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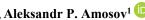
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Research Article

Destruction of Internal Anticorrosive Polymer Coatings of Oilfield Pipes during Operation

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Abstract

Introduction. Failure of equipment, specifically pipes in the oilfield complex, due to the development of corrosion processes leads to numerous losses, destruction of expensive components, disruption of technological processes and, as a result, environmental damage. The use of anticorrosive coatings as an internal protection of oilfield pipes offers many advantages and can significantly reduce the rate of corrosion, but does not provide a complete solution to this problem. Destruction of internal anticorrosive polymer coatings (IACPC) occurs for numerous reasons. The causes and mechanisms of destruction are insufficiently investigated. Therefore, the aim of this work was to analyze the destruction of internal anticorrosive polymer coatings using practical examples, which made it possible to form and identify the main causes of damage and degradation of coatings during operation.

Materials and Methods. A complex of laboratory studies was carried out to study the damage to internal polymer anticorrosive coatings during operation and to establish the main causes of destruction. The initial phase of the investigation involved a detailed examination of the materials related to the accident circumstances, including the operating conditions of the coated pipeline (composition of the operating medium, temperature, pressure, and presence of mechanical impurities), operation time, and type of polymeric material used. The second phase involved laboratory testing of the coating, which included the determination of layer thickness, dielectric continuity, adhesive strength (by the normal separation method), investigation of thermokinetic properties by means of differential scanning callometry (DSC), study of the coating structure using scanning electron microscopy.

Results. Practical examples of the destruction of internal anticorrosive coatings of oilfield pipes were analyzed. For each case, characteristic signs of degradation of the anti-corrosive coating were identified. Changes in the microstructure of the coatings, as well as the formation of corrosion products, were observed depending on the type of destruction. The focus was on studying the degree of polymerization of the coating, both using the traditional method of determining the ΔTg parameter using DSC, and based on indirect signs detected during microscopic studies.

Discussion and Conclusion. The practical cases of damage to the internal anticorrosion coating of pipes of the oil and gas complex considered in the article allowed us to divide the causes of destruction into three groups: operational, technological and defects during transportation, storage and construction and installation works. Based on these findings, we have formulated recommendations for manufacturers to ensure maximum performance from their coatings. It is noted that the compliance with the presented recommendations makes it possible to obtain internal anticorrosive polymer coatings with a minimum guaranteed lifespan of 15 years, as demonstrated by the successful operations of pipelines in Western Siberia, such as those operated by Surgutneftegaz PJSC and LUKOIL - Western Siberia LLC.

Keywords: internal anticorrosive polymer coating, destruction of the coating, adhesive strength, operational defects, peeling of the coating, corrosion products, cracking, blistering

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Научная статья

Разрушение внутренних антикоррозионных полимерных покрытий нефтепромысловых труб при эксплуатации

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Аннотация

Введение. Отказ оборудования — труб нефтепромыслового комплекса — по причине развития коррозионных процессов приводит к многочисленным убыткам, разрушению дорогостоящих комплектующих, нарушению работы технологических процессов и, как следствие, экологическому ущербу. Применение антикоррозионных покрытий в качестве внутренней защиты нефтепромысловых труб имеет много преимуществ и позволяет значительно снизить скорость коррозии, но не обеспечивает полного решения данной проблемы. По многочисленным причинам происходят разрушения внутренних антикоррозионных полимерных покрытий (ВАКПП). Недостаточно исследованными являются причины и механизмы разрушения. Поэтому целью данной работы стало проведение анализа разрушений внутренних антикоррозионных полимерных покрытий на практических примерах, что позволило сформировать и выделить основные причины повреждения и деградации покрытий при эксплуатации.

