

Influence of aqueous sodium chloride solutions on operational properties of epoxy coatings

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Highlights

- A permanent decrease in the operational properties of the brine aged coatings was shown.
- FTIR and DSC studies have documented the degradation of the brine aged epoxy material.
- A significant growth of destruction and roughness of the brine aged coatings was found.
- Silver crackings were revealed on the surface of the coatings aged for 1008 h - 1680 h.
- An original, universal method of multi-criteria studies of coating properties was used.

Abstract

The main goal of the research presented in the article is to assess the impact of the destruction (degradation) of epoxy coatings, caused by the influence of a 25% aqueous solution of sodium chloride (brine), on the operational properties that determine the coatings reliability (durability). Samples of two-layer epoxy coatings (obtained from powder paints) were aged by immersing them in brine for a maximum period of 1680 h. The following criteria were used to assess the operational properties of the coatings: thickness, roughness and surface morphology, hardness, water absorption (mass increase), surface free energy. The FTIR and DSC tests performed showed a progressive development of the oxidation processes of the epoxy with the ageing period. The long-term impact of the brine resulted in the destruction of the coatings in the form of: craters, grooves, microcracks, including silver cracks. The contact of the coatings with brine also increased their: surface roughness (Ra, Rz, Rmax), thickness, mass, surface free energy, and decreased hardness and heat resistance.

Keywords

epoxy coating, operational properties, ageing with brine, destruction.

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1. Introduction

The polymer coatings of technical objects during their use in natural conditions are influenced by various types of harmful operational factors, both climatic and environmental. Among the climatic factors, the strongest destruction of polymer coatings is caused by solar UV radiation, which primarily contributes to the degradation of the coating material and to the initiation of surface cracking of silver coatings [27]. On the other hand, the dominant environmental factors include hard erosive particles (stones, gravel), causing: erosion, abrasion and scratching of the coatings [12], as well as aggressive media.

The aggressive media contributing to the strong destruction of polymer coatings include salt spray (occurring in the coastal area), as well as an aqueous solution of sodium chloride (the so-called brine), which is commonly used in winter to prevent the formation of a layer of ice on the road surface [40].

Operational factors synergistically influencing polymer coatings (climatic and environmental) cause their destruction, both chemical (degradation) and physical, manifested in the form of: craters, etchings, cracks, blisters, interlayer delamination and surface roughness increase [17]. Moreover, the impact of operational factors leads to the loss of durability of the adhesive bonds between the primer coat

and the substrate [41], as a result of the development of undercoating corrosion [29].

Operational factors in the initial period of use of polymer coatings cause a progressive loss of their gloss and colour change, thus deteriorating the decorative properties of the coatings [30]. In subsequent stages, due to the increasing physical destruction of the coatings with the passage of their service life, as well as the degradation of the chemical structure of the polymer coating material, deterioration of the barrier properties of the coatings, determining their reliability, is observed [17].

The reliability of polymer coatings is primarily determined by their tightness, conditioned by the optimal proportion of fillers and pigments, limiting the porosity of the coating-forming material [11]. The reason for the formation of pores is the development of ageing processes in the structure of the coatings, mainly under the influence of climatic factors, and above all, solar UV radiation [13]. Pores can also be generated by the influence of environmental factors in the form of: mechanical loads [35], microorganisms [42] and aggressive media, including aqueous solutions of sulphuric acid [15] and sodium chloride [18].

The reliability of polymer coatings significantly depends on the type of coating resin used for their production, which was confirmed

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by the test results presented in the paper [2]. The coatings are made of laminates produced on the basis of epoxy or polyester resin. The research proved that epoxy resin coatings showed greater resistance to abrasion and scratching [2].

The mechanical wear resistance of polymeric materials (protective coatings) is also determined by their hardness, the increase of which generally increases their resistance to abrasion and scratching. The authors of the work [30] investigated the impact of thermal fatigue and ageing on the hardness of polymer-ceramic composites, confirming the high hardness stability of new silorane composites, which translates into their high resistance to abrasive wear, compared to traditional composites.

Reliability tests of multi-layer polymer coatings protecting the floor of military cars against destruction caused by an explosion (e.g. grenade) are presented in the paper [36]. Effective protection against this type of rapidly increasing mechanical loads was provided by a coating consisting of three layers, the first of which was a glass composite (6 mm thick), the second was an aluminium sheet (12.5 mm thick), and the third was an aramid composite (2,5 mm thick).

Increasing the tightness of polymer coatings, which determines their reliability, is achieved by modifying the physical structure of the coating material by supplementing with various types of fillers, with optimal dimensions and mass fraction [9]. Microfillers ensuring good barrier properties of coatings include, among others: glass microspheres [12], silicon dioxide (silica) [23], titanium dioxide [38], zinc [24].

In this article, an epoxy primer coating modified with a micro-filler in the form of zinc dust and zinc monoxide is considered.

The reliability of polymer protective coatings is particularly effectively improved by addition of various types of nanofillers, among which the most commonly used is silicon dioxide (the so-called nanosilica) [7]. The composition of polymer coatings is also enriched with nanoparticles of: zinc [6], copper [14], titanium dioxide [31], aluminium trioxide [37], as well as silver nanoparticles, additionally acting as inhibitors of biological corrosion [28].

Titanium dioxide nanoparticles were used to modify the top layer of the epoxy coating system, the examination results of which are presented in this article.

The mass fraction of nanoparticles of fillers is generally ten times lower than in the case of using traditional microfillers. High tightness and good mechanical properties of polymer coatings (high resistance to: erosion, cracking, bending, impact, abrasion) are obtained when each of the filler grains is surrounded by the coating resin [11].

The introduction of nanofillers to the paints reduces the porosity of the coatings, thus improving their barrier properties, which translates into a reduction in the absorption of aggressive media. This was proved by the results of the research obtained in the work [10], showing a decrease in water absorption of epoxy coatings as a result of their modification with aluminium trioxide nanoparticles, with a simultaneous increase in their erosive resistance. It was also found that this type of modification of oxysilane coatings increased their resistance to the effects of salt spray [20].

The paper [37] showed that polymer coatings containing aluminium oxide nanoparticles, thanks to their high hardness and even distribution in the coating material, were characterized by increased resistance to abrasion and scratching.

