



UDC 620.193.2

<https://doi.org/10.17073/1997-308X-2025-6-65-82>

Research article

Научная статья



Mechanisms of failure in anti-corrosion polymer coatings on metallic surfaces of oilfield pipelines: Review

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Abstract. Corrosion is one of the primary causes of failure in oil and gas equipment, affecting not only its service life but also operational safety. In the Russian Federation, crude-oil production is increasingly complicated by the high water content of produced fluids, which significantly accelerates corrosion processes. The use of internal polymer coatings in pipelines partly mitigates this problem; however, the proportion of corrosion-related failures remains high. Effective protection of oil pipelines using polymer coatings requires a clear understanding of their degradation mechanisms, including under conditions that closely approximate field operation. Such understanding enables the development of effective solutions that help maintain the operating stock of oil wells in serviceable condition. This work summarizes the principal mechanisms of degradation of polymer coatings on metallic surfaces, including under exposure to aggressive environments. The key factors governing coating failure in oil pipelines are identified: diffusion and absorption of water molecules within the polymer matrix; disruption of molecular interactions in the polymer network; delamination due to loss of adhesion between the coating and the metal; interfacial corrosion; cathodic delamination; blister formation; and erosion-driven damage. The study presents results of the examination of various epoxy–novolac-based anticorrosion coatings removed from pipelines after field service and provides representative images of coatings at different degradation stages. The aim of the work was to consolidate current knowledge on the degradation mechanisms of polymer coatings on metals under diverse conditions and to refine the staged description of coating degradation in oil pipelines.

Keywords: internal anticorrosion coatings (IACCs), oil pipelines, production tubing, diffusion, degradation, delamination

Acknowledgements: This work was partially carried out within the framework of the State Assignment of the Institute of Strength Physics and Materials Science SB RAS, project FWRW-2022-0002.

For citation: Yudin P.E., Lozhkomoev A.S. Mechanisms of failure in anti-corrosion polymer coatings on metallic surfaces of oilfield pipelines: Review. *Powder Metallurgy and Functional Coatings*. 2025;19(6):65–82.

<https://doi.org/10.17073/1997-308X-2025-6-65-82>

Механизмы разрушения антикоррозионных полимерных покрытий на металлических поверхностях нефтепромысловых трубопроводов: обзор

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Аннотация. Коррозия является одной из главных причин выхода из строя нефтегазового оборудования. Помимо уменьшения его срока службы, она оказывает влияние на безопасность при его эксплуатации. В настоящее время добыча нефти в РФ осложнена обводненностью скважинной продукции, что в значительной степени интенсифицирует процессы коррозии. Применение внутренних полимерных покрытий трубопроводов частично решает данную проблему, однако доля отказов, связанных с коррозией, до сих пор остается на высоком уровне. Для эффективной протекторной защиты нефтепроводов с использованием полимерных покрытий необходимо понимание механизмов их разрушения, в том числе в приближенных к реальным условиям эксплуатации. Это позволит находить эффективные решения, способствующие поддержанию эксплуатационного фонда нефтяных скважин в работоспособном состоянии. В настоящей работе описаны основные механизмы разрушения полимерных покрытий на металлических поверхностях, в том числе при их эксплуатации в агрессивных средах. Выделены основные факторы, обуславливающие разрушение покрытий нефтепроводов: диффузия и абсорбция молекул воды внутри полимерной матрицы; нарушение связей внутри полимерной сети покрытия; отслоение покрытий из-за потери адгезии между ним и металлом; межфазная коррозия; катодное отслоение; образование пузырей; эрозионные процессы. Приведены результаты исследования различных антикоррозионных покрытий нефтепроводов на эпоксишоволачной основе после эксплуатации на месторождениях. Продемонстрированы изображения покрытий на различных этапах разрушения. Цель работы заключалась в обобщении механизмов разрушения полимерных покрытий на металлах в различных условиях и уточнении стадийности разрушения покрытий нефтепроводов.

Ключевые слова: коррозия, эрозия, полимерные покрытия, внутренние антикоррозионные покрытия (ВАКП), нефтепроводы, насосно-компрессорные трубы (НКТ), диффузия, деградация, расслоение

Благодарности: Работа частично выполнена в рамках государственного задания ИФПМ СО РАН, тема FWRW-2022-0002.

Для цитирования: Юдин П.Е., Ложкомоев А.С. Механизмы разрушения антикоррозионных полимерных покрытий на металлических поверхностях нефтепромысловых трубопроводов: обзор. *Известия вузов. Порошковая металлургия и функциональные покрытия*. 2025;19(6):65–82. <https://doi.org/10.17073/1997-308X-2025-6-65-82>

Introduction

All polymers are, in principle, permeable to well fluids encountered during oil production, and this permeability ultimately results in corrosion and delamination of internal polymer coatings (IPCs) used in oilfield pipelines [1]. The permeability of water, oxygen, and electrolyte ions through the coating is a fundamental characteristic governing the progression of coating degradation and the subsequent corrosion of pipeline steel [2]. The failure mechanism of IPCs includes:

- ingress of water and ions into the coating, where water diffuses through the polymer matrix and initiates changes in its properties;
- chemical degradation of the polymer molecular structure, in which water cleaves reactive sites within

the epoxy network, causing hydrolysis-induced chain scission;

- accumulation of water within micropores of the coating, forming pathways for ion transport and ultimately leading to coating delamination from the metal surface [2].

Water absorption (hydration) within epoxy coatings is one of the primary causes of failure in pipeline coating systems [3]. The uptake of water softens and plasticizes the polymer network, promotes blister formation, cracking, and localized delamination of the epoxy layer. During prolonged exposure to water and aggressive chemical species, water molecules displace polar interfacial bonds between the coating and steel, weakening adhesion. Underfilm corrosion represents the final stage of degradation, where the combined

effects of adhesion loss and osmotic pressure cause cracking and delamination, resulting in coating failure and a substantial reduction in pipeline service life [3].

The corrosion process is governed by anodic and cathodic reactions at the metal–polymer interface [4; 5]. Cathodic reactions at the metal surface generate hydroxide ions, producing a highly alkaline environment [6; 7] that can raise the local pH to values above 14 beneath the coating near the delamination front [7]. Cathodic delamination may therefore arise from:

- electrochemical reduction of the oxide layer [8];
- alkaline hydrolysis [9] or electrochemical degradation [10] of the interfacial polymer region responsible for adhesion;
- alkaline breakdown of interfacial bonds [8].

The interfacial polymer layer is also degraded by free radicals generated through Fenton-type reactions involving Fe^{2+} and H_2O_2 or organic peroxides [11; 12]. These peroxide intermediates form during oxygen reduction and react with iron cations in the electrolyte near the metal–polymer interface. Radical-driven degradation weakens interfacial adhesion and accelerates delamination [11; 12]. Cathodic polarization additionally promotes molecular hydrogen evolution at the metal surface [13; 14]. The evolution of molecular hydrogen gas at the metal–polymer interface can generate high interfacial pressures and additional mechanical stresses within the delamination zone. This effect is supported by the established correlation between the electrolytic hydrogen uptake current in the metal and the rate of cathodic delamination [13].

This review summarizes the general mechanisms of polymer-coating degradation on metallic surfaces in atmospheric environments or ionized water – where oxygen acts as the primary corrosive agent. It further examines the behavior of internal anti-corrosion coatings used in gathering pipelines, water lines, and tubing strings, and presents an updated staging model for IPC degradation in oil pipelines.

Cathodic delamination of coatings

A schematic representation of cathodic delamination is presented in [15] (Fig. 1), based on an experimental study of the degradation of a polybutadiene coating on steel exposed to a 0.5 M NaCl solution under a cathodic potential of -1.5 V for 1000 h [8]. At the edge of the delaminated region, a pronounced decrease in oxide-film thickness was observed compared with the central area [8]. The increase in pH at the delamination front promotes dissolution of the oxide layer; however, as the interfacial gap (the distance between the metal surface and the lifted coating) increases, the pH gradually decreases and the oxide layer thickens again.