Материалы и методы. Для изучения повреждений внутренних полимерных антикоррозионных покрытий в процессе эксплуатации и установления основных причин разрушения проводился комплекс лабораторных исследований. Первоначальным этапом исследования являлось подробное изучение материалов обстоятельства аварии: условия эксплуатации трубы с покрытием (состав эксплуатируемой среды, температура, давление, наличие механических примесей), наработка, тип применяемого полимерного материала. Второй этап — лабораторные исследования покрытия: определение толщины слоя, диэлектрической сплошности, адгезионной прочности (методом нормального отрыва), исследование термокинетических свойств посредством дифференциально-сканирующей каллометрии (ДСК), изучение структуры покрытия при помощи сканирующей электронной микроскопии.

Резульмамы исследования. Изучены практические примеры разрушения внутренних антикоррозионных покрытий нефтепромысловых труб. Для каждого исследуемого случая выявлены характерные признаки деградации антикоррозионного покрытия. Показаны изменения микроструктуры покрытий, а также образование продуктов коррозии в зависимости от характера разрушения. Делается акцент на исследовании степени полимеризации покрытия как с помощью традиционного метода определения параметра ΔTg с помощью ДСК, так и на основе косвенных признаков, обнаруженных в ходе микроструктурных исследований.

Обсуждение и заключение. Рассмотренные в статье практические случаи повреждения внутреннего антикоррозийного покрытия труб нефтегазового комплекса позволили разделить причины разрушения на три группы: эксплуатационные, технологические и дефекты в ходе транспортировки, хранения и строительномонтажных работ. Сформулированы рекомендации производителям, позволяющие получать покрытия с максимальными характеристиками, присущими используемому лакокрасочному материалу. Отмечено, что соблюдение представленных рекомендаций позволяет получать в условиях Западной Сибири внутренние антикоррозионные полимерные покрытия с гарантированным ресурсом не менее 15 лет (что подтверждается опытом успешной эксплуатации таких трубопроводов в ПАО «Сургутнефтегаз» и ООО «ЛУКОЙЛ – Западная Сибирь»).

Ключевые слова: внутреннее антикоррозионное полимерное покрытие, разрушение покрытия, адгезионная прочность, эксплуатационные дефекты, отслоение покрытия, продукты коррозии, растрескивания, вздутия

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Introduction. Failures of oilfield pipelines due to internal corrosion cause significant losses [1]. The main damage is caused by the destruction of essential components, leading to disruption of operational processes and high levels of economic and environmental harm [2]. To address this issue, various methods for protecting the inner surfaces of pipes have been developed. These include the use of corrosion inhibitors, corrosion-resistant steels, non-metallic materials, and internal anticorrosive coatings [3]. All these methods aim to reduce the rate of corrosion under specific operating conditions [4]. The most promising method to protect metal from corrosion is the use of anticorrosive polymer coatings, which prevent the impact of aggressive components of the transported medium on the inner surface of the pipe [5]. As a result, the destruction of metal caused by corrosion is significantly reduced, ensuring long-term, trouble-free operation of equipment [6]. Liquid and powder-based polymer coatings are two of the most reliable and versatile methods of protecting the inner surfaces of oilfield pipes [7]. Powder coatings based on epoxy resins are preferred due to their excellent performance and durability [8].

One of the main advantages of using anticorrosive polymer coatings is the possibility to use materials that are relatively inexpensive instead of more expensive options. For example, carbon steel pipes with a corrosion-resistant coating can be used instead of high-alloy steel pipes. In addition, due to the low roughness of the polymer coating, the flow rate of pipes increases [9], the formation of salt [10], asphalt-resinous and paraffin deposits decreases significantly [11]. Compared to the chemical method of protecting pipes (through the use of corrosion inhibitors), internal polymer-based coatings have several advantages. These include:

- 1. Internal anticorrosive polymer coatings are more effective, as they form a physical barrier between the aggressive environment and the metal. Inhibitors affect the corrosion process only in direct contact with the metal surface.
- 2. Polymer coatings have a longer service life, while the action of the inhibitor may cease when its concentration in solution is depleted.
- 3. In compliance with the technical regulations, anticorrosive coatings are easily applied to the inner surface of the metal. When using corrosion inhibitors, it is necessary to carefully calculate the concentration and method of introducing them into the working environment.