Modification of epoxy coatings with copper nanoparticles [14], with a grain diameter below 66 nm (with a mass fraction of 3.5%), resulted in a reduction of over 30% of the pore volume determined with the use of mercury porosimetry. In addition, an increase in the erosion resistance of modified epoxy coatings was observed, which also showed high thermal stability and resistance to UV radiation with a wavelength below 350 nm.

Research has shown that modifying polymer coatings with small-sized nanoparticles does not reduce their transparency, which allows them to be used for varnish topcoats. For example, the introduction of zinc monoxide nanoparticles into the structure of methacrylate coat-

ings (grain size $3\div 5$ nm and mass fraction $1\div 15\%$) did not reduce their transparency [24].

Polymer coatings modified with nanofillers and nanopigments (called nanocoatings), apart from increasing the tightness [8] (due to the reduction of their porosity), are characterized by: increased resistance to UV radiation [38] and mechanical factors [25]. Moreover, nanocoatings (thanks to their high tightness) show a high durability of adhesive connections with the steel substrate, as a result of limiting the penetration of aggressive media into the surface of the protected element, which may contribute to the development of undercoating corrosion [26].

The content of nanofillers in the structure of polymer coatings also improves their thermal stability [22] and resistance to biological corrosion [42]. Moreover, the work [29] showed a higher resistance to chemical degradation due to UV ageing of polymer coatings containing UV absorbers in the form of nanoparticles of titanium dioxide and/or zinc monoxide, compared to coatings modified with organic absorbers.

In order to increase the service life of polyurethane-epoxy coatings, nanoparticles of aluminium trioxide (grain size $d=20$ nm) or silica (grain size $d=16$ nm), the mass fraction of which was 3.5%, were introduced into the polyurethane top layer. Among the coatings aged at the climatic station in the period of 3 years, the lowest chemical and physical destruction, as well as the highest hardness and erosive resistance were distinguished by coating systems with a polyurethane topcoat modified with aluminium trioxide [16].

The epoxy coatings assessed in this article have found a wide application in anti-corrosion protection of elements of technical facilities, mainly exposed to the influence of aggressive media [34]. The recipe of these coatings is constantly being improved, inter alia, thanks to modifications with the use of various types of nanofillers, primarily in order to improve their barrier properties, mechanical and thermal [35].

Multilayer epoxy coatings reinforced with carbon fibres have been used to increase the reliability of coating system protecting the inner surface of railway wagons against damages caused by mechanical and chemical factors, which was demonstrated in the work [4]. The tested coating systems consisted of five to ten layers, made of composite epoxy coatings reinforced with carbon fibres. The best mechanical properties were obtained for the coating consisting of seven layers.

Increased resistance to soaking by aggressive media of the three-layer epoxy coating was obtained as a result of improving its tightness, thanks to the introduction of nanofillers to the structure of each layer [36]. The base layer was modified with aluminium oxide nanoparticles, the interlayer with graphene nanoparticles, and the top layer with silicon dioxide nanoparticles [36]. An increase in the resistance of this coating to UV radiation was also found, as a result of its reflection by silicon dioxide nanoparticles contained in the topcoat.

A significant improvement in the anti-corrosive properties of epoxy coatings was achieved after the addition of 2% (mass fraction) of cerium and graphene monoxide nanoparticles to their composition. The nanofillers sealed their structure, thus limiting the migration of aggressive media to the coating substrate [5].

The effective improvement of the resistance of epoxy coatings (containing zinc microfiller) to the influence of a 3.5% aqueous solution of sodium chloride was achieved by introducing 0.3% (mass fraction) of graphene nanoparticles into their composition [1].

Nanofillers were also used in the production of self-healing epoxy coatings based on: bio-epoxy resin, halloysite nanotubes and silicon dioxide nanoparticles [33]. Halloysite nanotubes (HNTs) were filled with bio-epoxy resin (by vacuum infiltration), and silicon dioxide nanoparticles were mixed with a hardener activated by UV radiation. Then, the filled halloysite nanotubes were mixed with the bio-epoxy resin (together with the hardener). When attempting to scratch the coatings halloysite nanotubes break, and the bio-epoxy resin they contain fills the crackings and comes into contact with the UV activated hardener overlaying the silicon dioxide nanoparticles, initiating the

curing reaction. Complete self-healing of cracks under the influence of sunlight was observed when the mass fraction of halloysite nanotubes filled with bio-epoxy resin was 40%. Moreover, the composite showed increased shielding ability against UV radiation, as well as increased thermal stability and good transparency. Therefore, the developed bio-epoxy composite can constitute an effective, self-repairing protective coating of technical objects exposed to scratching and the influence of solar UV radiation.

The anticorrosive properties of epoxy coatings can also be improved by adding to their composition a filler in the form of flake basalt (chemically inactive), the surface modified with aniline trimer. The addition of 10% (by mass) of this filler to the composition of epoxy coatings increases their corrosion resistance more than twice [39].

Epoxy coatings also effectively protect concrete elements exposed to UV radiation and an aqueous solution of sodium chloride [32].

The resistance of polymer coatings, protecting technical objects against the negative effects of aggressive media, is largely determined by the hydrophilicity of their surfaces, conditioned by the value of the contact angle Θ_C , characteristic for each type of coating, depending on the type of coating material, as well as the condition of the coating surface. On the surface of hydrophilic coatings for which the contact angle $\Theta_C=0^\circ$, complete spreading of the water drops takes place. It should be noted that the most advantageous in terms of protective properties are coatings with low wettability (called hydrophobic coatings), characterized by the contact angle $\Theta_C=90^\circ\div 180^\circ$. However, when the value of the contact angle $\Theta_C=180^\circ$, the polymer coating is completely water repellent [21].

The research showed that the contact angle Θ_C decreases with the increasing degree of ageing of the coatings surface, especially their surface layers, and the lower its value, the larger the area of the surface wetted with drops of aggressive media, which results in increased absorbability of aged coatings. On the other hand, the aggressive media absorbed into the coatings contribute to their swelling and the degradation of the chemical structure of coating material [19].

If the contact angle characteristic for a given coating is $\Theta_C=45^\circ\div 90^\circ$, the penetration of aggressive media (water) into its surface layers to a large extent depends on the chemical structure of the coating polymer and the geometry of the wetted surface roughness profile. The development of destruction processes in polymer coatings under the influence of climatic factors (mainly as a result of the influence of solar UV radiation) contributes to the reduction of the contact angle Θ_C that characterizes them, thus increasing the absorption of the coatings with aggressive media characteristic for the operational environment (e.g. acid rain, fog salt, brine) [19].

