

Article

The Influence of Battery Acid on the Destruction of Acrylic Coatings of Car Bodies

Danuta Kotnarowska

Department of Mechanical Engineering, Kazimierz Pulaski University of Technology and Humanities, 26-604 Radom, Poland; d.kotnarowska@uthrad.pl

Abstract: Renovation coatings of car bodies undergo destruction under the influence of operational factors. Like ultraviolet radiation, erosion, and aggressive media (among others, battery acid). This article concerns the evaluation of the influence of battery acid on the destruction of acrylic coatings previously non-aged, as well as aged climatically for 2 years. Ageing of the coatings with battery acid contributed to a degradation increase of their chemical structure. It was supported by a considerable increase in the polar component of surface free energy (SFE) of the coatings. In the case of prior climate ageing, the increase in the polar component was even higher. Moreover, the coating's ability to absorb battery acid increased, which induced blistering. The DSC method revealed that the action of battery acid caused more intense oxidation of coating material, and as a result, the brittleness increased, leading to chipping of the coating surface layers. This led to the increase in surface roughness, measured using an interferometric method. The coatings previously climatically aged for 2 years presented higher values of surface roughness parameters than the non-aged ones. The increase in the surface roughness contributed to a substantial decrease in the gloss of coatings. A sharp difference in colour escalating with the lengthening of the ageing period was also observed using the spectrophotometric method.



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Keywords: acrylic coating; climatic ageing; ageing with battery acid; physicochemical properties; destruction

1. Introduction

Acrylic coatings have found a widespread and sustained application as decorative-protective coatings of modern car bodies. Scientific development in the area of paints and varnishes for coatings of car bodies is presently focused on environmentally friendly coating materials. For this reason, volatile organic compounds (VOC) have been eliminated (or significantly reduced) from paint and lacquer formulas in the last 10 years. Moreover, approximately every five years, these formulas have undergone changes which primarily improve the quality of coatings. Therefore, conducting complete and long-lasting operational examinations on representative samples of coatings, which may last even 10 to 15 years, has no substantive grounds. What concerns the currently used new generations of coatings (nanocoatings especially) is necessary to test them in accelerated mode, enabling their quick operational life prediction in expected conditions [1–6].

Despite the progress in the fields of the production and application of polymer coating materials, problems still exist concerning their use for reliable and long-lasting protection of car bodies against operational environment influence. Coating life predicting is also a complicated question, since the complexity of the ENVIRONMENT-COATING-SUBSTRATE system results in a gap of an appropriate theoretical basis, as the component parts of the system and the relationships between them undergo constant changes. The changes concern the operational environment's aggressiveness as well as kinds of materials used for polymer coatings and also for substrates [6–13].

The kinetics of the destruction of polymer coatings resulting from operational environment influence (in the form of climatic factors and environment pollution) is not

presently recognized well enough [14–19]. It is caused mainly by the fact that polymer coatings, which protect the surface of technical objects against the destructive influence of the environment (environmental factors), also submit to the destruction of complex aetiology [16,17]. It results from the simultaneous action of chemical substances (operational liquids, acid rains, and brine), mechanical loads (constant and variable stresses, erosive particles impacts), and aggressive products of the metabolism of microorganisms, as well as climatic factors like sunlight, wind, and rain or hail [18–24].

It should be stressed that information resources in the area of the physico–chemical properties of protective–decorative polymer coatings, constituting the basis for their operational life increase, are continually updated by numerous researchers dealing with this subject [25–37]. This growing interest in the subject is the result of the growing requirements in regard to the reduction of the contents of volatile organic compounds (VOC), according to directive 2006/42/WE of the European Parliament and The Council. Moreover, the permanent introduction of new generation materials (nanofillers, nanopigments [27–36]) into the market forces examinations (especially accelerated) of coatings produced with the participation of nano-additives in order to evaluate their protective and decorative properties [32,34]. Nowadays, “smart polymer coatings” are also produced, which self-heal defects occurring in their structure under the influence of operational factors. This type of coating contains nanocontainers (nanotubes, nanocapsules), in which binders, hardeners, corrosion inhibitors, biocides, as well as other substances that repair coatings in the defected zone may be found. These nanocontainers may be made of different materials that are organic (polystyrene, urea–formaldehyde resin) and/or inorganic (silicon dioxide, calcium carbonate, halloysite). The introduction of special substances into the nanocontainers enables one to control final properties of the coatings. In this way, it is possible to obtain smart coatings that are antibacterial, antifouling, self-cleaning, anti-icing, colour-altering, or hydrophobic [22,26,30,35].

The operational life of polymer coatings protecting the surfaces of technical objects against the damaging influence of environmental factors predominantly depends on their properties, e.g., the degree of hydrophobicity, tightness, and the durability of adhesive joints [9,14,16].

Environmental factors, which include aggressive media and ultraviolet radiation, lead to the formation of nanopores, micropores, and megapores in the coating structure. With the progression of operation time, pores occurring in coating structure connect with each other, forming paths transmitting aggressive media to the steel substrate, and contributing to subcoating corrosion. As a result, it leads to the breaking of adhesive bonds between the substrate and the coating, which mainly determines its operational life [14,19,37–45].

Aggressive media permeation into a polymer coating material depends on the coating surface susceptibility to wetting, assessed on the basis of the contact angle θ_C value. The lower this value, the greater is the coating wettability, and the larger is its surface contact with aggressive media, which leads to higher absorption of these media by the coating. Aggressive media absorption into coatings contributes to their swelling and to the degradation of their chemical structure [15,24,25,40]. In the case when $\theta_C = 45\text{--}90^\circ$, water permeation into the coating’s superficial layers substantially depends on its chemical structure and surface roughness [17].

It should be stressed that the simultaneous action of aggressive media absorbed by the coatings and mechanical factors may promote the propagation of cracks in their structure [7,46]. Moreover, as a consequence of aggressive media absorption, the coating’s surface energy decreases, which also causes a decrease of the mechanical strength of the coating [3,9,16].

In the course of polymer coating’s service, continual degradation of the polymer material occurs, caused by the service environment to which the material is exposed, in the form of climatic and environmental factors. Among climatic factors, the most significant are as follows: sun radiation stimulating polymer photodegradation [24,25,47–50], thermal radiation causing its thermal degradation [49], and oxygen included in the air

generating oxidative degradation [5,50,51]. Environmental factors embrace, among others, components such as mechanical factors, causing mechanical degradation [51], as well as aggressive media in the form of acids, alkalies, or/and salts, contributing to the hydrolytic degradation of coating materials [31].

Destruction of coatings, caused by polymer material degradation, leads to the decrease in protective effectiveness of the coatings, which is tantamount to their operational life shortening [24,25,52].

