection of nitrogen exclusively on the modified sample. The presence of silicon and oxygen is associated with the formation of a siloxane network, whereas the appearance of nitrogen originates from the aminopropionitrile fragment of the AN molecule.

Elemental mapping (Figure 9b–e) revealed a homogeneous distribution of carbon, nitrogen, oxygen, and silicon across the investigated surface. The absence of localized

elemental enrichment indicates that the coating components are uniformly distributed over the substrate, confirming the chemical homogeneity of the deposited AN coating.

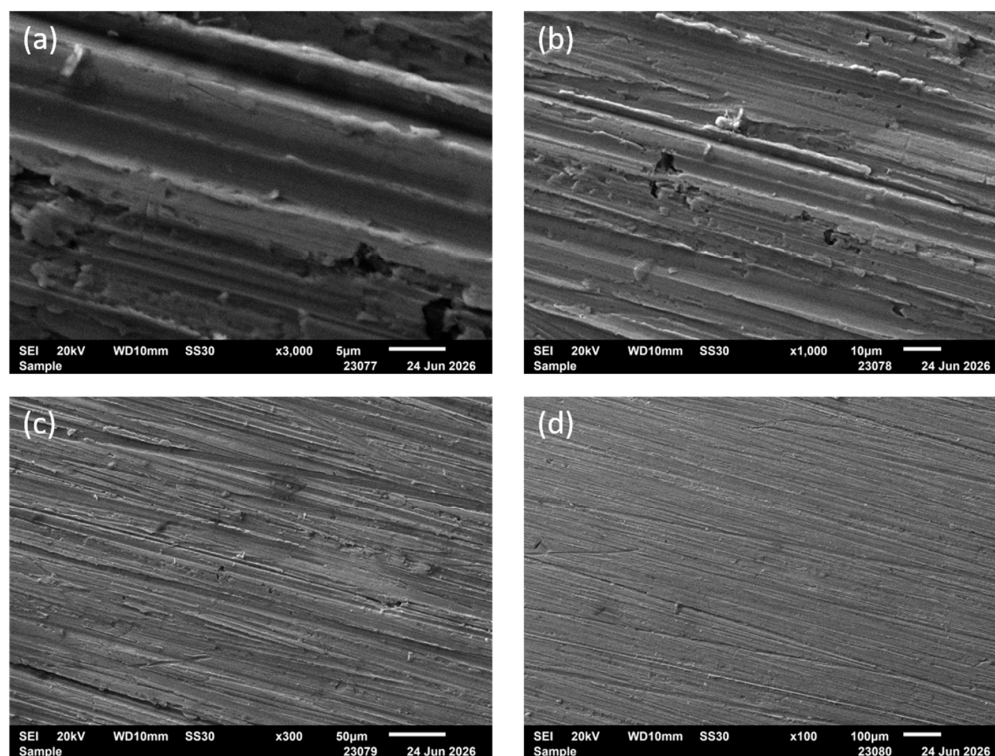


Figure 8. SEM micrographs of the AN coating deposited on the St20 steel surface at different magnifications: (a) $\times 3000$; (b) $\times 1000$; (c) $\times 300$; (d) $\times 100$.

Table 2. Elemental composition of uncoated steel and AN-coated steel (EDS analysis).

Sample	C	N	O	Al	Si	Mn	Fe	Total
Uncoated steel	2.02	-	-	-	1.40	0.30	97.55	100.0
AN-coated steel	7.48	1.28	4.50	0.61	1.40	-	84.73	100.00

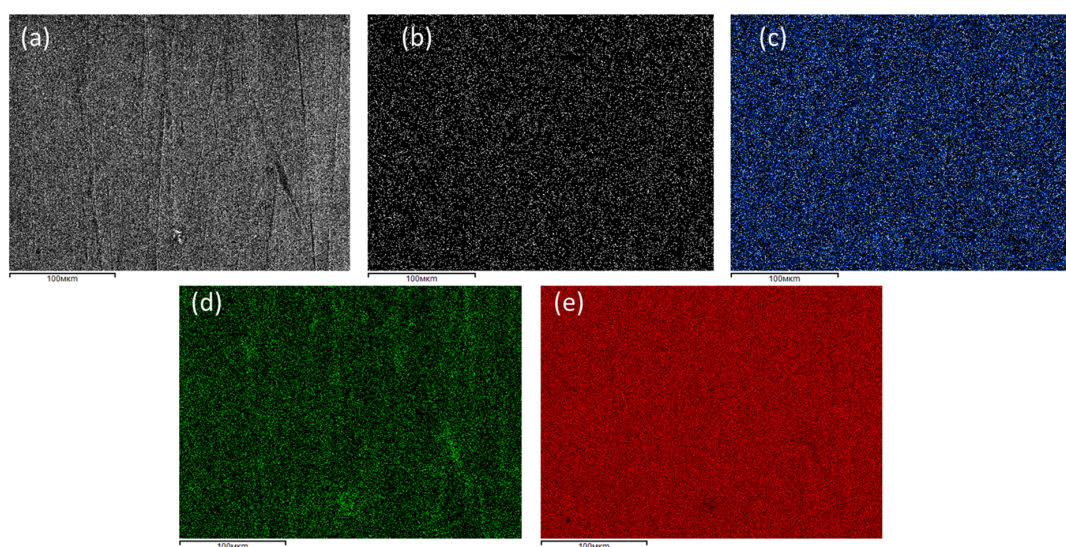


Figure 9. SEM micrograph and corresponding EDS elemental distribution maps of the AN-coated St20 steel surface: (a) SEM image; (b) C; (c) N; (d) O; (e) Si.