It should be emphasized that the reliability of polymer coatings is determined primarily by the durability of adhesive bonds between the coating and the substrate. It is reduced as a result of the development of undercoating corrosion as a result of the penetration of aggressive media into the usually steel substrate [26, 41].

Epoxy coatings considered in this paper, due to their high adhesion to the steel substrate, have found wide application as primer coatings [35].

The ageing of epoxy coatings (obtained from solvent-based paints) with an aqueous solution of sodium chloride results in the degradation of the coating material and the destruction of the coatings in the form of: crackings, etchings, pores and craters (reaching the substrate). Moreover, a significant increase in the surface roughness of the coatings was observed, assessed using the Ra and Rz parameters. The destruction of the coatings progressively increased with the increase of the concentration of the aggressive medium, which, in researches presented in the work [18], was 3%, 10%, 20 %.

Due to the insufficient collection of information contained in the world literature on the development of the processes of destruction of polymer coatings as a result of the influence of climatic factors and/or environmental factors, no effective method of forecasting their reliability (service life) has been developed so far. This is due to the fact

that the elements of the "Operational Environment - Coating - Coating Substrate" system are subject to constant changes, inter alia as a result of the continuous development of technology (nanotechnology) in the field of coating materials (polymer materials, fillers and pigments) and their application techniques, and also as a result of progressively increasing environmental pollution and increasing intensity of solar ultraviolet (UV) and thermal (IR) radiation [32].

Due to the development of technology in the area of paints and varnishes, pro-ecological powder paints are produced more and more frequently [35], and environmentally friendly curing of coatings with UV radiation is also used [3,].

This article presents the results of tests of epoxy coating systems made of innovative powder paints.

Due to the fact that the paint formula changes on average every five years, conducting long-term operational tests in order to determine the reliability (durability) of polymer coatings is substantially unjustified. Hence the necessity to carry out accelerated tests [29] of the operational properties of coatings, in conditions modelling the dominant climatic and/or environmental factors.

This article presents the results of research on the physicochemical properties of epoxy coating systems (used in the renovation painting of car chassis elements), which were subjected to accelerated ageing with a 25% sodium chloride aqueous solution, modelling brine used in winter to prevent road slippery. Brine is one of the dominant factors that destroy the polymer protective coatings of the car undercarriage components during its winter operation. Acceleration of ageing was obtained thanks to complete immersion of coating samples in this medium.

2. Research methodology

2.1. Materials and preparation of samples for testing

Epoxy coating systems, which are used to protect the components of the car chassis, were subjected to investigation.

Samples of epoxy coatings electrostatically deposited on the surface of steel plates with dimensions (160 x 80 x 2) mm were examined. The plates were cut out of sheets, made of calmed structural steel, S 235 JRG 2 (according to PN-EN 10025-1: 2007). The surface of the coatings (before applying the primer coat) was cleaned with an angle grinder (DWE4157), using sandpaper of P120 gradation. Prior to applying the primer, the surface of the steel plates was subjected to a degreasing process with an extraction solvent.

The samples of the coating systems were obtained by applying powder paint to the surface of the steel plates using the electrostatic spray method. Two layers of epoxy coatings were produced successively: a primer epoxy coating (grey) and an epoxy topcoat (blue).

The base coats were obtained from epoxy powder paint, modified with microfiller in the form of stabilized zinc dust (grain size 3÷4 μm and mass fraction 71%) and zinc monoxide (the so-called zinc white, with a mass fraction of 5%).

The topcoats were also obtained from epoxy powder paint. However, for its modification, nanoparticles of titanium dioxide were used, the mass share of which was 2%. The blue colour of the topcoats was obtained by using a mineral pigment with a grain size below 20 μm , consisting of sodium aluminosilicates combined with sulphur (Na6Al6Si6O24S4).

2.2. Methodology of accelerated ageing of epoxy coatings with brine

The effects of ageing of epoxy coatings as a result of the action of a 25% aqueous solution of sodium chloride (called brine) were investigated. In order to accelerate the examination, the coatings were fully immersed in a container filled with brine. The surface condition of the coatings was assessed after the appropriate test period, which was: 672 h (28 days), 1008 h (42 days), 1344 h (56 days) and 1680 h (70 days).

Table 1. Standard test methods for the physicochemical properties of epoxy coatings and the test equipment used

	Type of examination method	Apparatus
	Standard number	
Determination of the coating thickness	PN-EN ISO 2808:2020-01	Elcometer 456C
Method of geometric structure examination of coatings' surface	PN-M-04251:1987; PN-EN ISO 8501-1:2008	Hommel Tester T500 (by Hommelwerke)
Buchholz hardness test method	PN-EN ISO 2815:2004	Erichsen hardness tester

Table 2. Non-conventional examination methods of epoxy coatings and test equipment

Type of examination method	Apparatus
Study of changes in the chemical structure of an epoxy coating material	Spectrophotometer FT/IR-6200 (by Jasco)
Examination of the coatings thermal resistance	Thermal analyser LABSystem TG /DSC (by SETARAM)
Examination of the geometrical structure of the surface	Interferometric microscope Talysurf CCI (by Taylor Hobson)
Examination of the surface morphology of epoxy coatings	Scanning electron microscope with field emission SU-70 (by Hitachi)
Determination of the elemental composition of the surface layer of epoxy coatings	X-ray microanalyser with EDS energy dispersion by Thermo Scientific (Hitachi SU-70 microscope)
Examination of the epoxy coatings surface wettability	Goniometer G10 (by Krüss)

2.3. Methodology of epoxy coatings testing

The physicochemical properties of unaged and aged with brine epoxy coatings were assessed on the basis of results of performed standard tests of: thickness, surface roughness parameters (R_a , R_z , R_{max}), and hardness. The applied standard test methods and the test equipment assigned to them, are described in Table 1.

Non-conventional examination methods presented in Table 2 were used to assess the causes and effects of destruction (degradation of the coating material) of epoxy coatings aged with brine.