X-ray photoelectron spectroscopy (XPS) analysis [8] within the delaminated region revealed a metallic surface beneath the coating that was essentially free of oxide. According to the authors, this indicates that the surface oxide layer undergoes either reduction or dissolution. This process results in intraphase degradation of interfacial bonds and leads to interfacial separation along the metal/oxide boundary, with the oxide

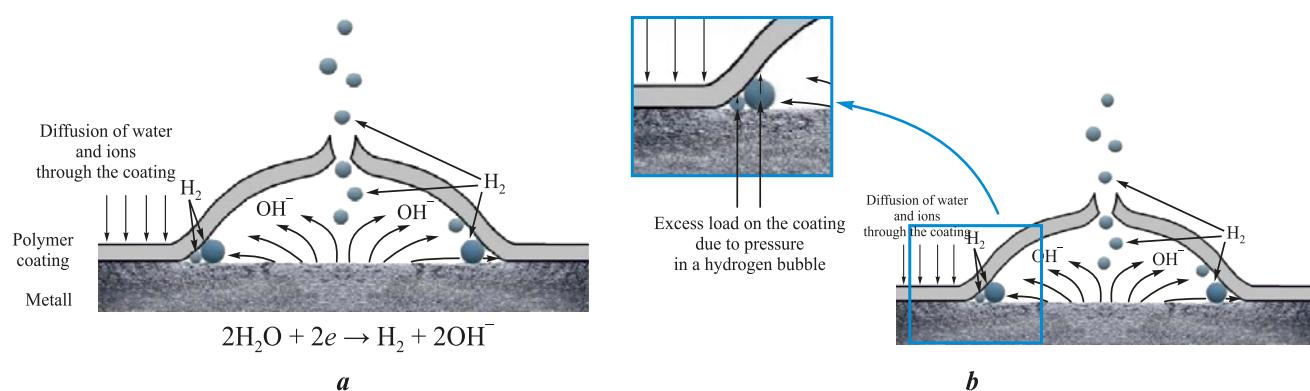


Fig. 1. Schematic representation of the processes occurring in a defective polymer coating and leading to cathodic delamination of the coating [15]

a – processes within the defect and beneath the delaminated coating; **b** – processes within the defect and beneath the delaminated coating, with detailed representation of the metal–polymer interface and the delamination zone

Рис. 1. Схема процессов, протекающих в дефектном полимерном покрытии и приводящих к катодному отслоению покрытия [15]

a – процессы в дефекте и под отслоившимся покрытием; **b** – процессы в дефекте и под отслоившимся покрытием с детализацией границы раздела металл–полимер и зоны отслоения покрытия

layer being removed together with the delaminated coating. Outside the interfacial separation zone, the coating detaches cleanly from the metal substrate without cohesive damage [8].

Anodic corrosion

Filiform corrosion, a form of anodic underfilm corrosion, has been observed on metals with polymer coatings exposed to a humid atmosphere, the aggressiveness of which is enhanced by artificial or natural contaminants such as sulfur dioxide or chlorides [16; 17]. This type of corrosion (Fig. 2) typically initiates at discontinuities in regions containing porosity and voids, mechanical defects, or areas of reduced coating thickness. Filiform corrosion is characterized by linear propagation paths, where local accumulation of water at the metal/coating interface triggers electrochemical processes [18; 19]. Localized anodic reactions on the steel are coupled with oxygen reduction, which in turn promotes cathodic degradation of adhesion at the interface.

Diffusion of reactants through polymer coatings

Fig. 3 illustrates the stages of coating delamination under high hydrostatic pressure as proposed in [20]. In an epoxy-varnish coating, the applied pressure significantly accelerates the diffusion of water toward the coating–substrate interface and leads to the formation of numerous small, water-filled blisters.

One of the most important degradation mechanisms is coating aging, which results in a loss of barrier performance and deterioration of mechanical properties. Aging occurs under the combined influence of elevated

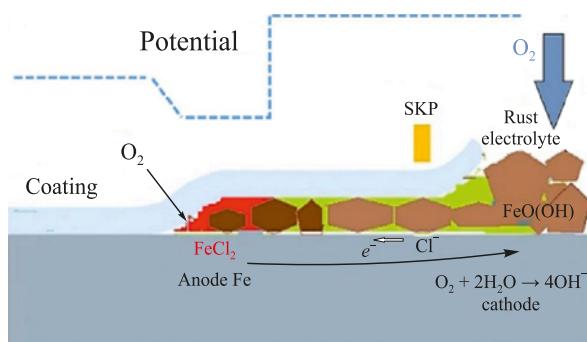


Fig. 2. Schematic representation of anodic delamination driven by corrosion, and the potential distribution along the metal–coating interface [16]

Рис. 2. Схема анодного отслоения покрытия под воздействием коррозии и распределение потенциала вдоль границы основы и покрытия [16]

temperature, chemically aggressive species, pressure, and mechanical loading [21]. Another critical failure mechanism is blister formation during decompression. As described in [21], gases penetrate the pores of the material at high pressure; when the pressure is rapidly reduced, the dissolved gases expand, generating blisters within the coating and causing its failure (Fig. 4, a). Corrosion also develops at sites where the coating is mechanically damaged (Fig. 4, b). In such cases, the base metal of the pipe is directly exposed to the aggressive environment, leading to active corrosion. When defects are present, the rate of corrosion progresses with similar intensity regardless of the coating type [21].

The authors of [22] investigated the effect of prolonged exposure (85 weeks) to hot water at 65 °C on epoxy powder barrier coatings used to protect metallic surfaces, including components of oil and gas equipment. It was shown that degradation of the coating begins after only 8 weeks, while oxidation of the substrate becomes noticeable after 182 days. Adhesion-strength measurements demonstrated that the bonding strength of the coatings decreases rapidly due to water-induced plasticization, but subsequently exhibits a slight recovery attributed to secondary crosslinking of the epoxy network [22].

A study presented in [23] examined the degradation mechanisms of coatings based on amine-cured epoxy novolac (EN) and bisphenol-F (BPF) resins under

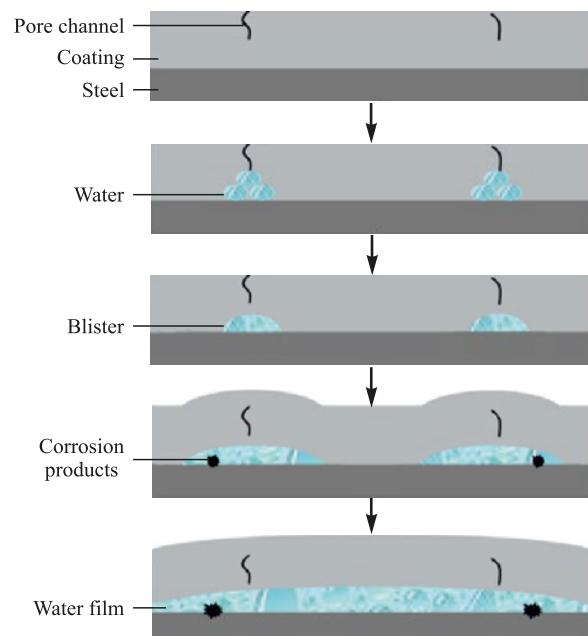


Fig. 3. Schematic representation of the coating-failure process under high hydrostatic pressure [20]

Рис. 3. Схематическое изображение процесса разрушения покрытий под высоким гидростатическим давлением [20]

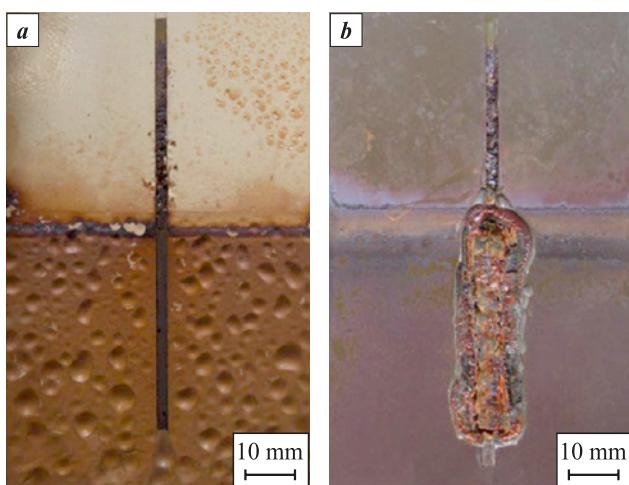


Fig. 4. Coating failure after corrosion autoclave testing [21]

a – blister formation caused by insufficient film thickness;
b – corrosion developing in a damaged coating

Рис. 4. Разрушение покрытия после коррозионных автоклавных испытаний [21]

a – образование пузырей из-за малой толщины пленки;
b – коррозия в поврежденном покрытии

high-pressure, high-temperature (HPHT) conditions. The coatings were subjected to autoclave testing. It was established that the degradation mechanisms of EN and BPF protective coatings under HPHT conditions are governed by the combined action of gas, hydrocarbon, and aqueous phases and their joint effects on the polymer structure and the substrate. In the gas phase, consisting of nitrogen and carbon dioxide, the coatings remain unchanged because no significant interaction or physical damage occurs. However, contact of the coating surface with hydrocarbons (*p*-xylene) results in solvent diffusion into the polymer matrix, which increases the free volume within the coating layer. Fig. 5 illustrates the mechanisms of coating degradation under HPHT exposure to *p*-xylene during autoclave conditioning, as well as during pressure release under decompression [23].