Ultraviolet radiation, which is part of the spectrum of sun radiation (UV-A range of wave length 315–400 nm), is the primary destructive factor in polymer ageing. It generates a photodegradation process of the superficial layers of polymer coatings of a radical nature, which is promoted by their structural defects in the form of pores and/or cracks. Oxidative ageing development of coating material has been documented in FTIR examinations by the intensity increase of the carbonyl group (C=O) band [1,5,24,25,32,34]. For example, in the case of acrylic coatings aged in a climatic station for one year, the band's intensity increase was stated for wavenumbers γ , equal to 1724 and 1690 cm^{-1} , both corresponding to carbonyl stretching frequency (carbonyl valence vibrations) [16]. Oxidized external sublayers of the topcoats show increased brittleness, which contributes to their chipping and the formation of pits, leading to an increase in the coating's roughness [15,24,25].

In the pits formed on the coating's surface, organic impurities and moisture settle, creating favourable conditions for the development of microorganisms in the form of viruses, bacteria, algae, and mould fungi. Products of their metabolism initiate the development of biological corrosion of polymer coatings [45]. It results in the generation of craters in coatings (reaching the substrate), as well as superficial etchings [1,2].

The coating's increased resistance to operational factors, including ultraviolet radiation, is achieved by nanoparticles' introduction to their structure, e.g., aluminium trioxide, titanium dioxide, or silicon dioxide [5,32,44,49]. It should be stressed that nanoparticles effectively fill nano- and micropores existing in polymer coatings, increasing their tightness, which limits aggressive media migration [15,25].

Coating-forming material is most frequently modified with nanoparticles of silicon dioxide (called silica) of a mass share from 3.5% [15] to 18% [5]. It is important that addition of nanofillers to the topcoat material only very slightly influences its transparency. For this reason, it is advisable to introduce nanofillers into paints for topcoats in order to improve the operational life of protective–decorative (multilayer) polymer coating systems [5,6,15,32].

During their service life, coatings of car bodies are often subjected to the influence of different operating fluids, e.g., diesel fuel, petrol, battery acid, or windscreen washing fluid [51].

The author of the presented paper in the work [16] discussed the destructive effects of diesel fuel contact with polymer coatings. Exposing the examined acrylic coating to diesel fuel resulted in ageing of the coating material, which included physical and chemical properties changes, such as thickness, hardness (acc. Buchholz), surface topography and roughness, gloss, and colour. The development of the ageing process in coatings under the influence of diesel fuel also resulted in a decrease of the contact angle θ_C characterizing coating susceptibility to wetting with water. Thereby, the contact area of water drops with the coating surface increased, which led to the increased absorbability of water by the coating material.

In turn, in the presented paper, on the basis of carried out investigations, the effects are discussed of the influence of another operating fluid, i.e., battery acid, on acrylic coatings applied for car renovation.

2. Materials and Methods

2.1. Materials

An evaluation of the influence of battery acid on coatings was carried out on the example of acrylic coating systems, which are commonly used in body and paint workshops

for the renovation of protective–decorative coatings applied on car bodies. Samples of the coatings were sprayed on surfaces of steel plates of dimensions $160 \times 80 \times 2 \text{ mm}^3$. The plates were cut from sheets of non-alloy structural steel S 235 JRG 2 (acc. PN-EN 10025-1:2007 [53]). Before undercoat application, the surfaces of the steel plates were prepared with P80 abrasive paper and then degreased with extraction solvent.

Samples of coating systems were obtained by air spraying of three successive kinds of polymer coatings, which were as follows: the acrylic base coating, the acrylic interlayer coating (red), and the top layer made of the acrylic lacquer.

The intermediate coating was pigmented with iron red, made of iron trioxide (Fe_2O_3) nanoparticles of dimensions $d \leq 60 \text{ nm}$.

After application, the coating systems were acclimatized for 10 days in the environment of a relative humidity equal to $65\% \pm 5\%$ and a temperature of $20 \pm 2 \text{ }^\circ\text{C}$ (according to the standard PN-EN 23270:1993 [54]). Then, preliminary examinations of their physical and chemical properties were carried out.

Subsequently, the examinations were made concerning the results of battery acid influence on the surface of coating systems. In the course of these examinations, cotton cosmetic pads soaked with battery acid were put on the surface of the examined coatings. The maximum period of coating exposure to battery acid action was 336 h. Two kinds of coating systems were subjected to battery acid action, specifically, the unaged climatically acrylic coatings (C0) and the acrylic coatings (C2) aged before (acc. PN-EN ISO 2810:2005 [55]) at a climatic station for the period of 2 years. The state of the coating surfaces subjected to battery acid action was evaluated after the lapse of the following periods: 48, 168, and 336 h.

2.2. Research Methodstsnle

Surface changes of acrylic coating systems (hereafter called “acrylic coatings”) under the influence of battery acid were evaluated on the grounds of the examination results of their physical and chemical properties. The following properties were taken into account: thickness, hardness, surface topography and roughness, gloss, colour, and contact angle θ_C of wetting the surface with aggressive media (diiodomethane and water), as well as resistance to oxidation.

The state of the coating surfaces was analysed based on their R_a and R_z roughness parameters and topography pictures. R_a and R_z parameters and the topography of acrylic coating surface were examined with a Taylor Hobson white-light interference microscope, Talysurf CCI 6000 (Taylor Hobson Precision, Leicester, UK), enabling optical measurements (acc. standards PN-M-04251:1987 [56] and PN-EN ISO 8501-1:2008 [57]).

Physical destruction of aged acrylic coatings was investigated using a Hitachi FESEM SU-70 (Hitachi, Tokyo, Japan).

Changes in chemical structure of acrylic topcoats that were aged at the climatic station were assessed using an infrared spectrophotometric method with a Jasco Inc. spectrophotometer FT/IR 6200 (Jasco Inc., Easton, MA, USA). The apparatus was controlled with a computer program, Spectra Manager, enabling mathematical and graphical processing of the obtained spectra. IR spectra were recorded with the help of a reflection method, using a single reflection ATR attachment of spectral range $\text{IR}\nu = 4000\text{--}600 \text{ cm}^{-1}$ and a resolution of 4 cm^{-1} .

Oxidation resistance of the coatings, which determines their thermal resistance, was examined using a LABSystem SETARAM TG-DTA/DSC apparatus (SETARAM Instrumentation, Caluire, France) were carried out by applying a dynamic method with a linear temperature increase, in the environment of oxygen as an oxidizing agent. Polymer samples, each of mass $3.0 \pm 0.5 \text{ mg}$, were heated in a platinum melting pot from 20 to $400 \text{ }^\circ\text{C}$ at the heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ and the oxygen flow rate of $60 \text{ mL}/\text{min}$. Based on obtained DSC curves, the temperature of oxidation onset of acrylic material was extrapolated. Measurement conditions were the same for all the samples, which enabled a comparison between DSC characteristics of the unaged coatings and coatings aged with battery acid.