3. Results and their discussion

3.1. Influence of ageing with brine on the degradation of the chemical structure of epoxy coating material

Ageing of epoxy coatings with brine increased the intensity of characteristic bands (appearing in the FTIR spectrum) of epoxy material contained in the surface layer of epoxy coatings (Fig. 1). This testifies changes in the chemical structure of the aged epoxy material [13].

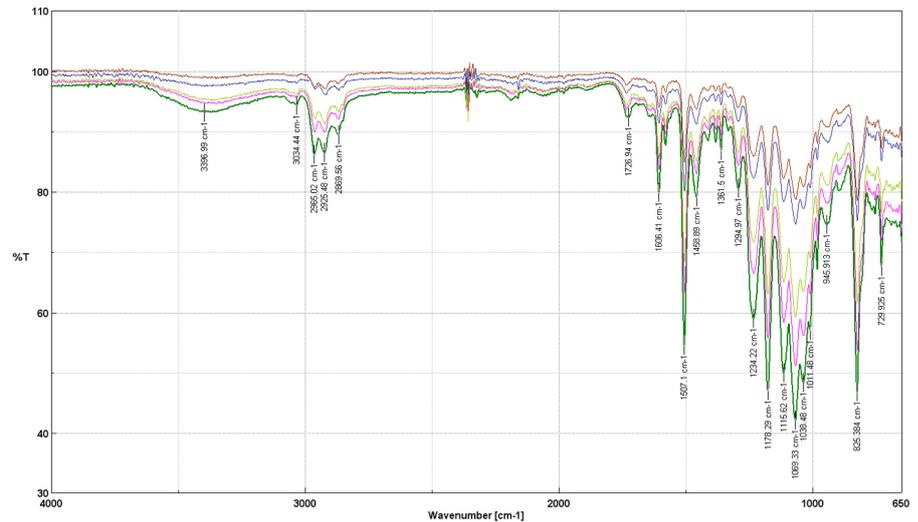


Fig. 1. Characteristics of the FTIR spectrum of an unaged epoxy coating (violet curve) and aged during: 672 h (blue curve), 1008 h (light green curve), 1344 h (pink curve) and 1680 h (green curve)

In the epoxy material, the intensity of the carbonyl group band ($C=O$), with the peak corresponding to the wave number 1726.94 cm^{-1} , increased by more than 3 times in the period of 1680 h. This proves a growth of the oxidation degree of the epoxy material.

Table 3. Temperature values of the energy effects in the epoxy topcoat determined on the basis of the DSC curves course

Ageing period t [h]	Temperature of energy effects [°C]		
	T_p temperature of the beginning of the oxidation process	T_1 temperature of the exothermic peak	T_k temperature of the end of the oxidation process
0	258	320	396
672	256	320	396
1008	255	325	396
1344	253	325	396
1680	243	325	396

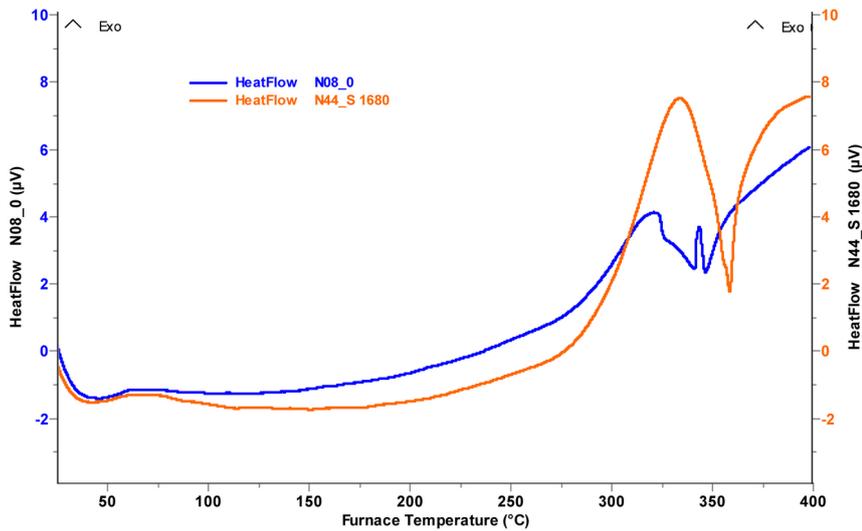


Fig. 2. Evolution of the DSC curve of an epoxy coating aged with brine in the period of 1680 h (orange curve) compared to the DSC curve of the unaged coating (blue curve)

The increase (almost 3 times) of the intensity of hydroxyl (OH) groups band (with a peak of 3396.99 cm^{-1}) of also documents the development of epoxy oxidation processes. On the other hand, the increase in the content of CH_3 groups (in the band with the peak corresponding to the wave number of 2925.48 cm^{-1}) proves the breaking of chemical bonds in the epoxy material [13].

3.2. Influence of ageing with brine on the thermal resistance of coatings

Differential scanning calorimetry (DSC) was used to assess the heat resistance of epoxy coatings. In the examination of the DSC characteristics, samples of epoxy coatings in the form of a powder, obtained as a result of abrasion of the top layer of the epoxy coating, were used. The average mass of the samples used in the examination was $(3.8 \pm 0.1)\text{ mg}$.

The course of the DSC characteristics (Fig. 2) shows that ageing with brine caused a progressive °decrease of the oxidation process onset temper-

Table 4. Surface topography of epoxy coatings

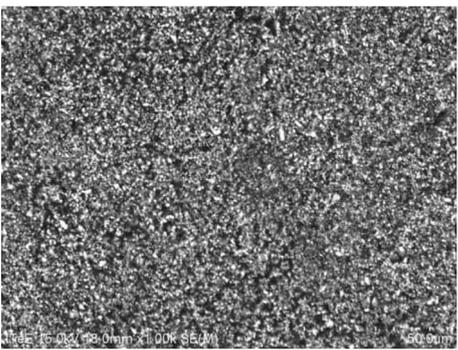
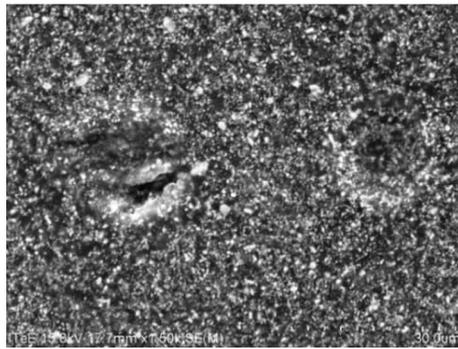
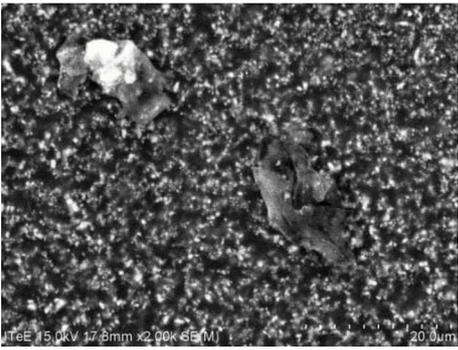
Type of coating	Epoxy coating surface topography
Unaged epoxy coating	
Epoxy coating aged with brine during the 1344 h	
Epoxy coating aged with brine during the 1680 h	