The study reported in [24], which involved simultaneous exposure to three phases (a gas phase, a hydrocarbon liquid phase, and mineralized water), investigated the influence of carbon dioxide (CO_2) present in the gas phase under HPHT conditions on the degradation of amine-cured epoxy novolac (EN) coatings. It was established that the combined action of the gas, hydrocarbon, and aqueous phases deteriorates the coating performance and leads to underfilm corrosion. When each phase was applied separately under low-pressure conditions, the EN network remained intact and essentially impermeable. However, in regions exposed to hydrocarbons, the joint action of *p*-xylene and CO_2 at elevated pressure and temperature causes

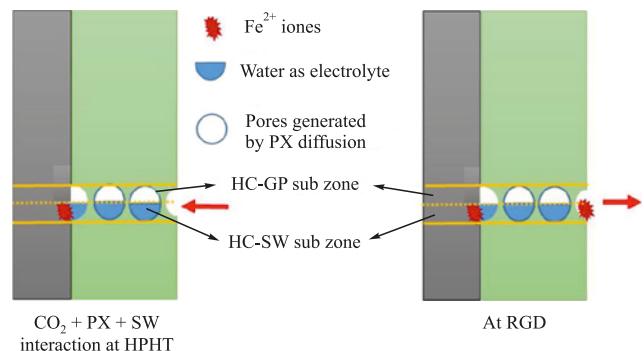


Fig. 5. Water ingress through the coating toward the metal and the migration route of iron ions toward the coating surface during decompression-driven pressure release [23]

Рис. 5. Проникновение воды через покрытие к металлу и путь ионов железа к поверхности покрытия при декомпрессионном сбросе давления [23]

a reduction in the glass-transition temperature, followed by softening of the EN network. This softening allows dissolved CO_2 to diffuse into the EN structure, forming microscopic voids at the coating surface (Fig. 6).

Comparative autoclave tests under high-pressure, high-temperature (HPHT) conditions were carried out in [25] or epoxy–siloxane hybrid coatings. These coatings were shown to outperform EN-based systems, which soften upon exposure to hydrocarbons (such as *p*-xylene), resulting in a reduction in glass-transition temperature and an accelerated diffusion of gases and ions.

The long polymer chains in siloxane-based coatings (EN-EPDMS) promote the uptake of water molecules, especially under high pressure. Such coatings tend to form unruptured blisters during rapid pressure release. In contrast, the coating modified with the short-chain 3-glycidyloxypropyltrimethoxysilane (EN-GPTMS) exhibited high resistance to decompression (Fig. 7).

Under the assumption that the coating remains intact and free of defects or inclusions, it can therefore be concluded that the primary initiating factor for coating degradation and the onset of corrosion is the diffusion of reactive species through the polymer layer (Fig. 8).

However, as noted by the authors of the review [26], many open questions remain regarding the swelling behavior of polymers and the complexity of describing diffusion processes that deviate from ideal Fickian diffusion (Fick's second law), among other issues (Fig. 9).

Overall, the degradation of a polymer coating is governed by the following processes and/or their combination.

- Diffusion and absorption of water molecules within the polymer matrix. These processes are influ-

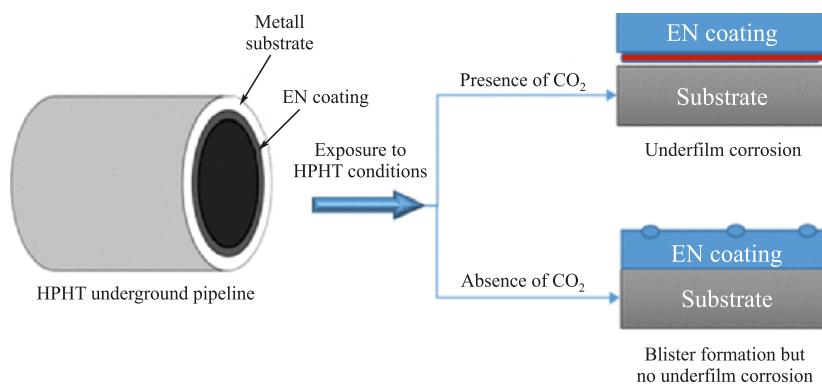


Fig. 6. Mechanisms by which the hydrocarbon and aqueous phases affect an epoxy–novolac coating under high-pressure, high-temperature conditions, in the presence and absence of carbon dioxide in the system [24]

Рис. 6. Механизмы воздействия углеводородной и водной фаз на эпоксидно-новолачное покрытие в условиях высоких давлений и температур при наличии углекислого газа в системе и без него [24]

enced by surface topography, polymer structure, and environmental conditions. Free volume and micro-cracks within the coating structure provide pathways for the diffusion of water molecules, which may follow Fickian, non-Fickian, and/or capillary diffusion regimes. As they move from the external coating surface toward the coating/metal interface, water molecules may either migrate freely or interact with polar segments of the polymer network. Water absorption by the polymer leads to structural instability of the polymer network (plasticization), promoting volumetric expansion, interfacial separation, and erosion of the coating [27–30].

- Disruption of van der Waals and hydrogen bonds within the polymer network as a result of interac-

tions between water molecules and polar segments of the polymer chain, which causes anisotropic expansion of the network. These volumetric changes and the associated stresses can irreversibly alter the coating microstructure, leading to the initiation and/or growth of microcracks within the coating and at the coating/metal interface [31–34].

- Fragmentation of polymer chains due to hydrolytic degradation of coatings containing hydrolysable bonds. In addition to hydrolysis of the polymer matrix, dissolution of coating components (such as pigments and additives) may occur, resulting in mass loss and structural changes. The hydrolysis process can further accelerate polymer degradation by altering the local pH in regions surrounding the reactive sites [35–37].

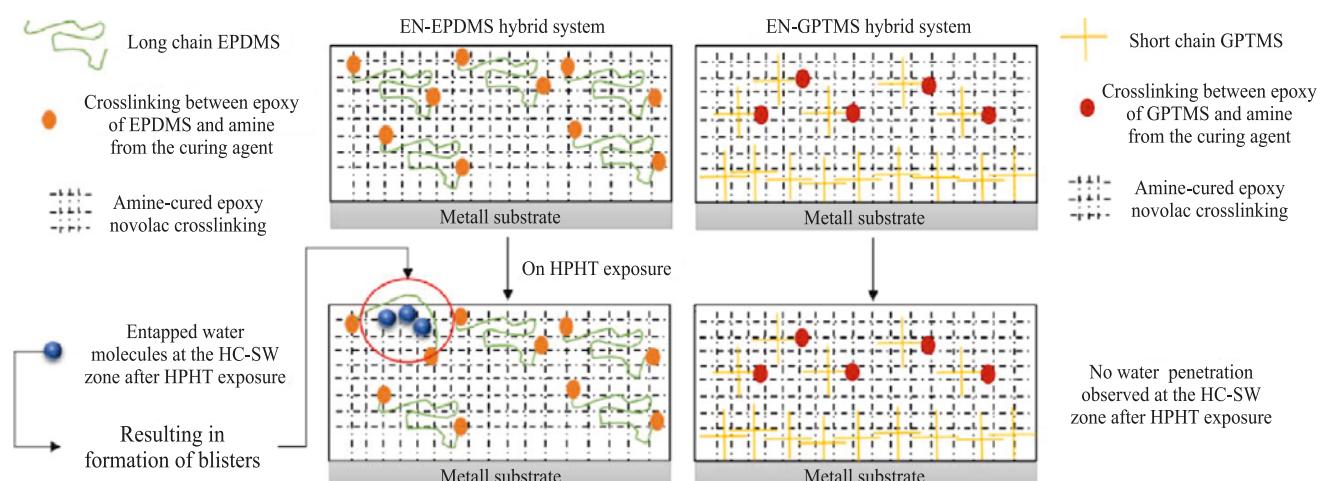


Fig. 7. Schematic illustration of crosslinking in EN-EPDMS and EN-GPTMS coatings before and after HPHT exposure [25]

The long and flexible EN-EPDMS chains exhibit trapped water molecules in the HC-SW region, which leads to the formation of unruptured blisters. By contrast, the short-chain, EN-GPTMS-crosslinked network shows no detectable changes under high-pressure, high-temperature exposure

Рис. 7. Схематическая иллюстрация сшивания EN-EPDMS и EN-GPTMS до и после воздействия HPHT [25]

Длинная и гибкая цепь EN-EPDMS демонстрирует захваченные молекулы воды в зоне HC-SW, что приводит к образованию нелопнувших пузырей. Напротив, короткая цепь в EN-GPTMS сшивкой структуре не показывает никаких изменений при воздействии высоких давлений и температур