The corresponding SEM micrograph (Figure 9a) demonstrates a continuous surface morphology without visible defects or discontinuities in the analyzed area. The combined SEM and EDS results therefore confirm the successful formation of a thin, continuous, and chemically homogeneous organosilicon coating on the St20 steel surface.

3.6. XPS Analysis of the Chemical Composition and Elemental States of the AN Coating

X-ray photoelectron spectroscopy (XPS) was used to study the chemical composition of the surface and the chemical states of the elements in the AN coating. The survey spectrum of the coating (Figure 10a) exhibits intense C 1s, O 1s, N 1s and Si 2p signals, confirming the presence of the main elements constituting the organosilicon coating.

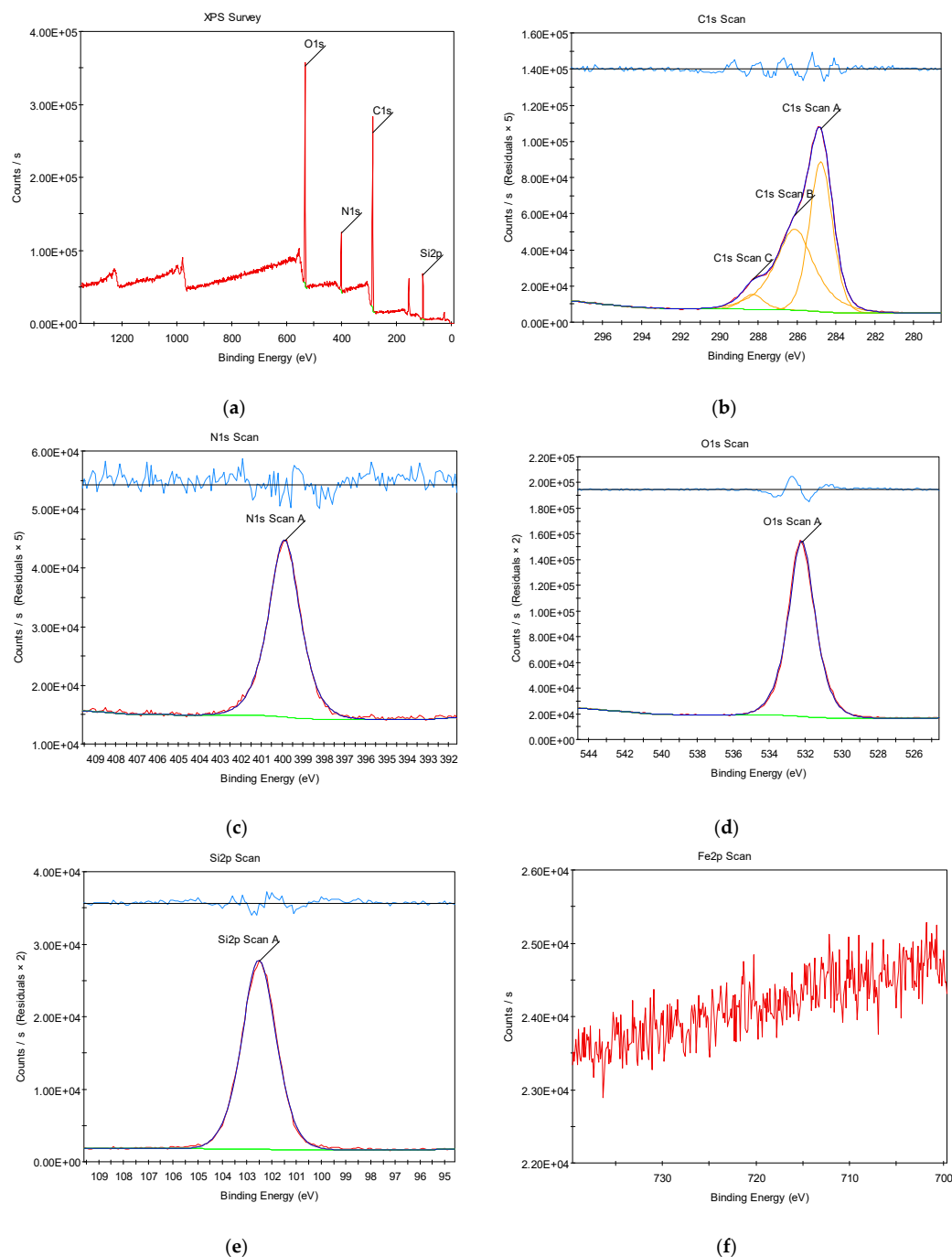


Figure 10. XPS characterization of the AN coating on the steel surface: (a) survey XPS spectrum; (b) high-resolution C 1s spectrum; (c) high-resolution N 1s spectrum; (d) high-resolution O 1s spectrum; (e) high-resolution Si 2p spectrum; and (f) high-resolution Fe 2p spectrum.