ature. For example, after the ageing period of 672 h, the oxidation onset temperature decreased by 2°C, and after ageing for 1680 h, it decreased by 15°C (Tab. 3). Increase of the exothermic peak on the DSC curves also proves the development of oxidation processes in the epoxy material aged with brine (Fig. 2). Thus, the thermal resistance of epoxy coatings decreased.

3.3. Influence of ageing with brine on the surface topography of epoxy coatings

Ageing of epoxy coatings with brine caused significant changes in their surface topography (Table 4).

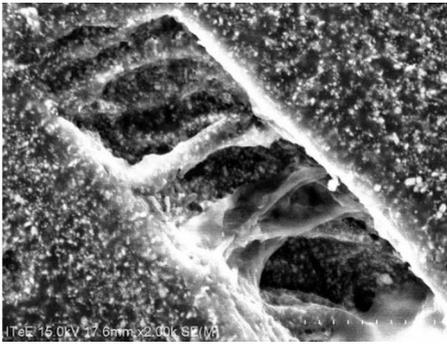
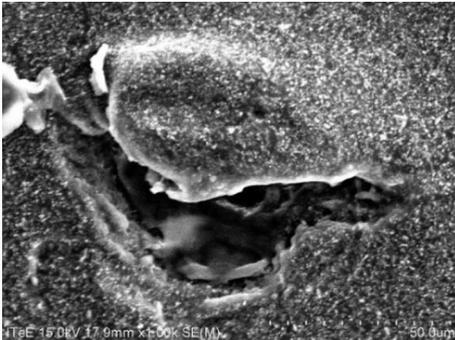
Table 5. Morphology of epoxy coatings aged with brine

Ageing period t [h]	Epoxy coating images obtained using SEM	Description of the destruction of the epoxy coating aged with brine
0		
672		<ul style="list-style-type: none"> • formation of craters in the topcoat
672		<ul style="list-style-type: none"> • release of topcoat fragments, • thinning of the top coat
1008		<ul style="list-style-type: none"> • cracking, • craters

The presented images of the surface topography of epoxy coatings aged with brine show that the surface destruction of the coatings was nonhomogeneous (Table 4).

3.4. Influence of ageing with brine on the surface morphology of epoxy coatings

Ageing of epoxy coatings with brine resulted in the destruction of their surface layers (Table 5) in the form of: craters, chippings, rarefactions, crackings. This was due to changes in the chemical structure of aged coatings. Table 5 shows the results of the coating morphology investigation obtained with the use of a scanning electron microscope (SEM).

1008		silver cracking the release of fragments of the topcoat (chipping), rarefactions in the top coat
1344		cracking of the top coat,
1680		cracking of the top coat

As a result of coatings ageing with brine, development of craters, chipping of coating fragments and rarefactions formation was observed in top coats after the period of 672 h. After ageing in the period of 1008 h new kinds of top coats destruction appeared in the form of crackings, including also silver crackings. Continuing of ageing (for 1344h and 1680 h) contributed to the further development of crackings in top coats.

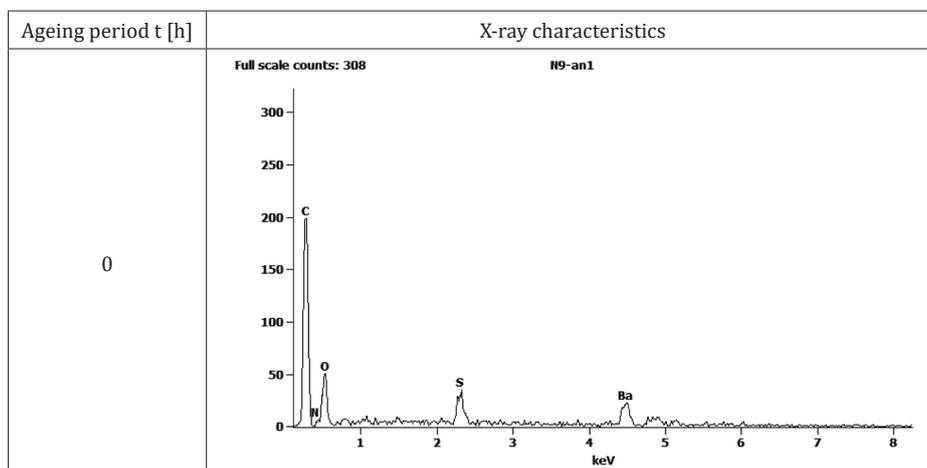
The chipping of coating components and the formation of craters in coating material was primarily influenced by the increase in the

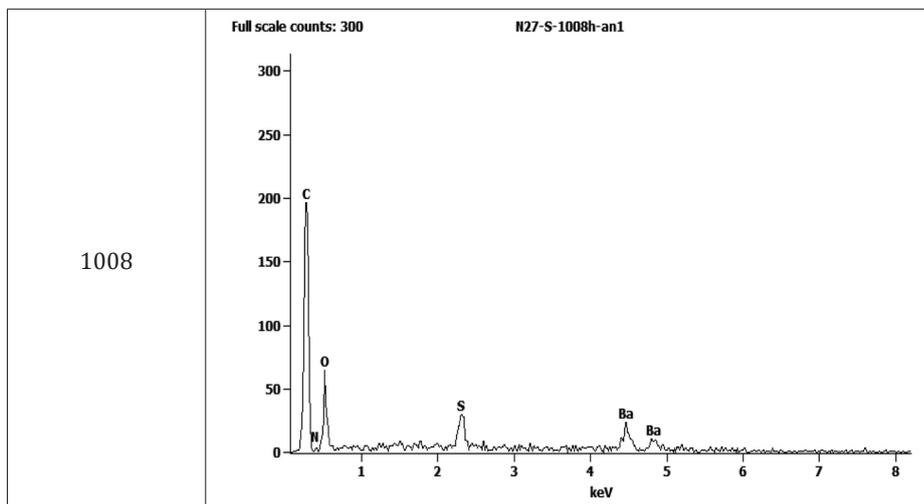
degree of oxidation of epoxy coatings aged with brine. On the other hand, the cause of cracking and the formation of rarefactions in the structure of the coatings was the breaking of chemical bonds (Fig. 1).