The thicknesses of the coatings were measured using an Elcometer 456CFN ultrameter (Elcometer, Aalen, Germany) (acc. PN-EN ISO 2808:2008 [58]), and their mean value was $115 \pm 1 \mu\text{m}$.

The Erichsen hardness tester (Erichsen, Ann Arbor, MI, USA) was used for measurements of the hardness of the coatings (acc. PN-EN ISO 2815:2004 [59]).

Contact angle θ_C was determined with the help of a Goniometr 190 (Rame-Hart Instrument, Succasunna, NJ, USA) equipped with a camera and using MicroScan software.

Gloss examinations (acc. PN-EN ISO 2813:2014-11 [60]) were carried out using a Konica Minolta Rhopoint IQ-S gloss meter (Konica Minolta, Tokyo, Japan).

The colour of the coatings was evaluated based on examination results obtained using a Konica Minolta CM-700d spectrophotometer (Konica Minolta, Tokyo, Japan).

Method of acrylic coatings ageing under the influence of the natural climatic conditions.

Climatic ageing of the coatings (acc. PN-EN ISO 2810:2005 [55]) took place on special racks where samples of the coatings were fastened after prior acclimatization. The racks with the samples were exposed for 24 months in a climatic station, situated on the grounds of the Mechanical Department in the University of Technology and Humanities in Radom (Central Poland).

The average annual climatic conditions during ageing of the coatings in the period of 2018–2019 were as follows [61,62]:

(a) Average annual air temperature:

10.4°C in 2018

10.9°C in 2019

(b) Atmospheric precipitation:

600 mm in 2018

500 mm in 2019

(c) Insolation:

1750 h in 2018

1599 h in 2019

Method of acrylic coatings ageing under the influence of battery acid

Effects were investigated of the ageing of acrylic coatings under the influence of a sulphuric acid water solution of pH = 8, which is characteristic for battery acid used in cars. The maximum period of battery acid influence on the acrylic coatings was 336 h. For this purpose, cotton pads soaked with battery acid were applied on the surface of the coatings. The evaluation of the state of coating surfaces was done after 48, 96, 168, and 336 h of ageing.

3. Results and Discussion

3.1. Evaluation of the Destruction of Acrylic Coatings Aged in Natural Climatic Conditions

IR spectroscopic investigations (FTIR) were carried out in order to evaluate the chemical destruction of acrylic coatings aged at the climatic station for the period of 2 years. Obtained results, presented in Figure 1 in the form of infrared transmittance spectra, showed a dependence between transmittance (T) of infrared radiation and wavenumber (ν). We documented changes in the chemical structure of the coatings, which was evidenced by the increase of the carbonyl groups (C=O) content, as it was stated in the band with the peak of the wave number $\nu = 1724 \text{ cm}^{-1}$. This band corresponds to the carbonyl groups' stretching frequency (carbonyl valence vibrations). The increase of this band intensity documents the development of the ageing oxidation of the acrylic material.

SEM examination of the surface condition of the acrylic coatings showed that, as the ageing period increases, the destruction degree of the surface increases too (Table 1a–d). As observed, climatic ageing leads to the chipping of filler and pigment particles from the surface of the coatings (Table 1c). Microcracks (Table 1b), craters (Table 1c), and etchings (Table 1c) appeared on the surface. The microcracks, which had a shape of parallel bands,

probably formed areas of silver cracks, which arose because of the destructive influence of UV radiation (Table 1d).

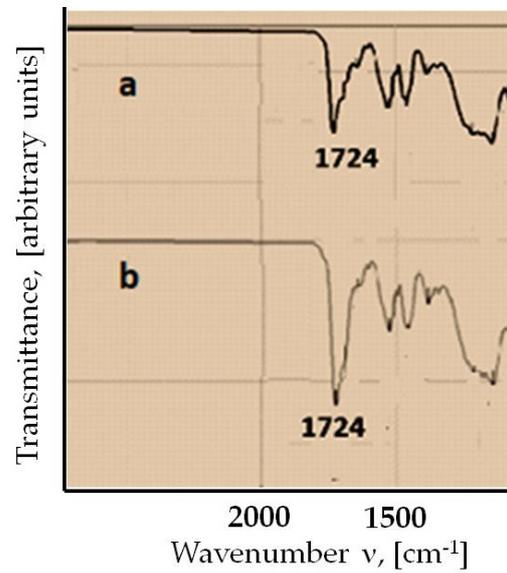


Figure 1. FTIR spectra of the non-aged acrylic coating (a) and of the same coating aged for 2 years (b).

Table 1. Surface morphology of acrylic coatings aged at the climatic station.

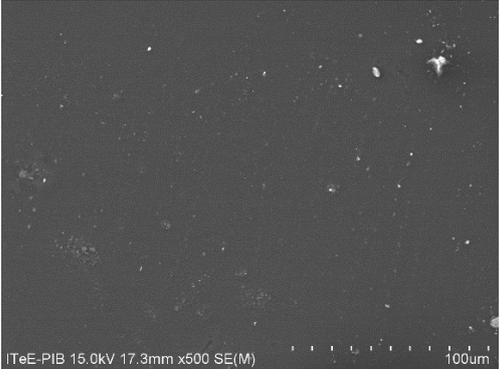
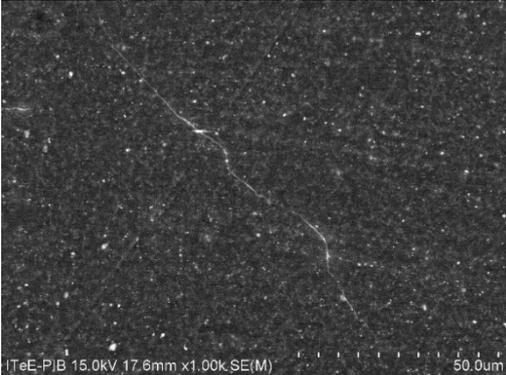
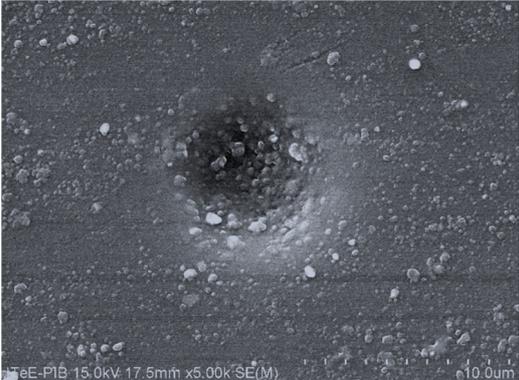
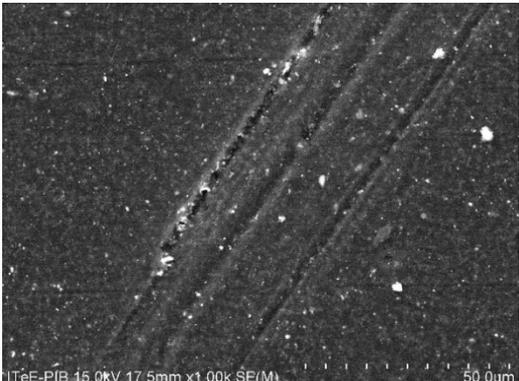
Ageing Period (Month)	Morphology of Acrylic Coating Surface
0	 <p data-bbox="842 1496 1342 1518">ITeE-PIB 15.0kV 17.3mm x600 SE(M) 100um</p> <p data-bbox="826 1532 1358 1561">a. Surface morphology of climatically non-aged coating.</p>
12	 <p data-bbox="836 1928 1342 1951">ITeE-PIB 15.0kV 17.6mm x1.00k SE(M) 50.0um</p> <p data-bbox="719 1964 1458 1993">b. Development of the cracking in the coating aged climatically for 12 months.</p>