The N 1s spectrum (Figure 10c) exhibits a single peak centered at 399.89 eV. This binding energy is consistent with the presence of nitrogen-containing functional groups derived from the AN precursor. Because only one unresolved N 1s component was observed, reliable discrimination between amino and nitrile nitrogen was not possible under the present experimental conditions. Nevertheless, the detected nitrogen signal confirms the incorporation of nitrogen-containing organic fragments into the organosilicon coating. The results of the quantitative analysis are presented in Table 3. Carbon makes the largest contribution to the surface elemental composition (42.67 at.%), whereas the content of oxygen, silicon, and nitrogen is 18.10, 7.97 and 6.95 at.%, respectively. The presence of silicon and oxygen indicates the formation of an organosilicon matrix, while the presence of nitrogen confirms the retention of nitrogen-containing functional groups derived from the precursor within the coating structure.

Table 3. Surface elemental composition of the AN coating determined by XPS.

Element	Binding Energy (eV)	Atomic Concentration (at.%)
C 1s	285.35	42.67
O 1s	532.26	18.10
Si 2p	102.84	7.97
N 1s	400.05	6.95

The absence of pronounced Fe 2p signals in the high-resolution spectrum indicates effective shielding of the metallic substrate by the formed coating and confirms the formation of a continuous surface layer. The high-resolution Si 2p spectrum (Figure 10e) is characterized by an intense peak centered at 102.52 eV (Table 4). This binding energy is characteristic of silicon bound to oxygen atoms in Si-O-Si and Si-O-C structures. The O 1s spectrum (Figure 10d) contains a dominant peak at 532.20 eV, corresponding to oxygen in Si-O-Si and Si-O-C bonds. These results indicate that oxygen is predominantly incorporated into the organosilicon matrix of the coating. The N 1s spectrum (Fig. 10c) exhibits a peak centered at 399.89 eV. Considering the structure of the precursor, 3-[(3-(triethoxysilyl)propyl)]-amino)propanenitrile, this signal can be attributed to the nitrogen atoms in the amino and nitrile functionalities of the molecule. Deconvolution of the C 1s spectrum (Figure 10b) revealed three major components (Table 4). The most intense peak at 284.77 eV corresponds to carbon in the C-C and C-H bonds of the aliphatic fragments. The component at 286.1 eV is assigned to carbon atoms bound to nitrogen and oxygen atoms (C-N and C-O). The third component, centered at 288.29 eV, can be attributed to carbon in the nitrile group (C≡N) and, partially, to oxidized carbon-containing fragments.

Table 4. Peak assignments of the high-resolution XPS spectra of the AN coating.

Spectrum	Peak	Binding Energy (eV)	Assignment
C 1s	A	284.77	C-C, C-H
C 1s	B	286.13	C-N, C-O
C 1s	C	288.29	C≡N and/or oxidized carbon species
N 1s	A	399.89	Nitrogen in amino and nitrile groups
O 1s	A	532.20	Si-O-Si, Si-O-C
Si 2p	A	102.52	Silicon in siloxane structures (Si-O-Si, Si-O-C)

Thus, the XPS results confirm the formation of a hybrid organosilicon coating on the steel surface, consisting of a three-dimensionally crosslinked siloxane matrix and organic fragments containing amine and nitrile groups. The presence of Si-O-Si and Si-O-C

bonds indicates the successful polycondensation of the hydrolyzed organosilane precursor, leading to the formation of a stable protective layer on the metal surface.

3.7. Surface Topography of the AN Coating by Atomic Force Microscopy

AFM characterization of the AN coating is presented in Figure 11. The two-dimensional topographic image (Figure 11a) reveals a relatively smooth and continuous surface morphology within the scanned $10 \times 10 \mu\text{m}$ area. The corresponding three-dimensional reconstruction (Figure 11b) provides a clearer visualization of the surface relief and indicates only limited nanoscale height variations. To further evaluate the surface topography, a height profile was extracted along the selected scan line shown in Figure 11c. The profile exhibits gradual height fluctuations without abrupt changes in the surface relief, indicating a relatively uniform surface morphology. AFM analysis of the optimized AN coating revealed no local cracks or pronounced surface defects after thermal treatment. Such defects were observed only during preliminary optimization under non-optimal processing conditions and were eliminated by optimizing the coating formation procedure.