3.5. Influence of ageing with brine on the elemental composition of epoxy topcoats

X-ray studies (similarly to FTIR and DSC studies) have documented an increase in the degree of oxidation of epoxy coatings aged with brine. A clear increase in the mass fraction of oxygen was found after

Table 6. X-ray characteristics of epoxy coatings





the coatings ageing for 1008 h (Table 6). Due to the dominance of the process of oxidized coating layers chipping, the share of oxygen in the tested coatings, assessed on the basis of X-ray examination, remained unchanged after a longer period of ageing of the coating samples with brine.

3.6. Influence of ageing with brine on the wettability of epoxy coatings

The length of the ageing period had a significant effect on the value of the contact angle of the coating while wetting with the measuring liquid (water or diiodomethane). Ageing of epoxy coatings with brine caused (along with the ageing period flow) a decrease in the value of the contact angle Θ_C (Table 7) with distilled water. After ageing for 1680 h, the value of the contact angle Θ_C decreased by 10%, thus increasing the contact area of water with the epoxy topcoat.

The obtained results indicate the hydrophilicity growth of aged epoxy coatings, which increases their susceptibility to soaking with aggressive media (water). It should be emphasized that long-term penetration of the coating with aggressive media may lead to the development of undercoating corrosion.

Table 7. Contact angle Θ_C values of epoxy coatings surfaces aged with brine

Ageing period t [h]	Contact angle Θ_C [°]	
	water	diiodomethane
0	88.18	51.69
672	86.22	59.42
1008	80.99	54.83
1344	80.10	58.62
1680	78.98	62.67

The contact angle Θ_C was used to determine the Surface Free Energy (SFE) of epoxy coatings. The Owens-Wendt method, which is commonly used to determine the surface free energy of polymer composite materials, including epoxy coatings, was used to calculate the SFE. In the research carried out with this method, distilled water (polar liquid), characterized by a high value of the polar component, and diiodomethane (non-polar liquid) as a dispersive liquid were used as measuring liquids.

Table 8. Effect of ageing of epoxy coatings with brine on the value of surface free energy and its components (dispersive and polar)

Ageing period t [h]	Surface free energy (SFE) γ_s [mJ/m ²]	Dispersive component of SFE γ_s^d [mJ/m ²]	Polar component of SFE γ_s^p [mJ/m ²]
0	35.53	33.33	2.20
672	32.59	28.91	3.68
1008	36.49	31.54	4.94
1344	35.28	29.37	5.91
1680	34.18	27.04	7.14

The obtained results of research on the surface free energy of epoxy coatings aged with brine (Tab. 8) showed a significant effect of their ageing period on the value of the SFE components, both polar and dispersive. The free surface energy decreased by 4% for epoxy coatings aged with brine in the period of 1680 h.

On the other hand, ageing with brine contributed to a significant increase in the value of the polar component of the surface free energy of epoxy coatings. After ageing in the period of 1680 h, its over three-fold increase was observed. It should be said with high probability that it was influenced by changes in the chemical structure of the epoxy material contained in the surface layer of epoxy coatings (Fig. 1).

3.7. Influence of ageing with brine on the thickness of epoxy coatings

Characteristic of the thickness increase of epoxy coatings aged with brine during the period of 1680 h is presented in Figure 3, while Table 9 shows the trend line equation and the value of the coefficient of determination R^2 of this characteristic.

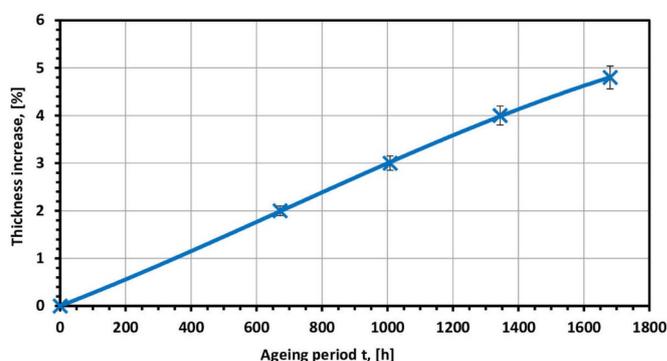


Fig. 3. Characteristic of the thickness increase of epoxy coatings aged with brine

The test results proved a progressive increase in the thickness of aged coatings, which after ageing in the period of 1680 h accounted for 5%, which was caused by soaking of the coatings with brine 6.

3.8. Influence of ageing with brine on the mass of epoxy coatings

The characteristic of the mass increase of epoxy coatings aged with brine during the period of 1680 h is presented in Figure 4, while Table 10 shows the trend line equation and the value of the coefficient of determination R^2 of this characteristic.

The conducted research shows that ageing with brine caused a progressive mass increase of epoxy coatings. After ageing of the coatings in the period of 1680 h, due to the penetration of brine into its interior, an increase in the mass of the coatings by 8% was observed.