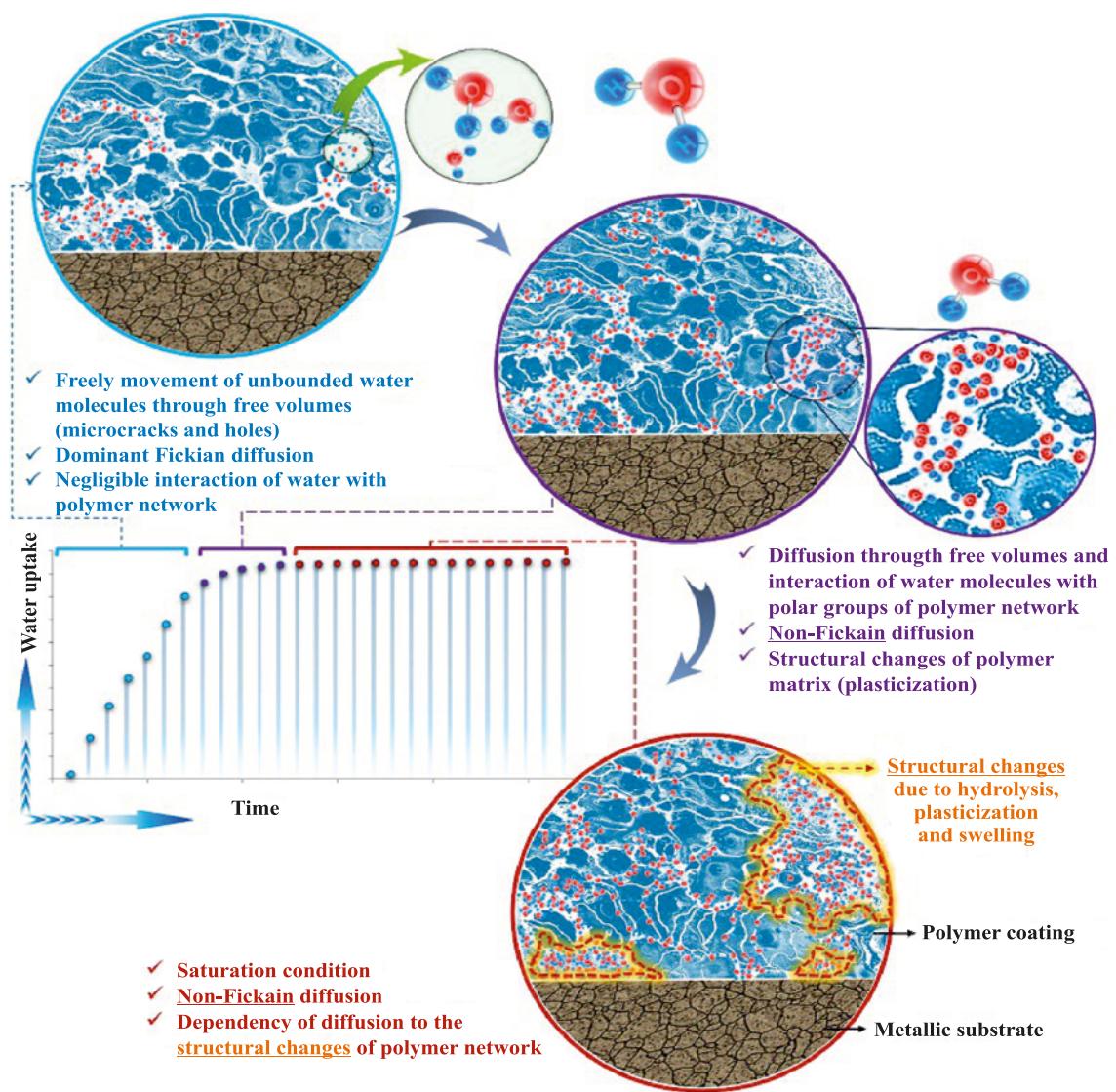


Fig. 8. Schematic illustration of changes in water uptake in polymer coatings as a function of exposure time [18]

Рис. 8. Схематическая иллюстрация изменения водопоглощения в полимерных покрытиях с течением времени [18]

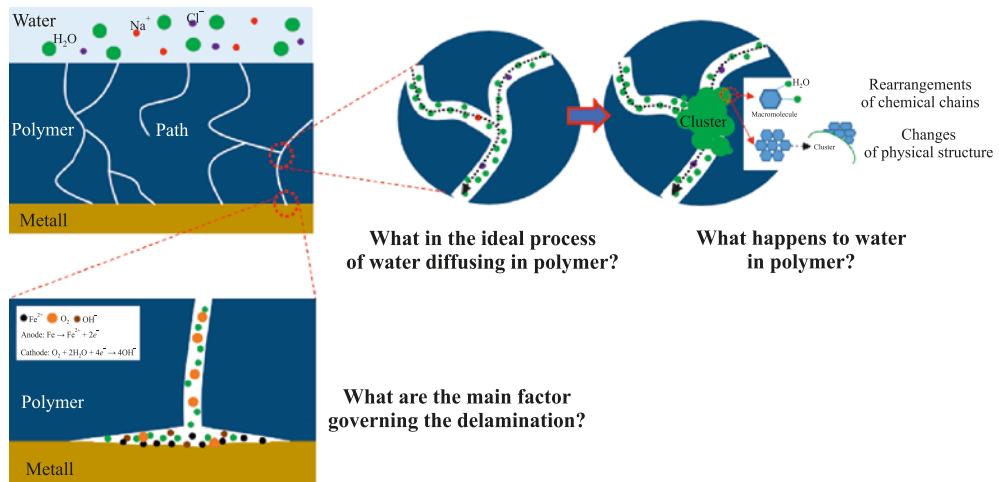


Fig. 9. Schematic representation of water diffusion through a polymer layer toward the metallic surface and the associated unresolved questions [26]

Рис. 9. Схема диффузии воды через слой полимера к металлической поверхности и связанные с этим вопросы [26]

- Delamination associated with loss of adhesion, driven by damage to molecular bonds between the coating and the metal, disruption of thermodynamic equilibrium at the metal–polymer interface, and the breakdown of mechanical interlocking and/or the development of osmotic pressure. Delamination is initiated by the permeation of water molecules through the coating to the metallic substrate, thereby compromising coating integrity and accelerating adhesion loss. Typically, delamination is preceded by plasticization and swelling of the coating, as well as changes in interfacial chemistry [38–41].

- Interfacial delamination caused by corrosion at the metal–coating interface. Variations in pH within the interfacial region disturb the thermodynamic equilibrium established by Lewis acid–base interactions, thereby reducing adhesion strength [18]. Corrosion at the metal/coating interface disrupts mechanical interlocking between the coating and the metallic substrate, further weakening adhesion. The accumulation of corrosion products in the interfacial gap generates mechanical stresses due to expansive forces (for example, the formation and growth of rust) [42]. Moreover, the hygroscopic nature of rust enhances moisture uptake, leading to dimensional changes and additional mechanical stresses within the coating. These stresses promote interfacial separation and cracking. Lateral expansion of the separated coating region, caused by growth of corrosion products, can also lead to blister formation [43].

- Cathodic delamination of polymer coatings, which is driven by the alkaline environment generated by cathodic reactions at the metal–polymer interface. As a result, the thermodynamic equilibrium at the interface is disrupted: alkaline species dissolve the thin

oxide layer on the metal and induce chemical degradation of the polymer via alkaline hydrolysis and reactive intermediates. This process also promotes substrate corrosion by disturbing the local charge balance and facilitating the transport of charged species. Ultimately, these mechanisms undermine the adhesion forces between the coating and the substrate [39; 44–46].

- Blister-induced delamination of the coating arises from water uptake and electrochemical reactions. The accumulation of water and dissolved species at the metal–polymer interface, together with the resulting osmotic pressure and mechanical stresses, reduces the adhesion of the coating to the metallic substrate and leads to interfacial delamination [47–52].

Erosion-corrosion processes

The processes described above, whose combined action leads to degradation of the protective polymer coating, proceed at a substantially accelerated rate when the coating is additionally exposed to flowing fluid during service. In [53], a comparison was made between the deterioration of barrier properties under flow conditions and under static immersion, using an experimental setup whose schematic arrangement is shown in Fig. 10.