Table 1. Cont.

Ageing Period (Month)	Morphology of Acrylic Coating Surface
18	 <p data-bbox="699 779 1485 831">c. Development of a crater and chippings in the coating as a result of climatic ageing for 18 months.</p>
24	 <p data-bbox="699 1243 1485 1294">d. Development of silver cracks on the coating surface and its fragment chipping as a result of climatic ageing for 24 months.</p>

Acrylic coatings previously aged at the climatic station showed substantial destruction under the influence of accelerated acid rain ageing, which generated changes in their surface topography. Topography examples of coatings subjected to accelerated ageing with acid rain (water solution of sulphuric acid of pH = 5) are presented in Table 2. It is visible that changes in topography increased with the increase in the ageing period. This was caused by the increase of the coating's susceptibility to plastic deformation, which was associated with blistering [16].

3.2. Assessment of the Contact Angle θ_C of Acrylic Coatings' Surfaces

The operational life of protective acrylic coatings, which protect the surfaces of technical objects against the negative influence of environmental factors, depends strongly on the hydrophilicity of their surfaces, determining wettability of coatings with water. It should be stressed that, on hydrophilic surfaces, water drops fully spread, and the contact angle $\theta_C = 0^\circ$. In contrast, hydrophobic coatings of contact angle $\theta_C = 90^\circ\text{--}180^\circ$ are the most advantageous with regard to their protective properties. Of course, in the case when the angle $\theta_C = 180^\circ$, the polymer coating is fully non-wettable with water.

Permeation of aggressive media (aqueous solutions of acids, alkali, and salts) into the polymer material of coatings equally depends on their surfaces' susceptibility to wetting with water. The lower value of contact angle θ_C , the higher is the wettability of the coatings' surface with aggressive media; therefore, the surface contact with their drops is bigger, which results in higher absorptivity of coatings with these media.

Table 2. Surface topography of acrylic coatings subjected to acid rain influence (in accelerated examination).

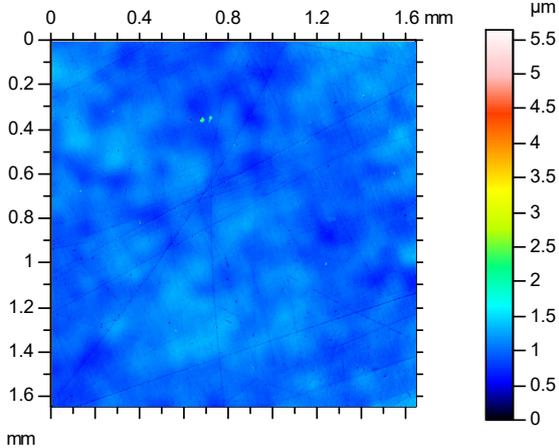
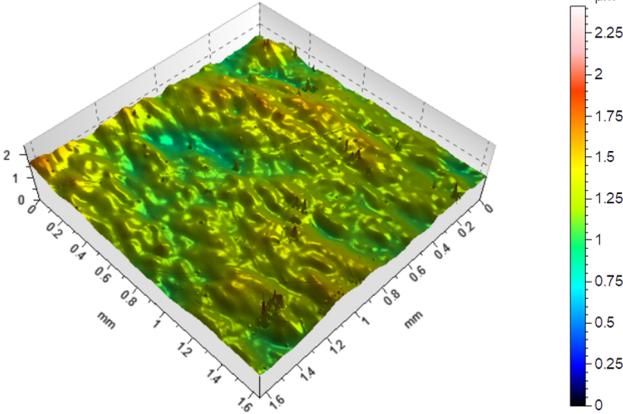
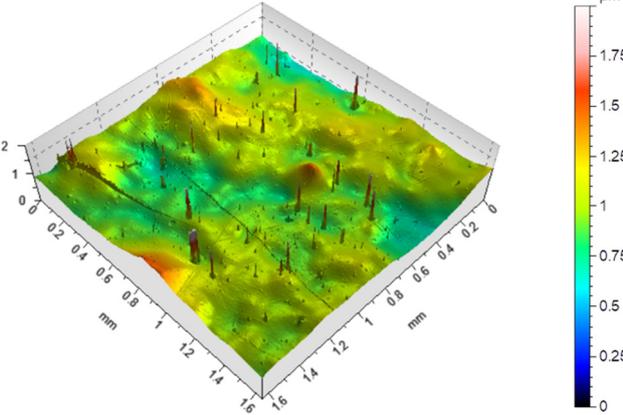
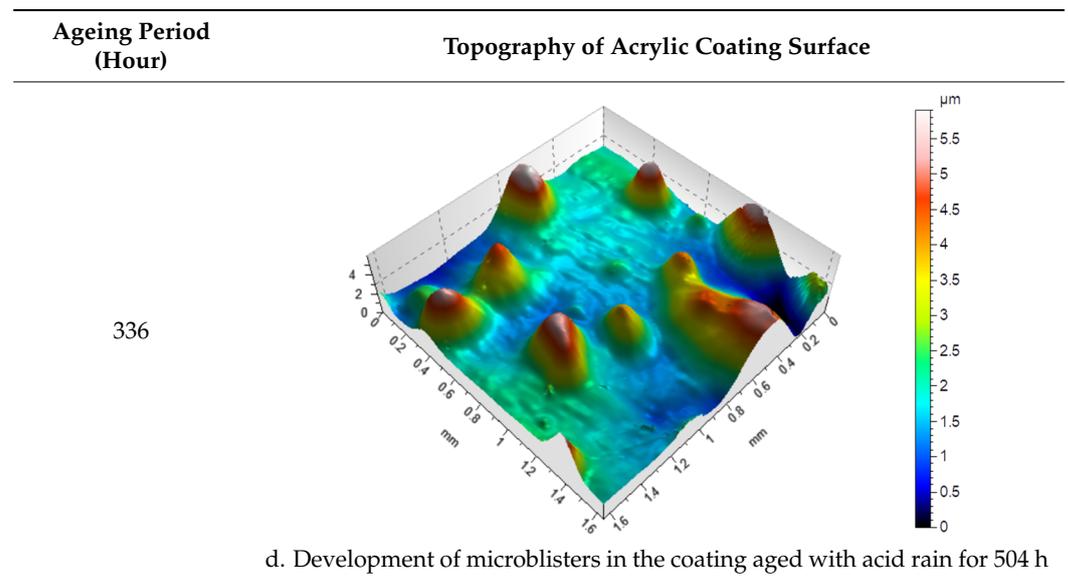
Ageing Period (Hour)	Topography of Acrylic Coating Surface
0	 <p data-bbox="842 880 1337 913">a. Topography of the non-aged coating surface</p>
168	 <p data-bbox="703 1361 1481 1395">b. Topography of the coating surface after ageing with acid rain for 168 h</p>
336	 <p data-bbox="703 1843 1481 1877">c. Development of microblisters in the coating aged with acid rain for 336 h</p>