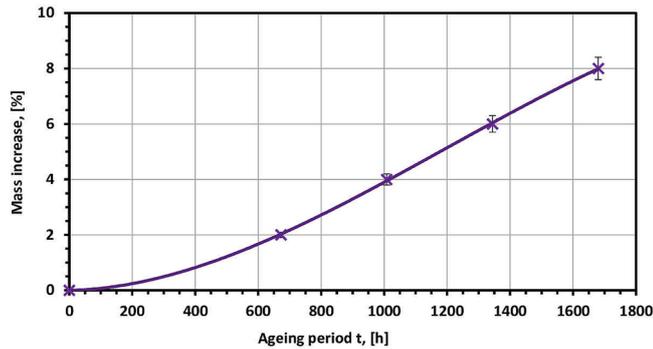


Fig. 4. Characteristic of mass increase of epoxy coatings aged with brine

Table 9. Equation of the trend line and the value of the coefficient of determination R^2 for the thickness increase characteristic of epoxy coatings aged with brine

Characteristic name	Mathematical model	Coefficient of determination R^2
Thickness increase	$y = -3E-10x^3 + 6E-07x^2 + 0.0027x + 0.0011$	0.9999

Table 10. Equation of the trend line and the value of the coefficient of determination R^2 for the mass increase characteristic of epoxy coatings aged with brine

Characteristic name	Mathematical model	Coefficient of determination R^2
Mass increase	$y = -1E-09x^3 + 5E-06x^2 + 0.0003x - 0.0027$	0.9999

Table 11. Equation of the trend line and the value of the coefficient of determination R^2 for the hardness (according to Buchholz) characteristic of epoxy coatings aged with brine

Characteristic name	Mathematical model	Coefficient of determination R^2
Buchholz hardness	$y = 9E-10x^3 - 7E-07x^2 - 0.0162x + 83.993$	0.9999

The reason for this was (among other things) an increase in the water absorption of the coatings, resulting from the reduction of the contact angle of the coating surface with water (Table 8).

3.9. Influence of ageing with brine on the hardness of epoxy coatings

The characteristic of Buchholz hardness measurements of epoxy coatings aged with brine in the period of 1680 h is presented in Figure 5, and in Table 11, the equation of the trend line and the value of the coefficient of determination R^2 of this characteristic are presented.

Ageing with brine resulted in a progressive reduction of hardness (according to Buchholz) of epoxy coatings. After ageing of the coatings in the period of 1680 h, the hardness decreased by 30%, which

was caused by an increase in the brittleness of the coatings as a result of an increase in their oxidation degree (Fig. 1, Table 3).

3.10. Influence of ageing with brine on the surface roughness of epoxy coatings

The impact of brine ageing on the surface roughness of epoxy coatings was assessed on the basis of examination of their parameters (R_a , R_z and R_{max}) of surface roughness. Ageing with brine in the period of 1680 h resulted in a significant increase in their value, which was caused by the chipping of components from the top layer of the coatings.

The characteristics of the R_a , R_z and R_{max} parameters of the surface roughness of epoxy coatings aged with brine in the period of 1680 h are presented in the figures 6 ÷ 8, while the equations of the trend line and the values of the coefficient of determination R^2 of these

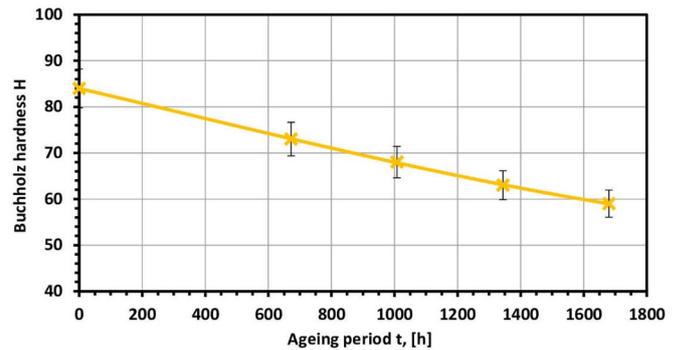


Fig. 5. Characteristic of Buchholz hardness of epoxy coatings aged with brine

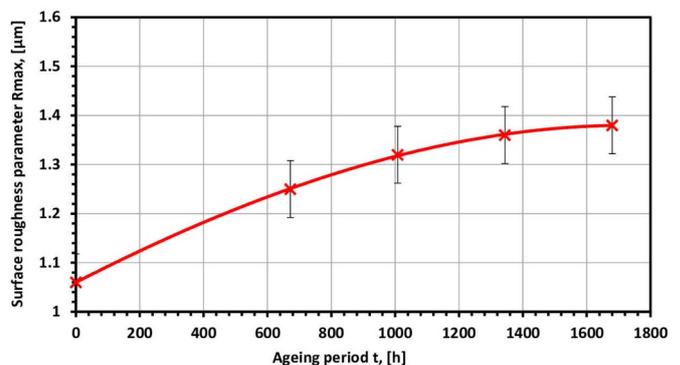


Fig. 8. Characteristic of the R_{max} parameter of the surface roughness of epoxy coatings aged with brine

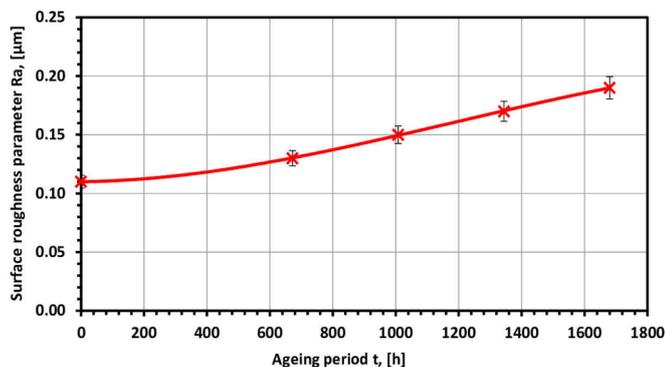


Fig. 6. Characteristic of the Ra parameter of the surface roughness of epoxy coatings aged with brine

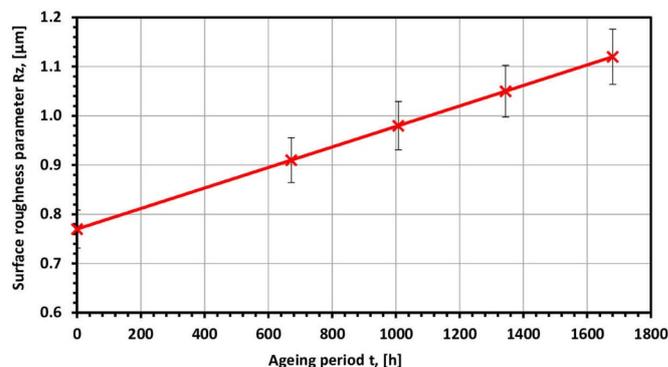


Fig. 7. Characteristic of the Rz parameter of the surface roughness of epoxy coatings aged with brine