The barrier properties of the coating during testing were evaluated using electrochemical impedance spectroscopy (EIS). The EIS measurements showed that the impedance modulus of the coating decreases much more significantly under flow, indicating that fluid motion along the protective coating accelerates water ingress into the coating [53]. A similar conclusion – that degradation of an organic coating accelerates when immersed in two different working fluids (DI water and 3.5 wt. % NaCl solution) under laminar-

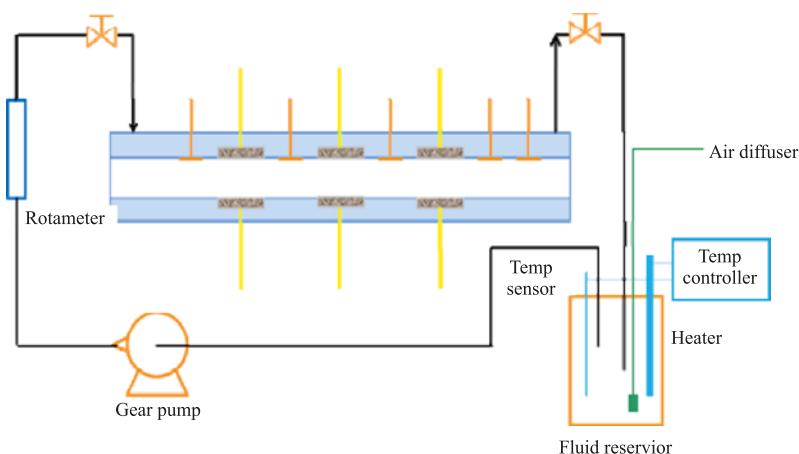


Fig. 10. Schematic diagram of the setup used to simulate fluid-flow effects on a polymer coating [53]

Рис. 10. Принципиальная схема установки, моделирующей условия воздействия потока жидкости на полимерное покрытие [53]

flow conditions compared with static immersion – was also reported by the authors of [54].

A review presented in [55] summarized existing research on tribocorrosion of coatings, i.e., their behavior under simultaneous action of erosive wear and corrosion. Under erosive flow, the authors distinguish three coating-damage mechanisms:

– surface damage, in which a defect in the passive film triggers repassivation and film reconstruction on the coating surface (Fig. 11, *a*):

– corrosive wear of hard coatings on metallic substrates, leading to the formation of pits and blistering of the protective coating, followed by mechanical damage and delamination (Fig. 11, *b*):

– abrasive action on the coating surface caused by the potential difference between the metallic substrate beneath the coating and entrained abrasive particles, which accelerates surface wear (Fig. 11, *c*).

In [56], the authors described the degradation mechanism of protective epoxy–novolac coatings exposed to erosion–corrosion. At the first stage, erosive attack produces microcracks exclusively around filler particles. These microcracks create a porous structure that allows the electrolyte to gradually penetrate deeper into the coating. At this stage, however, the coating still maintains sufficient barrier performance to prevent corrosion initiation.

At the second stage, the cracks begin to widen, and the barrier properties of the coating weaken under aggressive conditions (high temperature, low pH, presence of CO_2 and chlorides). The electrolyte penetrates further and reaches the metal–polymer interface. As a result, local corrosion initiates and produces corrosion products (iron oxides) within the pores of the coating. This decreases the coating resistance, as detected by electrochemical measurements.

At the third stage, the mechanical integrity of the coating is severely compromised. As underfilm corrosion continues to deepen and spread, the coating delaminates and its structure becomes increasingly porous. As a result, the access of aggressive species to the metallic substrate increases, leading to the initiation of new corrosion sites, and the coating ultimately loses its barrier functionality. All three stages of coating degradation are shown in Fig. 12.

Thus, the principal stages and regularities of polymer-coating degradation under high-pressure and high-temperature conditions, as well as under exposure to abrasive particles, have been examined. In most cases, the studies were conducted in atmospheric environments or in ionized water, where oxygen is the predominant corrosion-active species.

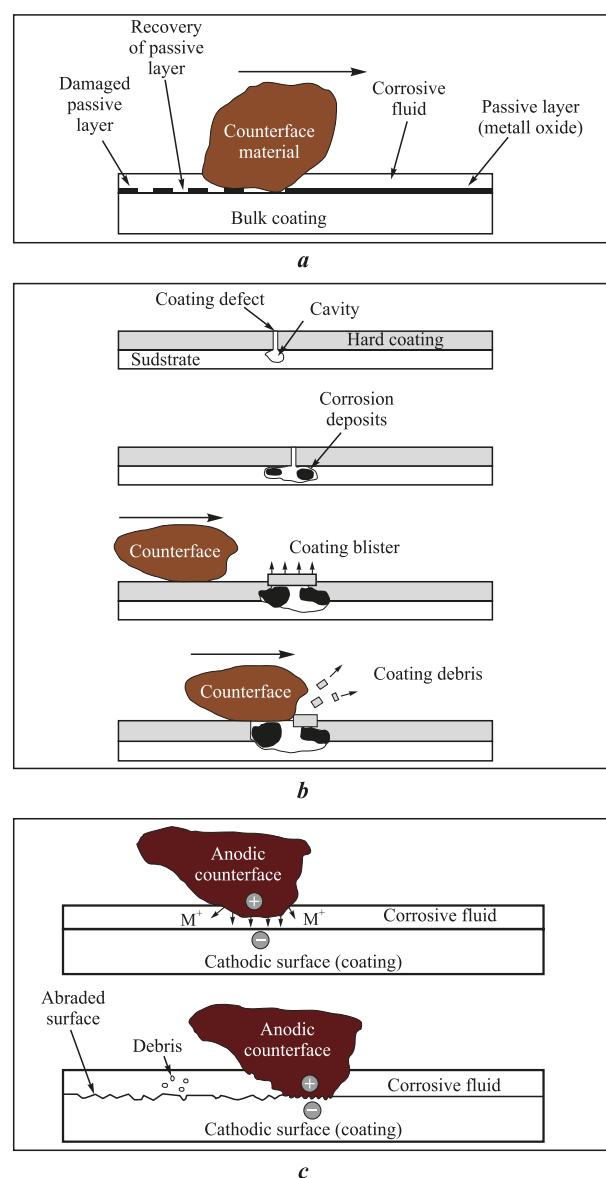


Fig. 11. Three coating–failure mechanisms under erosive conditions [55]

a – type-1 wear: corrosion of hard coatings on metallic substrates, in which damage to the passive film leads to its repassivation and regeneration on the coating surface;

b – corrosive wear of hard coatings on a metallic surface, resulting in pitting and blistering of the protective coating, followed by mechanical damage and delamination;

c – abrasive action on the coating surface caused by the potential difference between the metallic substrate beneath the coating and entrained abrasive particles, which activates surface wear of the coating

Рис. 11. Три механизма разрушения покрытия в условиях эрозионного воздействия [55]

a – износ 1-го типа: коррозия твердых покрытий на металлических подложках, при которой повреждение пассивной пленки приводит к повторной ее пассивации и регенерации на покрытии;

b – коррозионный износ твердых покрытий на металлической поверхности, приводящий к образованию пittingов и вздутию защитного покрытия и в результате – к его механическому разрушению и отслоению;

c – абразивное воздействие на поверхность покрытия, вызванное разнозаряженностью металлической подложки под покрытием и абразивными частицами, в результате чего происходит активация истирания поверхности покрытия

Degradation of internal anticorrosion coatings in oil pipelines

A review of degradation mechanisms of internal anticorrosion coatings (IACCs) used in oil-gathering collectors, water pipelines, and production tubing strings was previously carried out in [57]. All coatings examined were based on epoxy–novolac systems with different ratios of epoxy film-forming components to novolac resin. Powder coatings were applied by electrostatic spraying, whereas liquid coatings were applied using airless spraying followed by drying or polymerization.

Several processes occur simultaneously within the coating: diffusion of corrosion-active species, degradation of interfacial adhesion, and destructive changes within the polymer matrix that lead to a reduction of cohesive strength. The intensity of these processes depends strongly on temperature and increases sharply as the temperature approaches the glass-transition temperature (T_g) (taking into account its depression caused by water uptake). Therefore, the behavior of these coatings must be considered specifically in their glassy state [58].

At the present stage of research, coating degradation can be represented by the following sequence (Fig. 13). In the first stage, the polymer undergoes water uptake, accompanied by significant changes in its physical and mechanical properties: T_g decreases by approximately 30 °C at 1.5 wt. % water uptake, while tensile strength decreases by about 20 % [58]. This initial stage proceeds relatively rapidly and can be described by the diffusion equation [26]:

$$q(t) = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left\{ -\frac{(2n+1)^2 \pi^2 D}{4l^2} t \right\},$$

where $q(t)$ is the average concentration of the penetrant across the polymer layer at time t , s; D is the diffusion coefficient for a constant source into a polymer layer of thickness l , cm^2/s .

The values of D lie in the range of $1.0 \cdot 10^{-9}$ to $5.0 \cdot 10^{-8} \text{ cm}^2/\text{s}$ and depend on the chemical composition of the film-forming component and curing agent, the degree of crosslinking, the type and loading of fillers, as well as the pressure and temperature of the environment.