Given that corrosion inhibitors are acidic chemical solutions, their use can adversely affect the properties of tubing materials. When an inhibitor comes in contact with a metal surface of a pipe, as well as when it penetrates a threaded connection of a "tubing nipple – coupling", metal destruction through the mechanism of hydrogen cracking may occur [12].

Nevertheless, polymer anticorrosive coatings also have a number of disadvantages, which include: aging of the polymer base, diffusion of the transported medium through the coating, and relatively low impact strength [5].

The effectiveness and durability of an anticorrosive coating depend on a variety of factors that influence its protective ability. One of the most significant indicators of a coating's quality is the adhesion strength between the polymer and the metal substrate, which depends on the application technology. The quality of the materials used, compliance with correct preparation techniques for the metal surface, and the coloring process play a crucial role in determining the adhesive strength. Additionally, temperature drying conditions are essential [13]. Along with the above requirements, the stability of the protective properties of the polymer coating does not always depend on the coating itself, but is also determined by the operating conditions and parameters [9]. The main technological factors contributing to the IACPC degradation and premature destruction can include: disruption of well operation due to a sharp drop in the temperature of the pumped product or pumping of the product at a temperature higher than the design temperature; excess pressure; the presence of high corrosion activity of the extracted products; incorrectly selected type of coating for specific operating conditions.

There are frequent cases of damage to the polymer coating during scraping (cleaning) of the borehole from the formed asphalt-resin-paraffin deposits. The use of an improperly designed scraper contributes to the violation of the integrity of the surface layer of the coating. Scratches and protruding burrs are formed, which reduce the barrier properties of the polymer coating during further operation.

The existing literature [14] on the issues of internal protection of oilfield equipment using polymer coatings only considers a small part of the problem and does not reflect the full picture of the IACPC destruction. It is important to note that depending on changing factors such as operating conditions, the type of polymer material used, technological operations of preparation and coating, the destruction of the anticorrosive coating may have a different character. Thus, due to the complexity of the kinetics of the coating destruction process and the lack of a practical basis, it is not always reliably possible to determine the true cause of coating damage. Numerous studies conducted by the authors on oilfield pipes allowed us to consider some new specific examples of IACPC destruction during operation and identify the main causes leading to degradation and failure of internal anticorrosive coatings, taking into account new factors.

Materials and Methods. The following samples with damage to the internal anticorrosive coating were selected as samples for the study:

- 1. A fragment of tubing $\emptyset73\times5.5$ mm with damage to the coating in the form of blisters along the entire length of the sample. The tubing failed after 934 days of operation (Fig. 1 a, b).
- 2. A fragment of tubing $\emptyset73\times5.5$ mm with the destruction of the coating in the form of extensive areas with detachments and blisters localized mainly in the nipple part of the tubing. The time to failure was 146 days (Fig. 2 a, b).
 - 3. A fragment of tubing $\emptyset73\times5.5$ mm with a different color of the inner coating (Fig. 3 a, b).
- 4. A fragment of the pipeline $\emptyset 325 \times 8$ mm, with the coating destroyed, exposing the metal substrate, and a through defect in the pipe (Fig. 4 *a*, *b*).
- 5. A fragment of the pipeline $\emptyset159\times8$ mm with the formation of numerous blisters of the coating and its destruction (Fig. 5).