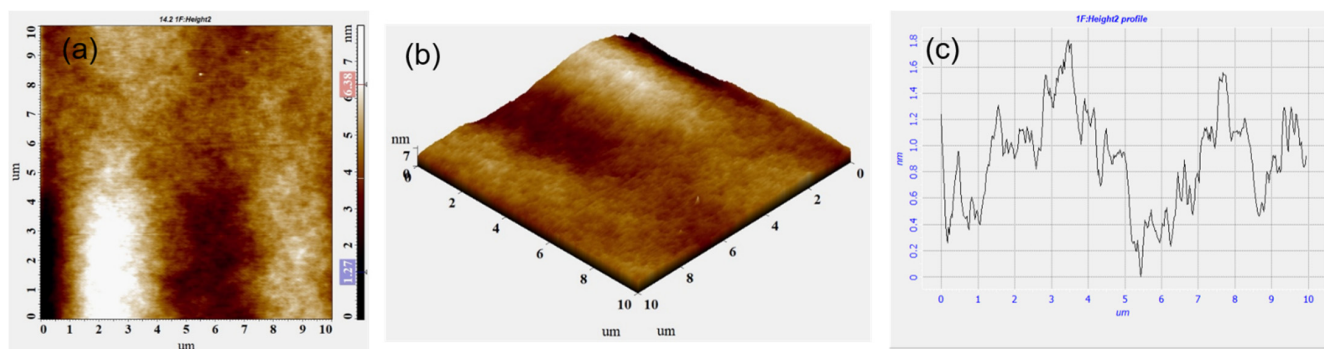


Figure 11. AFM characterization of the AN coating surface: (a) two-dimensional topographic image; (b) three-dimensional surface reconstruction; (c) height profile measured along the line shown in (a).

Although AFM does not directly provide coating thickness, the limited surface height variations are consistent with the formation of a continuous organosilicon coating. This interpretation is supported by the independently determined average coating thickness of $84 \pm 5 \text{ nm}$ obtained by optical reflectance analysis using ThinFilmID software. The AFM observations are also consistent with the SEM and EDS results, which indicate the formation of a homogeneous AN coating on the steel surface.

The combination of AFM, XPS, and corrosion test results suggests a close relationship between the surface organization of the AN coating and its protective performance. AFM analysis revealed a continuous surface with low roughness and no evidence of large defects or coating discontinuities, while XPS confirmed the formation of a cross-linked organosilicon network containing Si–O–Si bonds and nitrogen-containing organic fragments. Such structural organization is expected to reduce the number of preferential pathways for electrolyte penetration and thereby enhance the barrier properties of the coating. A similar relationship between molecular organization, surface characteristics, and corrosion protection has been reported for other organosilicon and organic protective systems. In particular, Neupane et al. [32] demonstrated that AFM and XPS analyses provide complementary information on the organization of surface layers and that a higher degree of molecular ordering is closely associated with improved corrosion resistance. Although the investigated system differs from the present organosilicon coating, the observed correlation between surface organization and protective performance is consistent with our results and supports the proposed mechanism of corrosion protection. The presence of Si–O–Si and Si–O–C bonds indicates the successful polycondensation of the hydrolyzed organosilane

precursor, leading to the formation of a stable organosilicon network. Although direct spectroscopic evidence for the formation of interfacial Si–O–Fe bonds was not obtained in the present study, the interaction of hydrolyzed organosilanes with hydroxylated steel surfaces through covalent Si–O–metal bonding is well established in the literature. Therefore, the adhesion of the AN coating to the steel substrate is interpreted on the basis of the accepted hydrolysis–condensation mechanism together with the observed continuous coating morphology and its protective performance.

The introduction of nitrile groups is expected to influence the organization of the forming organosilicon layer owing to their high polarity and large dipole moment. The presence of nitrile functionalities may promote stronger dipole–dipole interactions between neighboring molecules, leading to a more compact molecular arrangement and a denser siloxane network after hydrolysis and condensation. Such structural organization can reduce the free volume within the coating, hinder electrolyte penetration, and thereby contribute to improved barrier properties. In addition, the increased polarity of the AN molecule may favor interactions with subsequently applied paint coatings, contributing to enhanced interfacial adhesion in multilayer protective systems.

3.8. Electrochemical Characterization of the AN Coating

To provide a quantitative assessment of the corrosion protection performance of the optimized AN coating, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were performed in two electrolytes: the model solution MS1 (GOST 9.502) and formation water (BR), representing laboratory and oilfield service conditions, respectively.

The potentiodynamic polarization curves (Figure 12) demonstrate that deposition of the AN coating modifies the electrochemical behavior of the steel surface in both electrolytes. In the model electrolyte (MS1), the corrosion potential (E_{corr}) shifts from -625 ± 10 mV for bare steel to -532 ± 10 mV after coating deposition, indicating a decrease in the thermodynamic tendency of the substrate toward corrosion. Simultaneously, the corrosion current density (i_{corr}) decreases from 18.4 ± 0.8 to 17.4 ± 0.8 $\mu\text{A cm}^{-2}$, corresponding to a slight reduction in the corrosion rate from 0.21 ± 0.03 to 0.20 ± 0.03 mm year⁻¹. Although the decrease in corrosion rate determined from the Tafel analysis is relatively small, the positive shift in the corrosion potential indicates that the AN coating alters the electrochemical response of the steel surface and partially suppresses the anodic and cathodic corrosion reactions.