Table 2. Cont.



Carried out investigations have indicated that the influence of battery acid on surfaces of acrylic coatings changed the values of their contact angle θ_C . In order to measure the value of contact angle θ_C for the surface of acrylic coatings, distilled water and diiodomethane were used as model measuring liquids. The values of free surface energy (SFE) and the polar and dispersive components for these liquids are known and presented in Table 3. Ten drops (of a volume of 5 mL each) of the liquids were applied in sequence with a micropipette to the surfaces of all acrylic coatings tested. Then, the value of contact angle θ_C for each of the 10 drops was measured.

Table 3. Surface free energy (SFE) of water and diiodomethane.

Measuring Liquid Kind	SFE (mJ/m ²)	Polar Component of SFE (mJ/m ²)	Dispersive Component of SFE (mJ/m ²)
Water	72.8	51	21.8
Diiodomethane	50.8	0	50.8

The influence of battery acid on the surfaces of acrylic coatings contributed to their contact angle θ_C decrease, in the case of water as well as diiodomethane (Table 4).

Table 4. Contact angle θ_C of the acrylic coatings: C0: unaged; C-AK: unaged, subjected to battery acid (AK) action for 336 h; C2-AK: aged climatically for 2 years and then subjected to battery acid action for 336 h.

Symbol of the Coating	Period of Ageing with Battery Acid (AK) (h)	Contact Angle θ_C (°)			
		Water		Diiodomethane	
		θ	δ_θ	θ	δ_θ
C0	0	66.50	3.91	51.92	1.66
C0-AK	336	56.91	2.77	47.74	4.04
C2-AK	336	55.59	6.98	52.34	4.30

Coatings aged climatically for 2 years and then aged with battery acid for 336 h showed a decrease of the contact angle θ_C value by 16%, whereas coatings aged only with battery acid for 336 h showed a decrease of the contact angle θ_C value by 14%. These results

document the increase of acrylic coatings hydrophilicity under the influence of ageing with battery acid, which is tantamount to the increase of the contact area of an aggressive medium drop with the coating surface. Therefore, the increase of coating susceptibility to absorb water (together with impurities) was observed, which migrates to the steel substrate and contributes to development of substrate corrosion.

Moreover, as a result of soaking of acrylic coatings with battery acid, their capacity for plastic deformation increases, which may result in microblisters development (Table 1c,d).

Subjecting acrylic coatings to battery acid action also caused an increase in their surface free energy (SFE) (Table 5). The coatings after battery acid action showed a value of the SFE polar component 40% higher than non-aged coatings, which testify to a bigger chemical degradation of aged coatings. In the case of the coatings climatically aged beforehand and then subjected to battery acid action, the value increment of the SFE polar component was higher by 58%.

Table 5. Surface free energy (SFE) of the acrylic coatings (description acc. Table 4).

Symbol of the Coating	Period of Ageing with Battery Acid (AK) (h)	SFE γ^s (mJ/m ²)	Polar Component γ^p_s (mJ/m ²)	Dispersive Component γ^d_s (mJ/m ²)
C0	0	44.50	11.31	33.20
C0-AK	336	51.39	15.86	35.53
C2-AK	336	50.81	17.85	32.96

3.3. Assessment of the Thickness of Acrylic Coatings

Battery acid action caused a thickness increase of 10% of the coatings previously aged climatically for 2 years. However, the thickness of the non-aged climatically coatings practically did not change after battery acid action.

The influence of battery acid action on the thickness of acrylic coatings is presented in Figure 2, while mathematical models of the thickness characteristics are presented in Table 6.

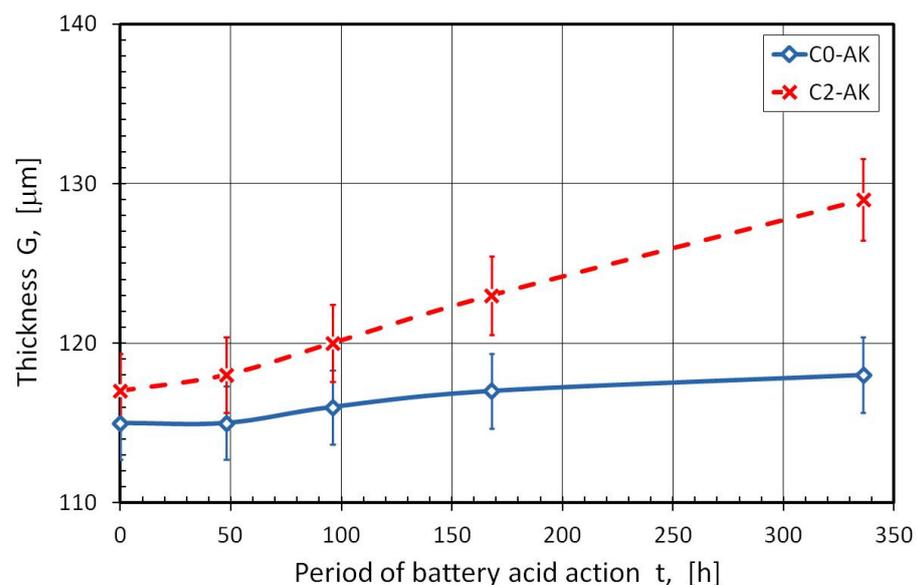


Figure 2. The influence of battery acid action on acrylic coatings thickness. C0-AK: the coating aged with battery acid; C2-AK: the coating before ageing with battery acid, previously aged climatically for 2 years.

Table 6. Trend line equations and the values of the determination coefficient R^2 of thickness characteristics of acrylic coatings.