Fig. 1. Damage to the internal anticorrosive coating: a, b — coating blistering

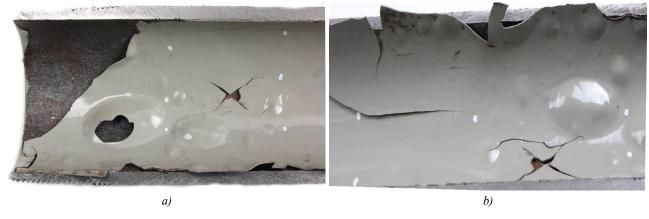


Fig. 2. Destruction of the internal anticorrosive polymer coating: a — blistering of the coating; b — cracking of the coating



Fig. 3. Different shades of the internal anticorrosive coating of the tubing: a — light brown shade of the coating; b — dark brown shade of the coating



Fig. 4. Damage to the internal anticorrosive coating of the pipeline $\emptyset 325 \times 8$ mm: a—general view of the destruction of the coating; b—burns of the coating



Fig. 5. Destruction of the internal anticorrosive coating of the pipeline Ø159×8 mm

In order to identify the reasons for IACPC failure, a comprehensive analysis of the study was conducted in two stages. The first stage was a detailed study of the operating conditions of the coated pipe (composition of the operated medium, temperature, pressure, presence of mechanical impurities), operating time and type of polymer material used.

The second stage included laboratory studies of the coating: visual inspection, determination of the thickness of the inner coating according to GOST 31 993–2013, control of dielectric continuity according to ASTM G62, determination of adhesive strength by the pull-off adhesion strength method according to GOST 32 299–2013, investigation of thermokinetic properties by means of differential scanning callometry (DSC). Microstructural studies were carried out using a scanning electron microscope "TESCAN VEGA3 SBH" equipped with a detachable device for energy dispersion analysis.

Results. Microstructural studies of the anticorrosive coating of the tubing (sample No. 1) revealed complete detachment of the coating from the metal with the development of corrosion processes. This indicated that the formation of a corrosion layer with a thickness of approximately 122 microns was due to the prolonged penetration of aggressive components of the transported medium into the metal substrate (Fig. 6). Studies have not revealed any significant deviations or imperfections in the coating, such as local areas with reduced thickness or the presence of shot particles underneath the coating layer. These findings were consistent with the common occurrence of such phenomena during the shot blasting process of the metal surface prior to applying an anti-corrosion system. Based on these results, it could be concluded that the destruction of the coating through this mechanism was not the cause of the observed corrosion processes in this particular case [16]. These signs indicate damage to the anticorrosive coating caused by the operational impact due to the downhole work carried out to remove impurities and plugs in the tubing trunk using chemical reagents — hydrochloric acid treatments. It was also impossible to exclude an overpressure in the system, as a result of which gas penetrated into the coating volume as a result of diffusion permeability and its sharp expansion, which contributed to the destruction of the coating by decompression mechanism with the formation of blisters [1].

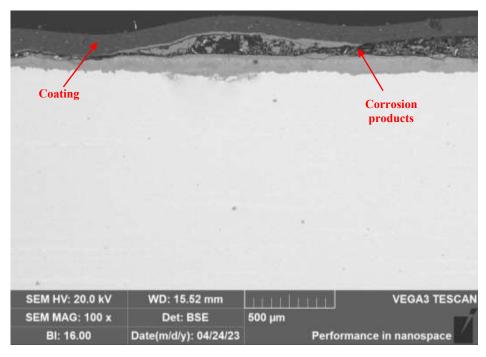


Fig. 6. Microstructural studies of the anticorrosive coating in the area of its damage

According to the results of the study of the tubing fragment (sample No. 2), no deviations were found in areas where the coating remained intact. However, there was a two-fold decrease in the adhesive strength of the coating in the nipple area compared to the central part of the tube. The thermokinetic characteristics were determined by differential scanning spectroscopy (DSC) with determination of the glass transition temperature (Tg) of the coating along the entire length of the tubing. The results of the analysis did not reveal a significant variation in Tg values of the studied areas, which may indicate uniform heating during the polymerization of the coating.

Microstructural analysis of the anticorrosive system has established that the peeling of the coating occurred along the primer layer and was characterized by a cohesive nature of destruction. In addition, oxide particles were present on the surface of the metal of the pipe and the detached part of the coating (Fig. 7, Table 1). In this case, inclusions of iron oxides on the inner surface of the pipe may have formed due to inadequate cleaning and surface preparation prior to coating.