A similar tendency is observed in formation water (BR). The corrosion potential changes only slightly, from -600 ± 10 mV to -595 ± 10 mV, while the corrosion current density decreases from 164 ± 15 to 153 ± 15 $\mu\text{A cm}^{-2}$, accompanied by a reduction in the corrosion rate from 1.9 ± 0.2 to 1.8 ± 0.2 mm year⁻¹. Although the protective effect is less pronounced than in the model electrolyte, the coating maintains its corrosion-inhibiting action under the considerably more aggressive conditions of formation water, characterized by higher ionic strength and a more complex electrolyte composition.

Electrochemical impedance spectroscopy provides a more sensitive assessment of the barrier properties of the coating. As shown in the Nyquist plots (Figure 11), deposition of the AN coating results in an increase in the diameter of the capacitive semicircle in both electrolytes, indicating an increase in the resistance of the steel/electrolyte interface to charge transfer. In the model electrolyte, the charge-transfer resistance (R_{ct}) increases from 850 ± 50 $\Omega \cdot \text{cm}^2$ for bare steel to 1160 ± 50 $\Omega \cdot \text{cm}^2$ after coating deposition. At the same time, the corrosion current density obtained from impedance fitting decreases from 20.2 ± 0.8 to 12.3 ± 0.8 $\mu\text{A cm}^{-2}$, while the corrosion rate decreases from 0.21 ± 0.03 to 0.15 ± 0.02 mm year⁻¹. These changes correspond to a protection efficiency of approxi-

mately 30%, confirming the ability of the AN coating to hinder electrochemical corrosion processes under standard laboratory conditions.

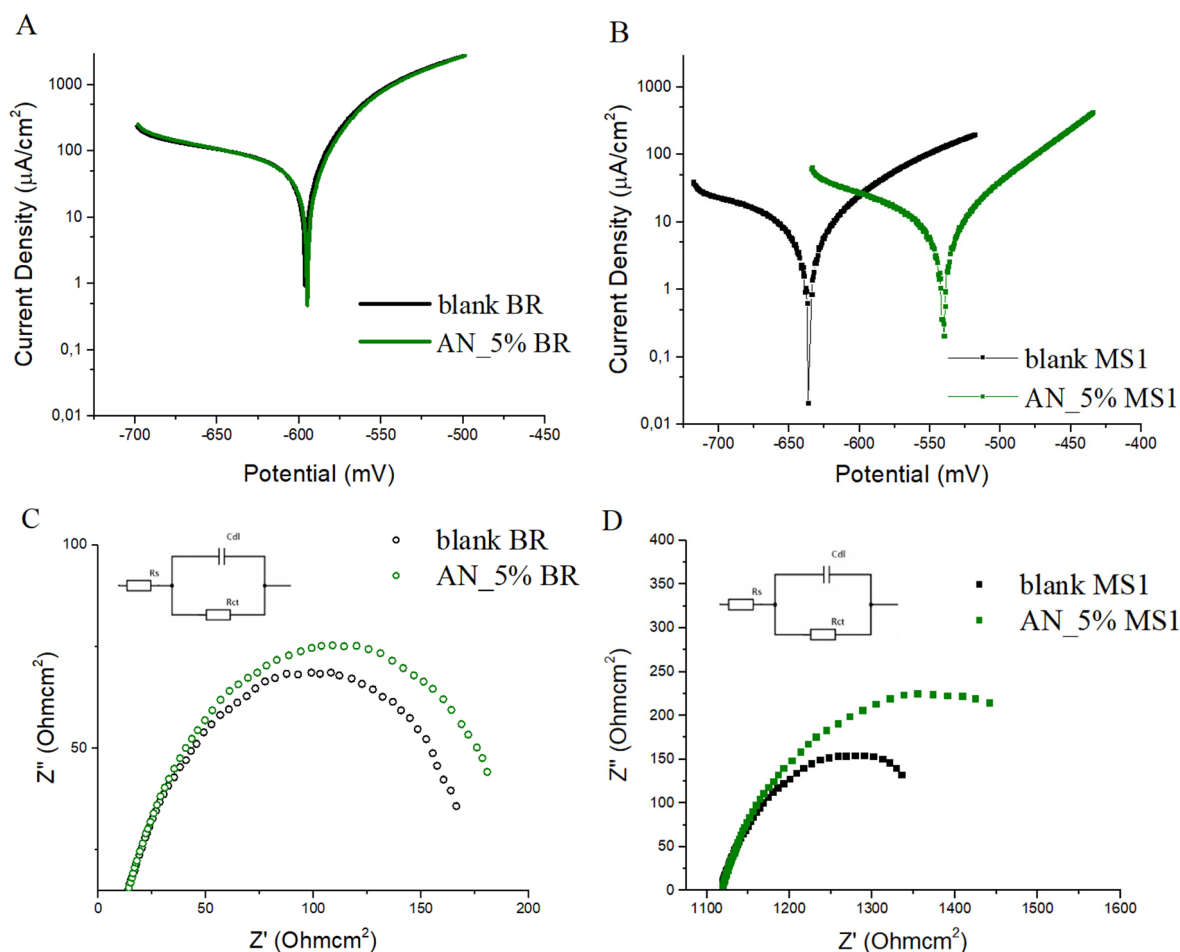


Figure 12. Tafel plots (A,B) and Nyquist diagrams (C,D) with equivalent circuit for calculation for samples of steel grade St20 with applied coatings marked with a solution of 5% AN in MS1 and formation water BR.