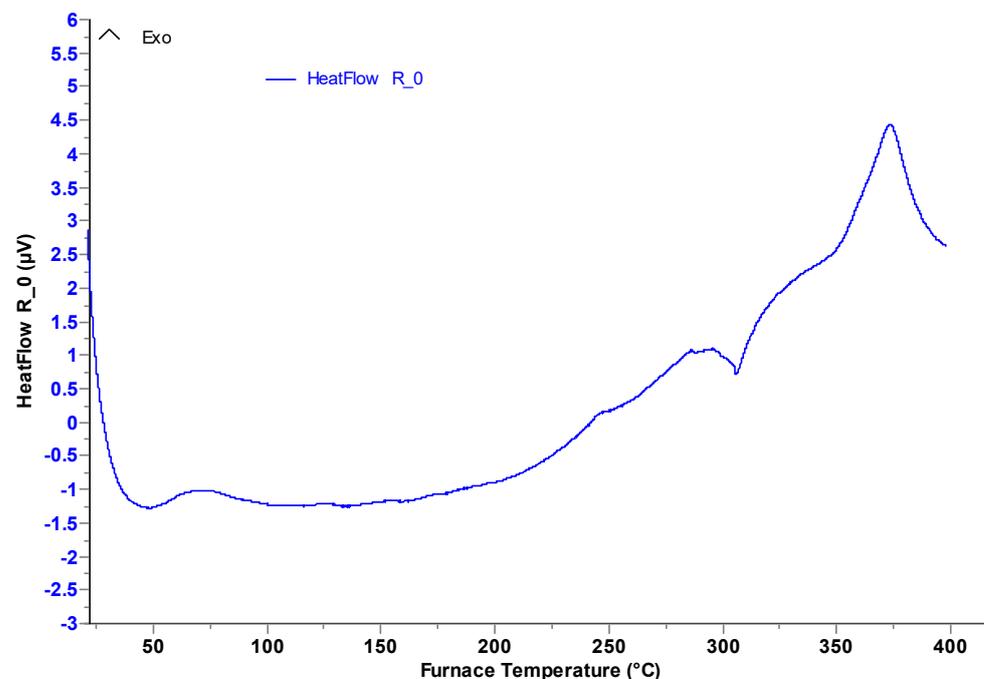
Symbol of the Coating	Mathematical Model of Thickness Characteristics	Determination Coefficient R^2
C0-AK	$y = -10^{-5} x^2 + 0.0145 x + 114.75$	0.9589
C2-AK	$y = 0.0368 x + 116.63$	0.9962

The reason that the thickness of the coating increases (Figure 2) after being subjected to battery acid is probably highly linked to the increase in the porosity of the aged coatings and their soaking in battery acid, because earlier examinations of polymer coatings aged with aggressive media showed the generation of micro- and nanopores in coating material [24,25], the dimensions of which increased with the increase of the ageing period. These pores developed in the coatings that were soaking with aggressive media, which contributed to their thickness increase (as a result of coating swelling). The same process very likely occurred in the case of the coatings described in the present article, which were soaked in battery acid.

Moreover, coatings aged with battery acid show increased susceptibility to blistering (Table 2) and cracking (Table 1). With ageing period, these pores, together with microcracks, form paths in the coating material, which conduct aggressive media to the metallic substrate, which causes its corrosion.

3.4. Evaluation of the Oxidative Resistance of Acrylic Coatings

Oxidative resistance of acrylic coatings was determined using differential scanning calorimetry (DSC). Based on obtained DSC curves (Figures 3 and 4), the following values of temperature were determined: oxidation onset temperature T_g , exothermic peak temperature T_1 , endothermic peak temperature T_2 , and the thermal degradation end temperature T_k of acrylic coatings.

**Figure 3.** DSC characteristics of unaged acrylic topcoat material.

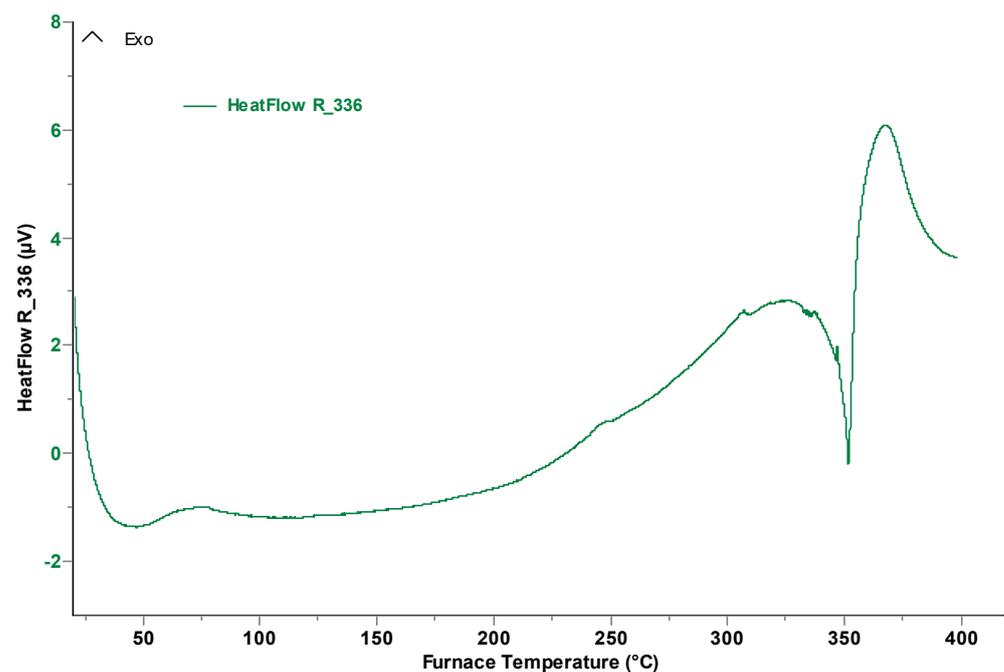


Figure 4. DSC characteristics of acrylic topcoat material aged with battery acid for 336 h.

DSC examinations also bring information about the nature of reactions running during the thermal degradation of acrylic coatings. Reactions of rearrangement and oxidation trigger exothermic peaks; whereas, endothermic peaks refer mainly to depolymerisation processes running in the acrylic material.

Results of DSC measurements showed that oxidation of non-aged acrylic coatings runs the most intensively at temperature $t = 374\text{ }^{\circ}\text{C}$, corresponding to the exothermic peak temperature; whereas, for the coatings aged with battery acid for 336 h, the exothermic peak occurs at temperature $t = 368\text{ }^{\circ}\text{C}$, which is lower by 1.6% in comparison with this temperature for non-aged coatings.