The considered example was a frequent case of destruction of the polymer coating associated with a violation of the technological processes of preparing the inner surface of the pipe before painting.

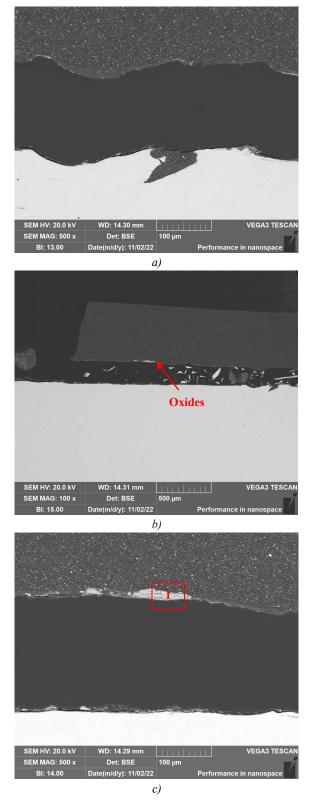


Fig. 7. Microstructural studies of the coating in the area of its destruction: a — peeling of the coating from the metal; b — presence of a layer of oxides; c — chemical composition of oxides

Table 1 Chemical composition of the oxide layer, weight %

Element/Area	С	О	Si	Mn	Fe
1	19.10	27.31	0.83	0.24	50.78

Upon visual inspection of the inner surface of the tubing (sample No. 3), it was found that the anticorrosive coating had a different shade. No visible coating defects, such as blisters, separations, or cracks, were found. However, when determining the dielectric continuity in the area with the dark brown coating (Fig. 3b), numerous breakdowns were detected, indicating a possible violation of the polymer's integrity due to the presence of microcracks. Taking into account the results of the conducted research, it could be concluded that the heterogeneity in the shade of the anticorrosive coating was likely due to under-polymerization during the drying process. Polymerization is achieved through exposure to high temperatures in specialized ovens, where chemical reactions between polymer chains take place. To ensure uniform heating of the coating during the curing process, it is essential to maintain a constant temperature. Any violation of the temperature-time polymerization regime directly affects the rate of chemical reactions, and as a result, can lead to the destruction of the polymer.

Quite often, there are cases of damage to the anticorrosive coating caused by human error. The formation of coating damage occurs accidentally and it is impossible to predict their occurrence in advance. These defects can occur at different stages, from the production of pipes to their transportation to the consumer. Specifically, the following factors can contribute to the occurrence of these defects: improper selection of coating material for operating conditions, mechanical damage due to lifting and lowering operations or scraping, violations of regulations during transportation and storage of coated pipe products, and the influence of human error.

As an example, we can consider damage to the powder-based inner coating caused by repair work on Ø325x8 mm pipeline (sample No. 4). The damage to the coating was severe, leading to the exposure of the metal substrate and the formation of a through defect in the pipe. External signs, such as the presence of blisters and a change in the color of the coating to black, indicated an additional temperature effect on the pipe at temperatures above 250°C (Fig. 4 a). In this case, welding work carried out during repair of the pipeline resulted in the formation of burns and burnouts in the coating (Fig. 4 b), due to violation of integrity and continuity of the coating. As a result, the transported medium could easily penetrate through the polymer layer to the metal of the pipe, activating corrosion processes. The intensity of corrosion in a pipeline could be increased by the presence of corrosive substances in the transported fluid, such as dissolved gases like CO₂ and H₂S. It could also be influenced by factors such as the velocity of the fluid flow, temperature, and pressure within the pipeline.