In formation water, the impedance measurements reveal a similar but less pronounced behavior. The charge-transfer resistance increases from 125 ± 10 to $165 \pm 10 \Omega \cdot \text{cm}^2$, whereas the corrosion current density decreases from 176 ± 15 to $156 \pm 15 \mu\text{A cm}^{-2}$, resulting in a reduction in the corrosion rate from 2.0 ± 0.2 to $1.8 \pm 0.2 \text{ mm year}^{-1}$. The corresponding protection efficiency is approximately 10%. The lower improvement observed in formation water is expected because of its substantially higher corrosivity, elevated ionic strength, and the presence of multiple dissolved salts, which facilitate electrolyte penetration and accelerate electrochemical reactions at the metal surface.

The electrochemical parameters presented in Table 5 quantitatively confirm the protective effect of the AN coating observed in the polarization and impedance measurements. The most pronounced improvement was achieved in the model electrolyte (MS1), where the coating produced a significant increase in the charge-transfer resistance (R_{ct}), accompanied by a reduction in the corrosion current density (i_{corr}).

The increase in R_{ct} together with the decrease in corrosion current density confirms that the AN coating hinders charge transfer across the steel/electrolyte interface and acts as an additional barrier against electrolyte penetration. These electrochemical results are in good agreement with the surface characterization data. SEM observations demonstrated the formation of a continuous coating on the steel surface, AFM analysis revealed a relatively

uniform surface morphology, while XPS confirmed the enrichment of the surface with silicon-containing species and the formation of an organosiloxane interfacial layer. The consistency of the structural, morphological, and electrochemical results indicates that the deposited AN coating forms a compact interfacial film capable of retarding electrochemical corrosion processes.

Table 5. Electrochemical parameters of uncoated and AN-coated St20 steel obtained from Tafel polarization and EIS measurements in the model electrolyte (MS1) and formation water (BR).

Electrolyte	Sample	E_{corr} (mV)	i_{corr} ($\mu\text{A cm}^{-2}$) Tafel	CR (mm Year $^{-1}$) Tafel	i_{corr} ($\mu\text{A cm}^{-2}$) EIS	CR (mm Year $^{-1}$) EIS	R_{ct} ($\Omega \cdot \text{cm}^2$)
MS1	Bare steel	-625 ± 10	18.4 ± 0.8	0.21 ± 0.03	20.2 ± 0.8	0.21 ± 0.03	850 ± 50
	AN coating	-532 ± 10	17.4 ± 0.8	0.20 ± 0.03	12.3 ± 0.8	0.15 ± 0.02	1160 ± 50
BR	Bare steel	-600 ± 10	164 ± 0.8	1.9 ± 0.02	173 ± 15	2.0 ± 0.2	125 ± 10
	AN coating	-595 ± 10	153 ± 0.8	1.8 ± 0.02	156 ± 15	1.8 ± 0.2	165 ± 10

It should be emphasized that the improvement in the electrochemical parameters is moderate rather than dramatic, which is consistent with the ultrathin nature of the coating, whose average estimated thickness is only 84 ± 5 nm. Unlike conventional thick barrier coatings, the developed AN film is intended to function as an organosilane primer, chemically bonded to the steel surface, rather than as a standalone corrosion-protective coating. Its primary role is to establish a stable interfacial layer that reduces electrolyte access to the metal surface, enhances interfacial stability, and provides a chemically active surface for the subsequent application of organic coating systems.

Although the present study was not intended to establish a direct relationship between the nitrile functionality and the electrochemical response, the observed increase in charge-transfer resistance and the reduction in corrosion rate are consistent with the formation of a more compact interfacial organosiloxane network expected for nitrile-functionalized silane precursors. Overall, the electrochemical results obtained in both media confirm that the AN-derived coating provides measurable improvement in the corrosion resistance of steel while maintaining its protective performance under conditions representative of oilfield environments. These findings support the potential application of the developed coating as a chemically active primer layer in multilayer corrosion-protection systems for oil production and petroleum processing equipment.