It should be noted that ageing of the acrylic coatings with battery acid contribute to the increase of their oxidation intensity, which was supported by the increase of the exothermic band area (of the peak corresponding to temperature of $t = 368\text{ }^{\circ}\text{C}$) in comparison with the non-aged coating. Moreover, a mass loss in the temperature range $T_p - T_k$ occurred. In the case of non-aged coatings, the mass loss ran to 20%. Oxidation processes occurring in the coatings in the time of ageing with battery acid for 336 h contributed to the increase of their mass loss by up to 27%. It was stimulated by intensive development of oxidation in the coatings aged with battery acid (Table 7).

Table 7. Thermal properties of the acrylic coatings.

Symbol of the Coating	Characteristic Values of Temperature (on DSC Curve) (at Heating Rate of $10\text{ }^{\circ}\text{C}/\text{min}$ in Oxygen Atmosphere) ($^{\circ}\text{C}$)				Mass Loss in Temperature Range $T_p - T_k$ (on TG Curve)	
	T_p	T_{END} T_1	T_{EGZ} T_2	T_k	Δm (mg)	Δm (%)
C0	156	307	374	396	0.703	19.5
C0-AK-336 h	156	351	368	396	0.968	27.0

3.5. Assessment of the Hardness of Acrylic Coatings

Results of Buchholz hardness tests of acrylic coatings subjected to battery acid action are shown in Figure 5, while mathematical models of hardness characteristics are presented in Table 8.

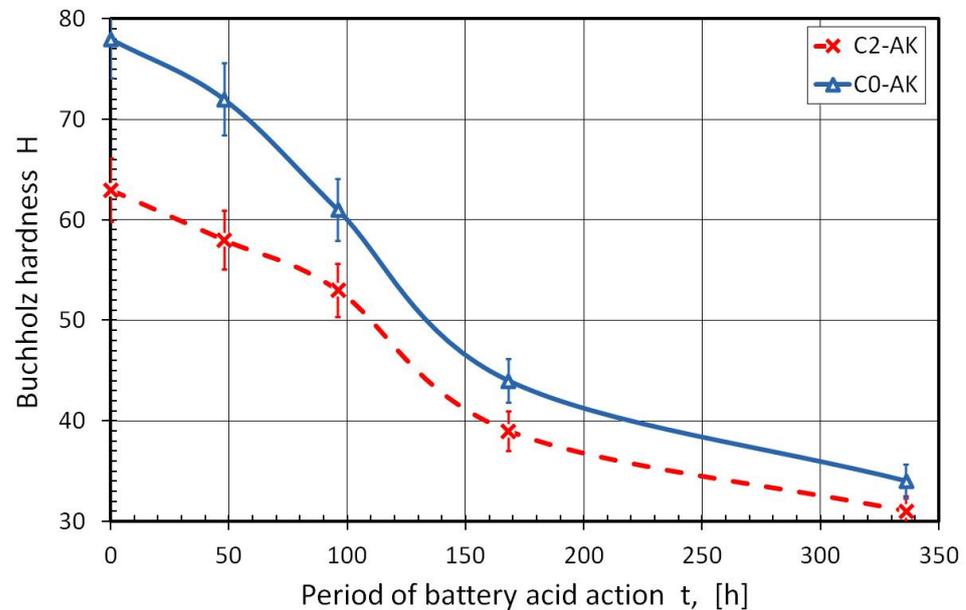


Figure 5. Buchholz hardness of acrylic coatings subjected to battery acid action.

Table 8. Trend line equations and the values of the determination coefficient R^2 of hardness characteristics of acrylic coatings.

Symbol of the Coating	Mathematical Model of Buchholz Hardness Characteristics	Determination Coefficient R^2
C0-AK	$y = 0.0003 x^2 - 0.2571 x + 80.481$	0.9786
C2-AK	$y = 0.0002 x^2 - 0.169 x + 64.541$	0.9723

Changes in the chemical structure of acrylic coatings under the influence of battery acid (Points 3.2 and 3.4) contributed to their Buchholz hardness decrease. It was also found that the rate of hardness loss of acrylic coatings, aged climatically for 2 years, was higher than of unaged coatings, which resulted in the decrease of the aged coatings' resistance to scratching and erosion [23–25].

3.6. Assessment of Surface Roughness Parameters of Acrylic Coatings

Results from investigations of battery acid's influence on acrylic coatings indicated that coatings previously aged climatically for 2 years show higher values of surface roughness parameters than non-aged coatings. This is associated with the higher susceptibility of the climatically aged coatings to have fragments chipping from superficial layers. This is caused by the higher oxidation degree of acrylic resin in the case of climatically aged coatings, since the spectroscopic IR investigations proved the increased content of carbonyl groups in the coatings aged climatically compared with the non-aged coatings (Point 3.1). Ageing with battery acid also increased the oxidation degree of the acrylic coatings, which was documented by DSC examination (Point 3.4).

The characteristics of surface roughness parameters R_a and R_z of acrylic coatings subjected to battery acid action are shown in Figures 6 and 7, while mathematical models of characteristics of R_a and R_z roughness parameters are presented in Tables 9 and 10.

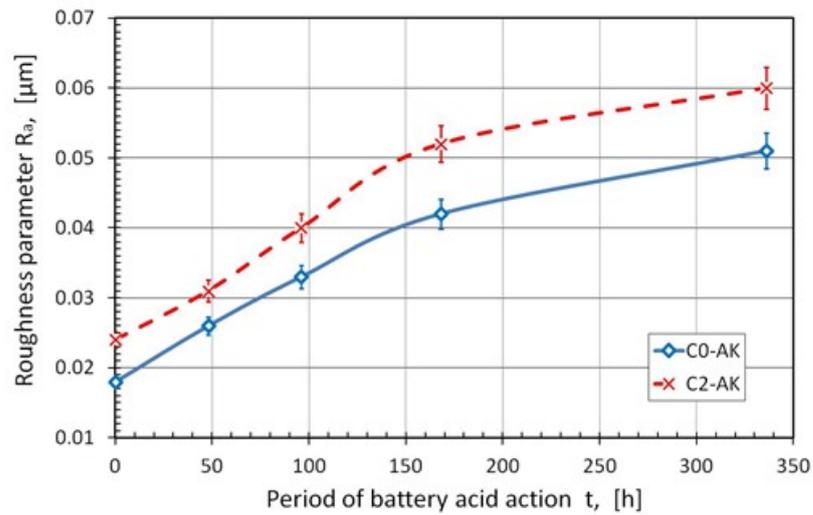


Figure 6. Influence of battery acid action for 336 h on the Ra surface roughness parameter of acrylic coatings.