Table 12. Equation of the trend line and the value of the coefficient of determination R^2 of the Ra parameter of the surface roughness characteristic of epoxy coatings aged with brine

Characteristic name	Mathematical model	Coefficient of determination R^2
Ra parameter	$y = -1E-11x^3 + 5E-08x^2 + 3E-06x + 0.11$	0.9999

Table 13. Equation of the trend line and the value of the coefficient of determination R^2 for the parameter Rz of the surface roughness characteristic of epoxy coatings aged with brine

Characteristic name	Mathematical model	Coefficient of determination R^2
Rz parameter	$y = 0.0002x + 0.77$	1

Table 14. Equation of the trend line and the value of the coefficient of determination R^2 for the Rmax parameter of the surface roughness characteristic of epoxy coatings aged with brine

Characteristic name	Mathematical model	Coefficient of determination R^2
Rmax parameter	$y = -1E-11x^3 - 6E-08x^2 + 0.0003x + 1.0599$	0.9999

characteristics are presented in Tables 12÷14. Ageing with brine resulted in a progressive increase in the Ra Rz and Rmax parameters of epoxy coatings, which after ageing in the period of 1680 h increased by 73%, 45% and 30%, respectively.

4. Summary

The conducted literature study shows that the current range of knowledge concerning the operational properties of polymer coatings exposed to brine during use, prevents the effective design of reliable protective and decorative coatings of technical devices.

The main reasons for this are the constant changes in the composition of coatings, caused by the development of nanotechnology in the field of nanofillers and nanopigments used for their modification, as well as the growing pro-ecological requirements in the field of paint and varnish production.

The speed of these changes is in contradiction with the traditional exploitation tests of the protective effectiveness of coatings, the duration of which in the case of innovative coatings can be even several years. The solution to this problem are accelerated tests used in conditions of intensified operational exposures caused by climatic and environmental factors. The degree of intensification of these exposures should be selected in such a way as to be adequate to the exposures affecting the actual period of several years of operation of the device protected with a given protective and decorative coating.

This article presents the results of accelerated (multi-criteria) tests of the variability of the physicochemical properties of epoxy coatings,

such as their thickness, mass (water absorption), hardness, surface roughness, heat resistance, water wettability.

Epoxy coating systems, consisting of a base layer modified with zinc microfiller and a top layer modified with nanoparticles of titanium dioxide, were subjected to multi-criteria tests of coating properties, determining their operational characteristics.

The epoxy coatings were aged by immersing them in a 25% aqueous sodium chloride solution (called brine). The maximum period of ageing with this medium was 1680 h.

Unconventional tests were used to determine the conditions for the destruction of brine-aged epoxy coatings, which include: FTIR infrared spectroscopic tests, DSC differential scanning calorimetry tests, tests of the surface morphology of the coatings performed with the use of scanning electron microscopy, tests of the geometric structure of the surface of the coatings with the use of an interferometric microscope, testing the angle Θ_C of wetting the surface of the coatings with a model liquid (water or diiodomethane).

The observed increase in brittleness of the top layer of brine-aged epoxy coatings, which progressively increased with the ageing time, was caused by the development of oxidation processes of the epoxy material. This is evidenced by an over 3-fold increase in the intensity of the C=O carbonyl group band (with a peak corresponding to the wave number 1726.94 cm^{-1}), disclosed in FTIR studies. Moreover, a more than 2-fold increase in the intensity of the OH hydroxyl group band (with a peak of 3396.99 cm^{-1}), also documenting the development of oxidation processes of epoxy topcoats. On the other hand, increasing the intensity of the CH_3 group band (with a peak corre-

sponding to the wavenumber of 2925.48cm⁻¹) indicates the breaking of chemical bonds in the epoxy material.

The chipping of the components of the top layers of the coatings, as a result of the increase in the degree of their oxidation, resulted in a significant change in the surface roughness profile.

For example, after 1680 h of ageing, the Ra parameter of surface roughness increased by 73%, the Rz parameter by 45%, and the Rmax parameter by 30%.

The effect of brine contributed to a reduction in the heat resistance of aged coatings, as it was found that the temperature of the beginning of the oxidation process (the beginning of thermal decomposition) decreased with the ageing time, as demonstrated in DSC tests. It was found that after 1680 h ageing, the temperature of the beginning of the oxidation process decreased by 15°C. Moreover, an increase in the intensity of the exothermic peak on the DSC curve was observed. This proves the development of epoxy oxidation processes with the passage of their ageing with brine. X-ray studies have also documented an increase in the susceptibility of epoxy coatings to oxidation due to ageing with brine. They showed a clear increase in the mass fraction of oxygen after ageing of the coatings over the period of 1008 h, determined on the basis of X-ray examinations.

After ageing with brine for 1680 h, a decrease in the hardness (according to Buchholz) of the coatings by 30% was also observed, which contributes to a decrease in their mechanical properties [25].

Ageing of epoxy coatings with brine caused a progressive (with ageing time flow) decrease in the value of the water contact angle

Θ_C on their surface, which after ageing for 1680 h decreased by over 10%. The obtained results indicate an increase in the hydrophilicity of epoxy coatings. Long-term penetration of the coatings with brine and its migration to the steel substrate may lead to the development of undercoating corrosion, as a result of which the coating will lose its adhesion to the steel substrate. Then it ceases to fulfil its protective (barrier) function and needs renovation.

The conducted research also revealed an over 3-fold increase in the value of the polar component of surface free energy in the case of epoxy coating ageing in the period of 1680 h. This was probably caused by significant ageing changes in the form of degradation of the chemical structure of the epoxy topcoat coating material.

It was also found that after ageing of the coatings in the period of 1680 h, their thickness increased by almost 5%, and their mass by 8%. The likely reason for this was the increase in wettability and porosity of the coatings (due to cracking of chemical bonds).

To sum up, the effect of brine on epoxy coatings resulted in deterioration of their operational properties, determining the coatings reliability, documented by: an increase in thickness and mass (water absorption), a decrease in hardness, a significant increase in the values of parameters (Ra, Rz, Rmax) of surface roughness, a decrease in the angle Θ_C of surface wetting with water, a decrease in the thermal decomposition onset temperature, as well as increase in the surface free energy and the degree of destruction (in the form of: crackings, silver crackings, rarefactions, craters).

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