3.9. Salt Spray Corrosion Resistance of the AN Coating

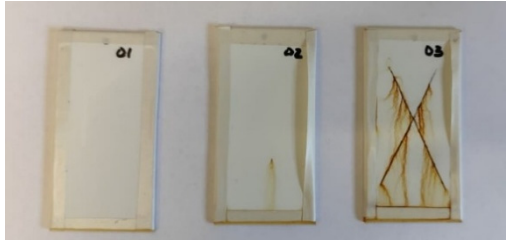
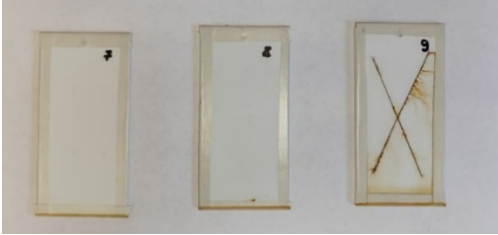
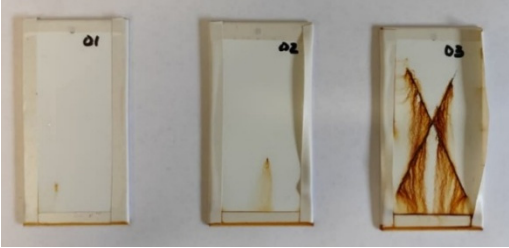
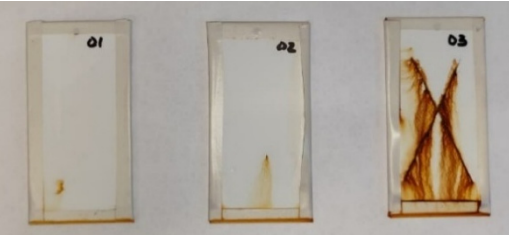
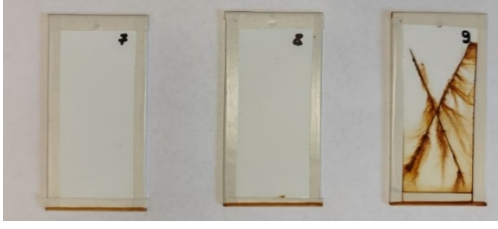
The appearance of the samples during salt spray exposure is presented in Table 6. No visible signs of corrosion were observed on samples with an intact AN coating throughout the entire testing period, which indicates the high barrier ability of the formed organosilicon layer. The AN-coated surfaces retained a homogeneous appearance without rust formation or evidence of coating degradation.

For samples containing an artificial cross-cut defect, the first signs of corrosion appeared within the damaged area. However, the corrosion process remained localized and did not result in significant propagation of corrosion products beyond the defect region. Such behavior indicates that the coating effectively limits the spread of corrosion from local defects while maintaining its protective properties over the remaining surface area.

The quantitative results of the salt spray test are summarized in Table 7. After 120 h of exposure, the AN-coated sample with an artificial defect had a significantly lower mass loss than the paint-coated steel. The mass loss for the AN + paint-coated sample was 0.0008 g/m^2 , whereas the corresponding value for the paint-coated steel reached 0.0047 g/m^2 . In addition, corrosion propagation from the defect did not exceed 0.05 mm

for the AN + paint coating, while a value of 0.35 mm was recorded for the paint coating on steel.

Table 6. Appearance of paint-coated and AN+ paint-coated steel samples before and after 120 h of salt spray exposure.

Exposure Time, h	Paint Coated Steel	Paint + AN Coated Steel
3		
24		
72		
120		

Reducing the mass loss of the metal substrate and limiting the spread of corrosion damage indicates an effective barrier effect of the organosilicon coating. The results obtained are consistent with the SEM, AFM, and RFES data, indicating the formation of a continuous layer with a homogeneous morphology and a developed siloxane structure. Probably, the protective effect of the coating is due to the formation of a dense Si–O–Si bond network, which makes it difficult for moisture and aggressive ions to penetrate to the metal surface.

Table 7. Results of salt-spraying testing of steel samples.

Sample	Mass Loss (g/m ²)	Corrosion Propagation (mm)	Maximum Scratch Width After Exposure (mm)
Paint coating	0.0047 ± 0.08	0.35 ± 0.04	1.2
Paint + AN coating	0.0008 ± 0.03	0.05 ± 0.01	0.6

Overall, the spray test demonstrated that the application of AN coating as an intermediate layer beneath the paint coating improves the corrosion resistance of the protective system. Even in the presence of an artificial defect, corrosion in the AN + paint coating system remained predominantly localized and developed with significantly lower intensity compared with samples protected only by the paint coating. These results indicate that the AN organosilicon layer provides an additional barrier of protection and effectively prevents corrosion propagation from the damaged area.

The combined results obtained using Raman spectroscopy, SEM-EDS, XPS, and AFM indicate that hydrolysis and condensation of the AN precursor lead to the formation of a continuous organosilicon layer on the steel surface. The formation of the crosslinked siloxane network, confirmed by the XPS, along with the homogeneous morphology revealed by AFM and SEM, enhances the coating's barrier properties. The improved corrosion performance of the AN + paint coating system under salt spray exposure suggests the organosilicon layer effectively acts as an adhesive-reinforced and protective intermediate layer, limiting the penetration of aggressive agents and preventing the spread of corrosion from damaged areas.