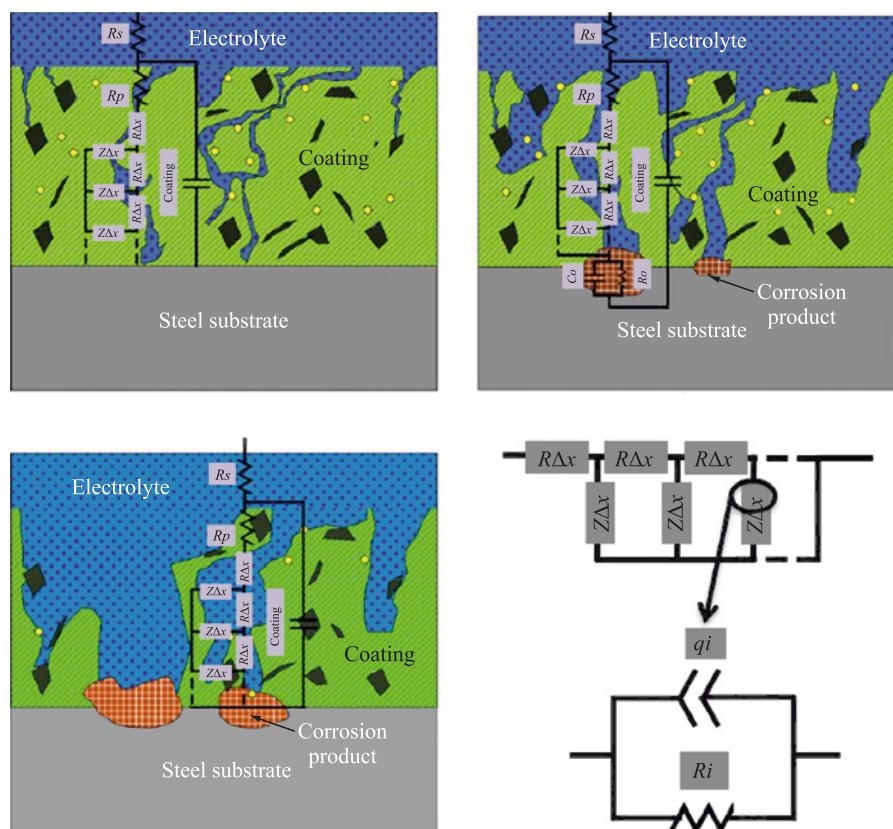


Fig. 12. Stages of polymer-coating degradation under erosive wear, together with the corresponding EIS equivalent circuits for each stage [56]

Рис. 12. Стадии разрушения полимерного покрытия в результате эрозионного износа, а также эквивалентные схемы EIS, соответствующие этим стадиям [56]

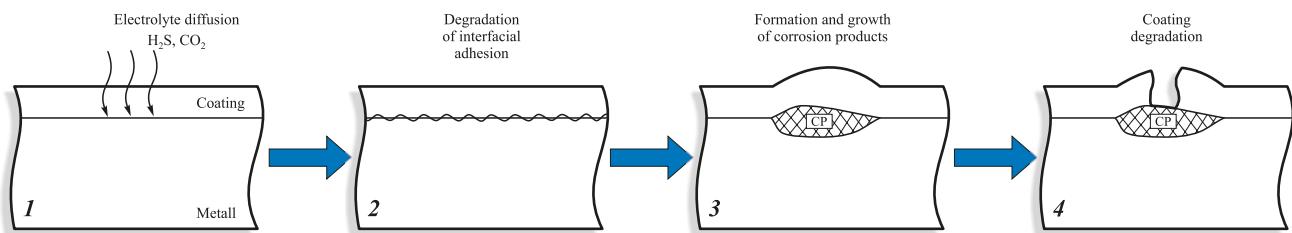


Fig. 13. Staged degradation process of internal protective coatings

Рис. 13. Стадийность процесса разрушения внутренних защитных покрытий

At the second stage, the coating undergoes degradation of interfacial adhesion, which is typically localized and appears as spots with a diameter of approximately ten coating-thicknesses (Fig. 14). This process is prolonged when the coating operates at temperatures below the wet glass-transition temperature (wet T_g) of the polymer and when no application defects are present. The key durability criteria include the initial adhesion strength, the diffusion coefficient, and the coating's resistance to chemical and physical degradation under service conditions – i.e., the retention of intrinsic coating properties that determine its barrier performance. For example, destructive changes in the polymer structure may produce microcracks that enable not only electrolyte diffusion but full mass transport through the coating.

During failure analysis of internal polymer coatings, it is often found that a significant reduction in service life results from violations introduced either during application or during operation. A common example illustrating how application technology influences the durability of internal coatings is the frequent occurrence of defects at the ends of production tubing. The application of coatings to tubing ends involves specific operations – make-up of the coupling and cleaning of the tube end and threads from factory lubricant (Fig. 15).

Conventional removal of lubricant by solvent cleaning and mechanical treatment is often incomplete, resulting in localized blistering and coating failure, even though the coating remains intact over the rest of the pipe surface (Fig. 16). In practice, complete removal of lubricant is reliably achieved only by high-temperature treatment (furnace heating or laser-based heat treatment). Characteristic features of this type of failure are its localization within approximately 100 mm of the pipe end and the presence of large blisters caused by the lack of adhesion in this region.

In this case, overheating is associated with operation at temperatures above the wet-state T_g of the coating. Visually, this failure mode differs little from the normal degradation mechanism; however, the service life may be reduced by more than a factor of ten under elevated-temperature operation.

The thermokinetic characteristics of the internal coating were determined in order to assess the degree of cure of the powder-based material using differential scanning calorimetry (DSC). Tests were carried out on specimens before and after conditioning at 90 °C for 24 h to remove moisture from the coating. The corresponding results are summarized in the table, and the DSC thermograms of the coating material are presented in Fig. 17.

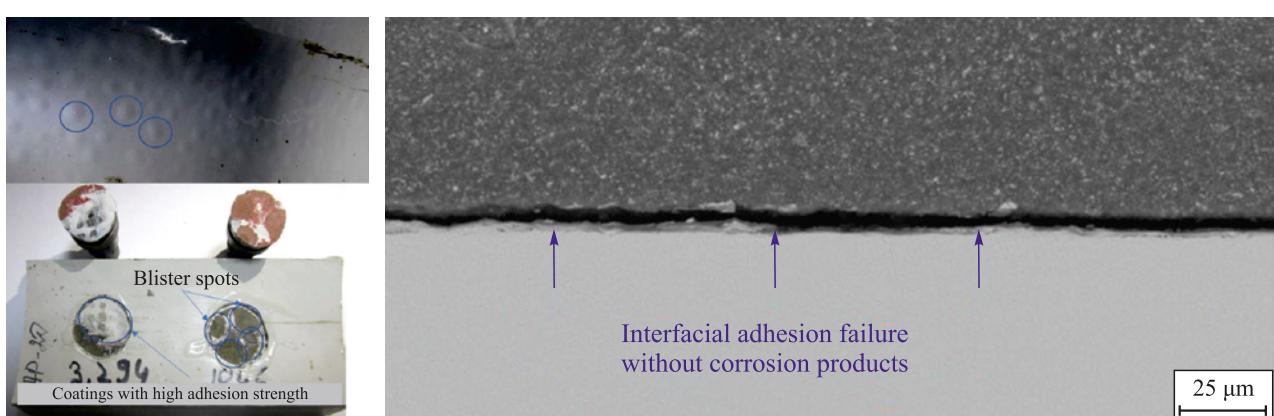


Fig. 14. Localized blistering of the coating after service (2nd degradation stage)

Рис. 14. Локальные вздутия покрытия после эксплуатации (2-я стадия разрушения)

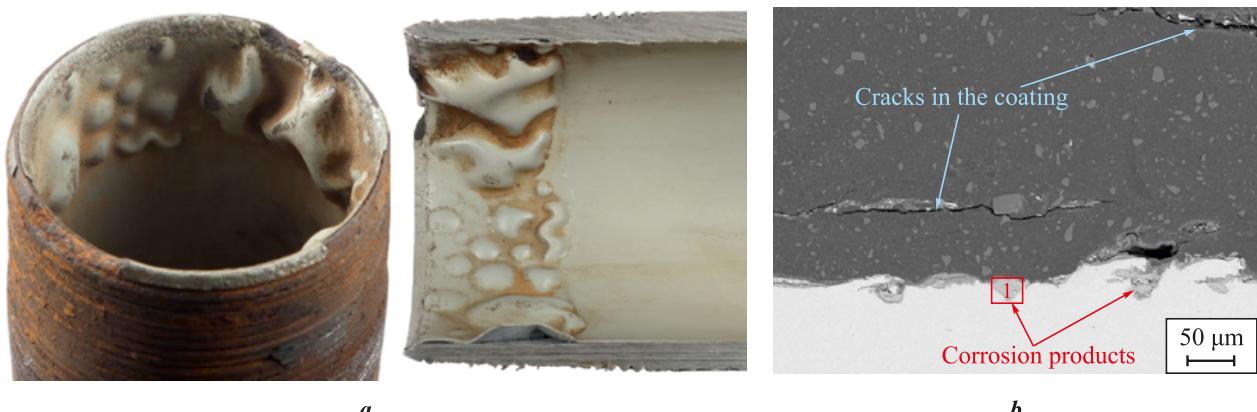


Fig. 15. Appearance of damage to the internal coating of production tubing in the nipple region caused by improper surface preparation prior to abrasive blasting (a), and microstructure of the damaged zone showing areas with corrosion products and cracking within the coating (b)