There are often cases where the destruction of an anticorrosive coating can have a complex mechanism and be accompanied by a combination of several factors. Microstructural studies of the Ø325×8 pipeline showed that the destruction of the coating occurred through the mechanism of decompressive peeling, which happened under the influence of a sudden pressure drop [1]. The penetration of gases through the coating reduced the barrier properties of the anticorrosive coating, leading to the development of corrosion on the pipe metal and the formation of corrosion products (Fig. 8). In addition, given the scale and nature of the destruction of the anticorrosive coating layer, it could be established that the main cause of damage to the pipeline was a local thermal effect applied from the inner surface of the pipe. In this case, high-temperature heating led to overheating of the internal anticorrosive coating and its destruction.

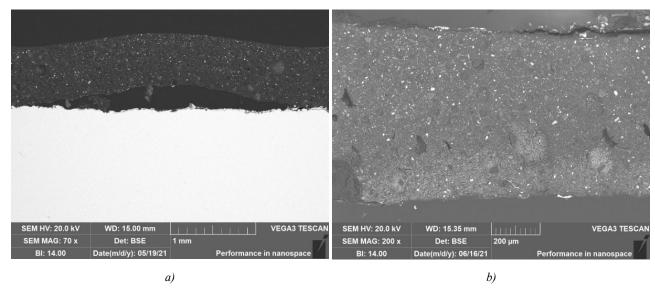


Fig. 8 Microstructural studies of anticorrosive coating in the field of destruction: a — peeling of the coating; b — destruction of the polymer coating

Discussion and Conclusion. Having studied practical examples of damage to internal anticorrosive coatings, it is possible to divide the causes of their destruction into three groups: operational, technological and defects formed during transportation, storage and construction and installation works.

Operational defects can be associated with various external influences, such as the use of hydrochloric acid treatments and the presence of mechanical impurities. The most common is exceeding the maximum permissible temperature for this type of coating (usually $20-30^{\circ}$ C below the glass transition temperature) or high partial pressures of hydrogen sulfide (H₂S) and carbon dioxide (CO₂).

A comprehensive assessment of the coating's ability to withstand operational impacts in the conditions of oil production and transportation can be conducted in accordance with GOST 58 346–2019¹ and regulatory documents developed on its basis²,³,⁴. Despite discrepancies in the methods of autoclave testing, all the presented documents can adequately assess the IACPC quality. However, predicting the resource of trouble-free operation based on them is impossible. The development of a model for accident-free resource forecasting is the most urgent task. It, in turn, is based on the accumulation, description and systematization of the causes of the IACPC destruction.

Technological defects include all defects and imperfections formed during the preparation of the pipe surface before painting and applying (polymerization) of internal coatings. Obtaining the necessary properties for a specific coating system is possible if the preparation requirements specified in Table 2 are met. For powder thermohardening coatings, criterion $\Delta Tg \le 3^{\circ}C$ must be met. It is possible to control the degree of hardening of liquid coatings only by indirect methods, for example, by comparing the Buchholz hardness of the controlled coating with the reference one.

Requirements for the inner surface

Table 2

Parameter Indicator		Standard	Test method	
Degree of degreasing	No more than	1	GOST 9.402	
Presence of oxides	Degree of purification, not less than	Sa 2.5	GOST R ISO 8 501–1	
Dustiness	Amount of dust, no more than 2 points		- ISO 8 502–3	
Dustiness	Size of the dust particles, no more than	2 class	130 8 302–3	
Roughness	Average height of microroughness Rz, microns, within	40–100	ISO 8 503–2	
Presence of water-soluble salts Salt content mg no more tha		20	ISO 8 502–6 ISO 8 502–9	

Defects that may occur during transportation, storage, construction, and installation can be minimized only with an increased focus on production quality and/or the implementation of inspection and construction control.

The compliance with the presented recommendations makes it possible to obtain IACPC with a guaranteed lifespan of at least 15 years under the conditions of Western Siberia, as confirmed by the successful operation of similar pipelines at Surgutneftegaz PJSC and LUKOIL – Western Siberia LLC.

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