3.10. Pull-Off Adhesion Performance

To evaluate the adhesion-promoting effect of the developed organosilane coatings, pull-off adhesion tests were performed on a multilayer coating system consisting of the St20 steel substrate, the organosilane interlayer, and a commercial acrylic paint coating. Representative specimens before and after testing are shown in Figure 13.

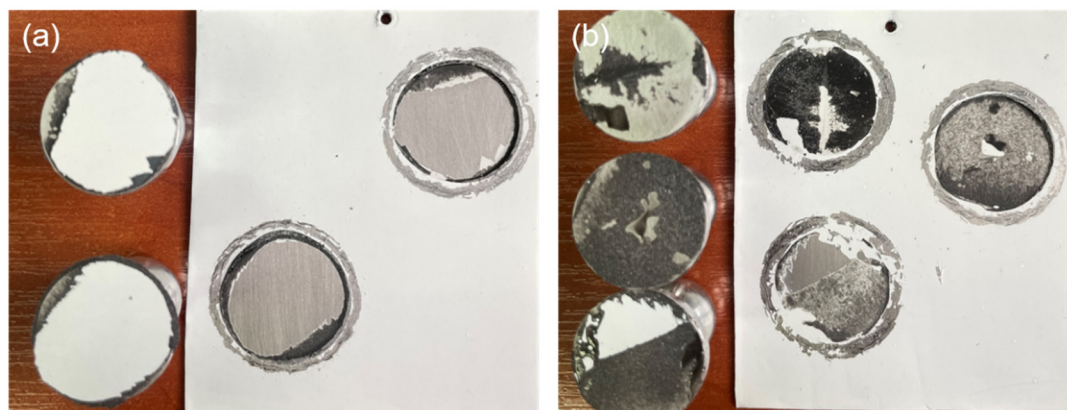


Figure 13. Representative fracture surfaces after pull-off adhesion testing of the acrylic coating system: (a) St20 steel treated with the AN organosilane interlayer (0.85 MPa); (b) untreated St20 steel (blank, 0.40 MPa).

The results demonstrate that the incorporation of the AN interlayer significantly improves the adhesion of the paint coating to the steel substrate. The AN coating exhibited the highest pull-off adhesion strength of 0.70 MPa, whereas the unmodified steel substrate (blank) showed a value of 0.40 MPa.

Visual examination of the fracture surfaces after pull-off testing (Figure 13b) revealed that failure was not exclusively localized at the steel/coating interface. In most cases, mixed failure involving both the coating and adhesive layers was observed, indicating effective interfacial bonding between the organosilane-treated substrate and the subsequently applied paint coating. The AN-coated specimens exhibited the smallest damaged area after pull-off, consistent with their higher measured adhesion strength.

The improved adhesion provided by the AN interlayer can be attributed to the formation of a continuous organosiloxane network strongly anchored to the hydroxylated steel

surface, while the nitrile-containing functionality promotes favorable interfacial interactions with the subsequently deposited acrylic coating. Although the detailed molecular mechanism requires further investigation, the present results clearly demonstrate that the introduction of the nitrile-functional organosilane enhances the adhesion performance of the coating system.

The improved interfacial adhesion is also consistent with the enhanced corrosion resistance observed in the electrochemical measurements and salt spray tests. A stronger and more stable coating/substrate interface reduces the probability of coating delamination and electrolyte penetration, thereby contributing to the overall protective performance of the AN coating.

4. Conclusions

The formation of an organosilicon coating based on 3-[(3-(triethoxysilyl)propyl)amino]propanenitrile (AN) on a steel surface was investigated. The optimal conditions for coating formation were established, including the composition of the hydrolysis solution, precursor concentration, surfactant content, and heat-treatment parameters. It was shown that hydrolysis and subsequent condensation of the AN precursor lead to the formation of a continuous organosilicon coating. Raman spectroscopy confirmed the preservation of the characteristic structural fragments of the precursor after coating formation, while AFM, SEM, and XPS demonstrated the formation of a homogeneous surface layer with low roughness and a cross-linked organosilicon network. Adhesion tests demonstrated that the AN coating significantly improves the adhesion of the paint coating to the steel substrate. Salt spray tests further showed that the AN coating, when used as an intermediate layer beneath a commercial acrylic paint, reduces the mass loss of the steel substrate and suppresses corrosion propagation from an artificial defect compared with the paint-only system. These results demonstrate that the synthesized AN compound is a promising precursor for organosilicon coatings and an effective adhesion-promoting protective interlayer for multilayer anticorrosion coating systems.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

The following abbreviations are used in this manuscript:

Abbreviation	Definition
AFM	Atomic Force Microscopy
AN	3-[(3-(Triethoxysilyl)propyl)amino]propanenitrile
AN coating	AN-based coating
APTES	3-Aminopropyltriethoxysilane
BR	Formation Water
EDS	Energy-Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
MS1	Model Solution 1 (GOST 9.502)
PAA	Protective Ability according to the Akimov Test
SDS	Sodium Dodecyl Sulfate
SEM	Scanning Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

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