Рис. 15. Внешний вид разрушения внутреннего покрытия НКТ в nippleльной части, обусловленного нарушением технологии подготовки поверхности перед дробеструйной обработкой (а), и микроструктура зоны разрушения с участками образования продуктов коррозии и трещин в покрытии (б)

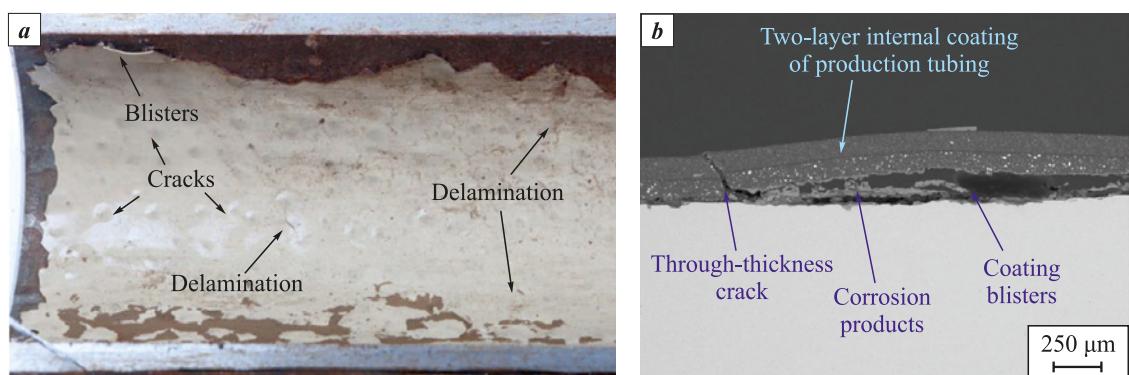


Fig. 16. Appearance of the internal coating of production tubing, Ø73×5.5 mm (after 512 days of service) (a), and the structure of the coating and corrosion products in the damaged region (b)

Рис. 16. Внешний вид внутреннего покрытия НКТ Ø73×5,5 мм (наработка 512 сут) (а) и структура покрытия и продуктов коррозии в области разрушения (б)

Based on the test results, the observed difference between the glass-transition temperatures determined in the first and second heating cycles for the as-received specimens is +13.8 and +12.7 °C, respectively, whereas after conditioning the difference decreases to +1.5 and +2.9 °C. This indicates that the coating absorbs moisture during service, which is a typical process for polymeric materials [58]. The absence of a curing peak in the DSC curves confirms that polymerization of the coating had been completed. The T_g values after conditioning (111–113 °C) match those of the as-received coating, demonstrating that no thermo-oxidative degradation occurred.

The third degradation stage is governed by the growth of corrosion products and depends on the diffusion coefficient and the corrosion resistance of the steel. This is a long-term process, and its duration is determined not only by the properties of the envi-

ronment and the coating but also by the absence of mechanical loading on the internal coating, which could otherwise rupture the blister (Fig. 18).

The composition and morphology of the corrosion products correspond to the governing corrosion pro-

Results of determining the degree of coating curing

Результаты определения степени отверждения покрытия

Specimen	T_{g_1} , °C	T_{g_2} , °C	$\Delta T_g = T_{g_2} - T_{g_1}$, °C
1 (as-received)	95,8	109,6	13,8
1 (conditioned)	107,8	109,3	1,5
2 (as-received)	99,8	112,5	12,7
2 (conditioned)	108,9	111,8	2,9
Requirements of GOST R 58346–2019			$-5 \leq \Delta T_g \leq +5$

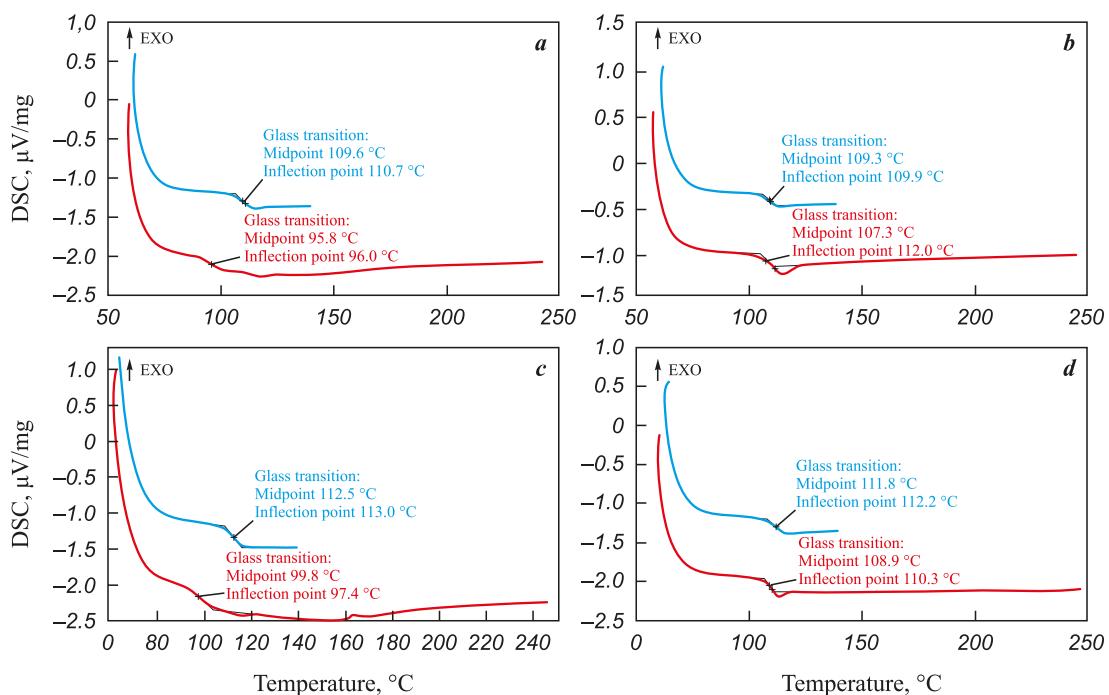


Fig. 17. DSC thermograms of the coating specimens:
a, c – specimens in the as-received state; b, d – specimens after conditioning
 Tg_1 – red curves, Tg_2 – blue curves

Рис. 17. Термограммы ДСК образцов покрытий

a, c – образцы в исходном состоянии; b, d – образцы после кондиционирования
 Tg_1 – красные кривые, Tg_2 – синие кривые

cesses. In CO_2 corrosion, the formation of FeCO_3 is observed; the carbonate inherits the steel microstructure because the reaction $\text{Fe}_3\text{C} + \text{CO}_2$ does not proceed, whereas α -Fe (ferrite) reacts with CO_2 to form iron carbonate (Fig. 19, a). Blister formation always precedes the growth of the corrosion-product layer, because this layer does not experience mechanical loading and cannot expand freely in the confined space. A corrosion-product layer enriched in chlorine is localized at the metal/corrosion-product interface (Fig. 19, b), which is characteristic of corrosion processes occurring

in oilfield tubing. The identical composition and morphology of the corrosion products indicate the absence of selective diffusion or differences in the diffusion rates of individual components through the coating.

The height of coating blisters may reach ten times the coating thickness, which indicates minimal destructive changes and preservation of elasticity. In the authors' experience, failures preceded by significant plastic deformation have not been observed even after long service periods (over 10 years); therefore, adhesion loss and blister formation always proceed

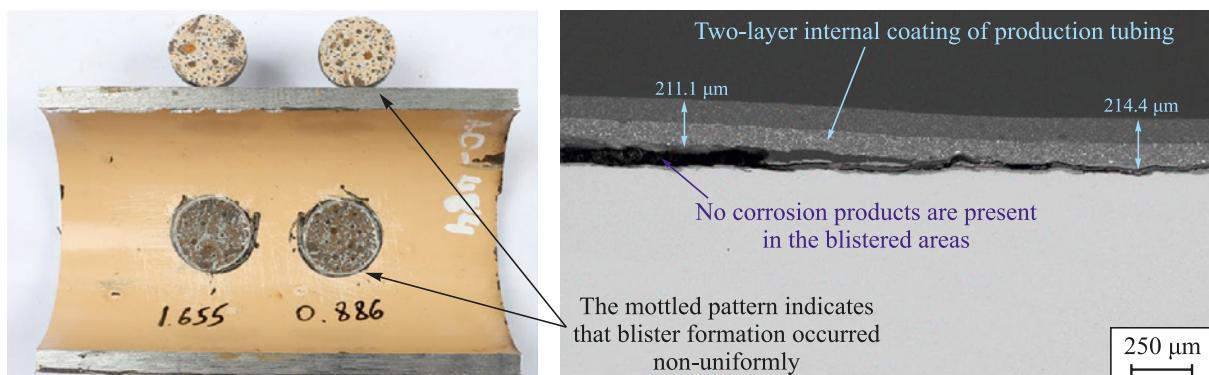


Fig. 18. A typical example of the appearance and structure of the coating at the third destruction stage

Рис. 18. Характерный пример внешнего вида и структуры покрытия на третьей стадии разрушения

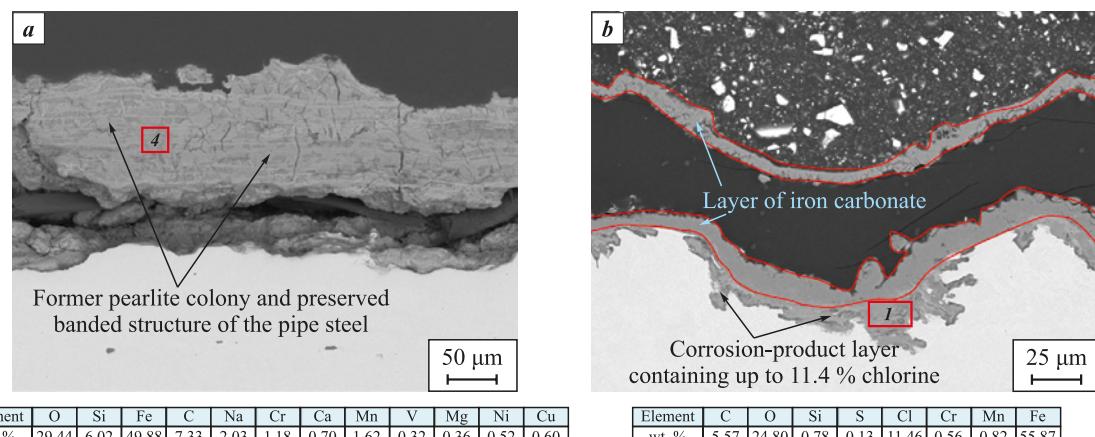


Fig. 19. Структуры продуктов коррозии под покрытием – карбоната железа (а) и хлора (б)
Красным прямоугольником обозначена зона элементного анализа в режиме СЭМ-ЭДС

faster than aging processes accompanied by a reduction in ductility.

The fourth degradation stage is associated with the rapid development of through-thickness pits. If the coating has not been exposed to elevated temperatures, then by the time this stage is reached substantial destructive changes have often occurred, causing the coating to become brittle and fail easily (Fig. 20). In the presence of coating defects, corrosion damage is intensified for two reasons:

– formation of a galvanic couple in which the blister center acts as the anode, followed by accelerated corrosion after pit initiation and the formation of an additional cathode–anode pair;

– all corrosive activity is concentrated in a single local area; the medium contains no Fe^{2+} ions (typically released during corrosion of uncoated pipe),

which otherwise act as inhibitors for corrosion processes. In such cases, the characteristic failure mode is through-wall pitting corrosion, whereas the coating remains intact on remote sections of the pipe (Fig. 21).

Conclusions

1. A comprehensive review of the degradation mechanisms of polymer coatings on metallic substrates has been conducted, including water diffusion and absorption within the polymer matrix, disruption of molecular interactions in the polymer network, adhesion loss and interfacial delamination, interfacial corrosion, cathodic delamination, blister formation, and erosion-driven damage.

2. It has been shown that the degradation of internal anticorrosion coatings in oil pipelines can be divided into four stages. At the first stage, water uptake and

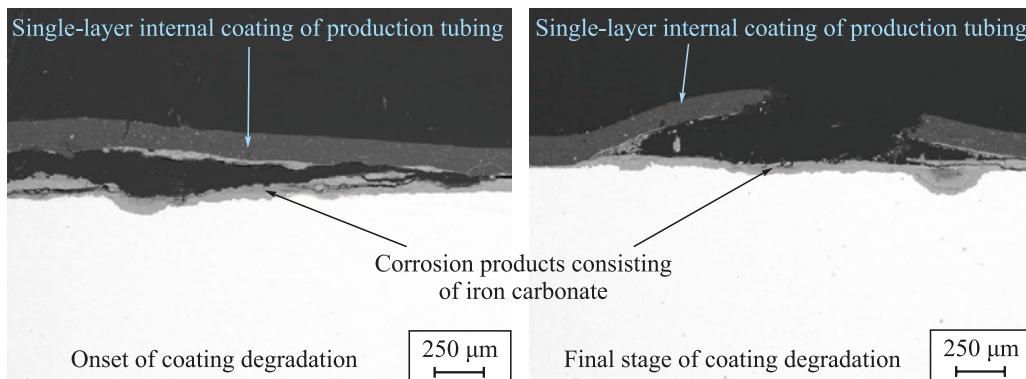


Рис. 20. Структура однослойного внутреннего покрытия НКТ $\varnothing 73 \times 5.5$ мм с наработкой 934 дня, а также продуктов коррозии

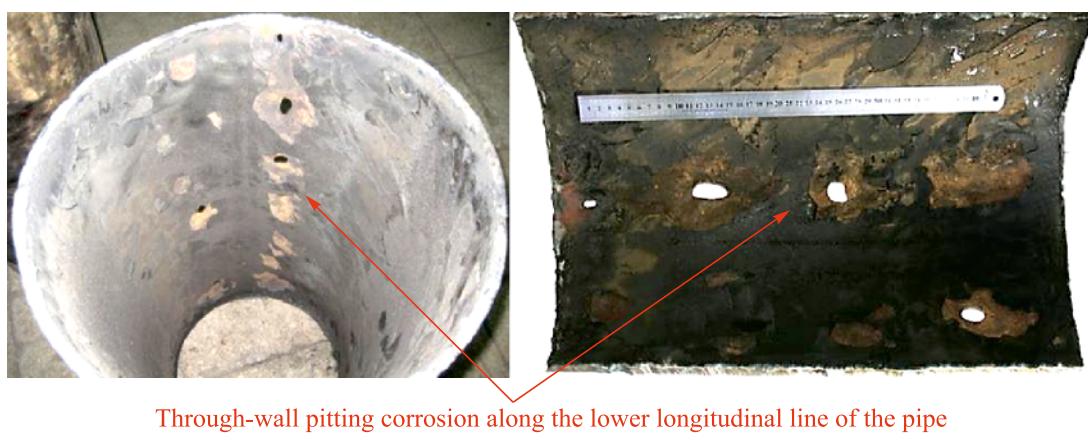


Fig. 21. Consequences of operating a pipeline with a degraded internal coating

Рис. 21. Последствия эксплуатации трубопровода с разрушенным внутренним покрытием

diffusion of transported species occur throughout the coating thickness. This is the shortest stage and can be described using Fick's diffusion equation. During the second stage, interfacial adhesion is degraded; this is the longest and the life-limiting stage in coating performance. The third stage involves blister formation and the development of corrosion products at the metal–coating interface. At the final stage, the blister ruptures, followed by the onset of aggressive through-wall pitting corrosion.

3. Based on the analysis of the composition and morphology of corrosion products beneath the coating and their comparison with corrosion products formed on similar pipe steels operated under comparable conditions, it has been established that diffusion selectivity is absent. No substantial limitation on the transport of any specific corrosion-active species was observed.

4. It has been demonstrated that visual inspection alone cannot reliably identify the root cause of coating failure, because overheating by only a few degrees above the wet-state glass-transition temperature of the polymer may significantly contribute to degradation. Although such overheating does not intensify thermo-oxidative processes and is not detectable by DSC or FTIR analysis, its presence reduces the coating service life by approximately an order of magnitude.

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<https://doi.org/10.17122/ngdelo-2025-1-77-90>

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P. E. Yudin – development of the main concept, formulation of the aim and objectives of the study, experimental testing of specimens, analysis of the research results, and formulation of the conclusions.
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П. Е. Юдин – формирование основной концепции, постановка цели и задачи исследования, проведение испытаний образцов, анализ результатов исследований, формулировка выводов.

А. С. Ложкомоев – подготовка текста статьи, корректировка текста.

Received 14.04.2025

Revised 20.04.2025

Accepted 21.04.2025

Статья поступила 14.04.2025 г.

Доработана 20.04.2025 г.

Принята к публикации 21.04.2025 г.