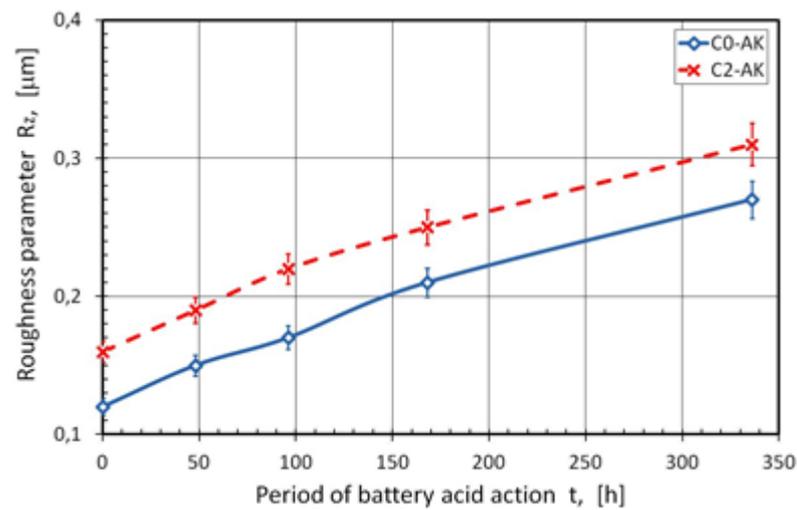


Figure 7. Influence of battery acid action for 336 h on the Rz surface roughness parameter of acrylic coatings.

Table 9. Trend line equations and the values of the determination coefficient R^2 of the Ra surface roughness parameter of acrylic coatings.

Symbol of the Coating	Mathematical Model of Ra Roughness Characteristics	Determination Coefficient R^2
C0-AK	$y = -3 \times 10^{-7} x^2 + 0.0002 x + 0.0178$	0.9997
C2-AK	$y = -3 \times 10^{-7} x^2 + 0.0002 x + 0.0228$	0.9922

Table 10. Trend line equations and the values of the determination coefficient R^2 of the Rz surface roughness parameter of acrylic coatings.

Symbol of the Coating	Mathematical Model of Rz Roughness Characteristics	Determination Coefficient R^2
C0-AK	$y = -5 \times 10^{-7} x^2 + 0.0006 x + 0.1202$	0.9985
C2-AK	$y = -6 \times 10^{-7} x^2 + 0.0006 x + 0.1607$	0.9990

3.7. Assessment of the Gloss of Acrylic Coatings

The results of gloss measurements showed that the influence of battery acid on acrylic coatings caused a substantial decrease in their gloss. The reason lies in the surface roughness increase of the coatings with increase of the period of battery acid action. It should be stressed that acrylic coatings previously aged climatically for 2 years showed a bigger loss of the gloss than non-aged ones. The coatings aged climatically showed significant destruction of their surface in the form of microcrackings, craters, and etchings (silver cracks), which influenced the surface topography, resulting in a gloss decrease. The coatings that were not aged climatically also showed a change in their surface topography (Points 3.1 and 3.6), resulting in a gloss decrease as well.

Battery acid's influence on the gloss of acrylic coatings at different angles (α) of light incidence are presented in Figures 8–10 (Figure 8 at $\alpha = 20^\circ$, Figure 9 at $\alpha = 60^\circ$, and Figure 10 at $\alpha = 85^\circ$), while mathematical models of gloss characteristics are given in Tables 11–13.

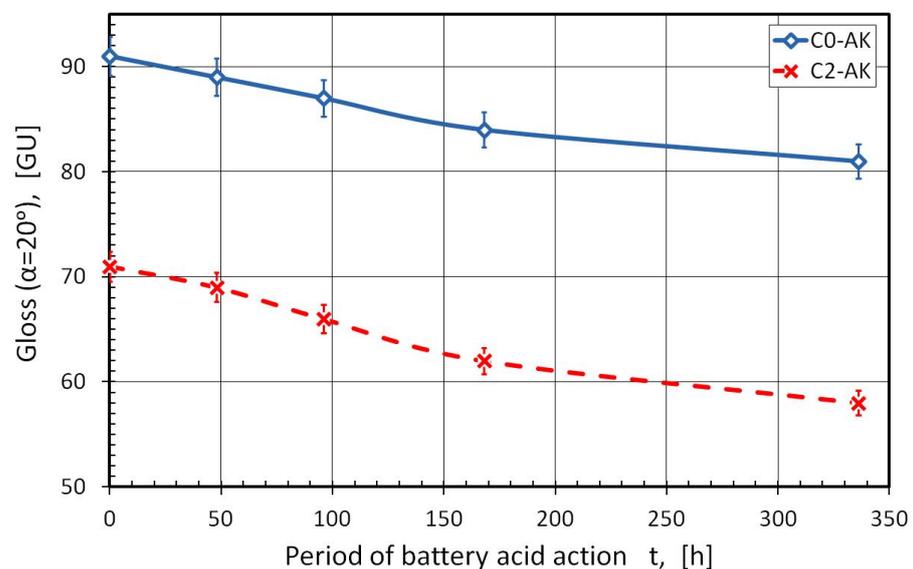


Figure 8. Influence of ageing with battery acid on the gloss of acrylic topcoats at $\alpha = 20^\circ$.

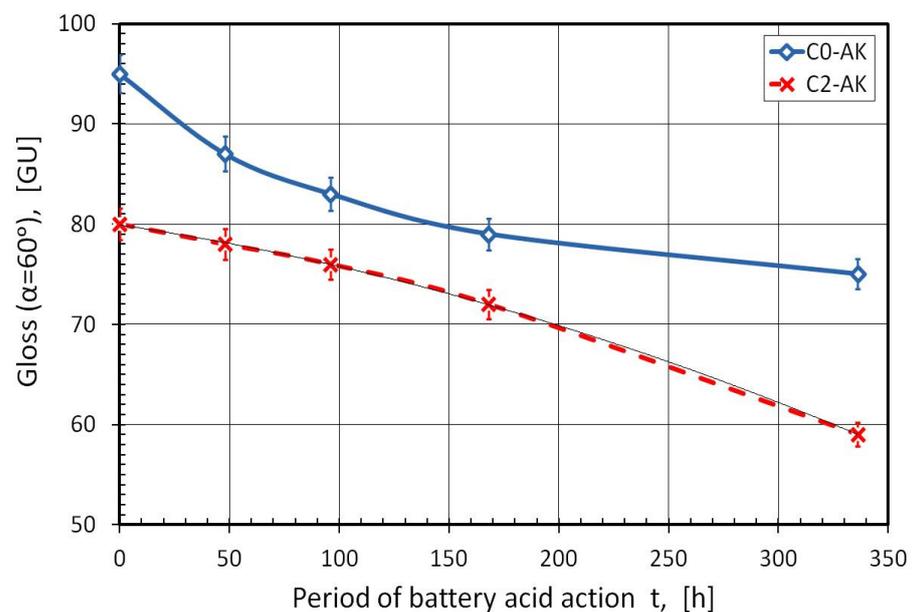


Figure 9. Influence of ageing with battery acid on the gloss of acrylic topcoats at $\alpha = 60^\circ$.

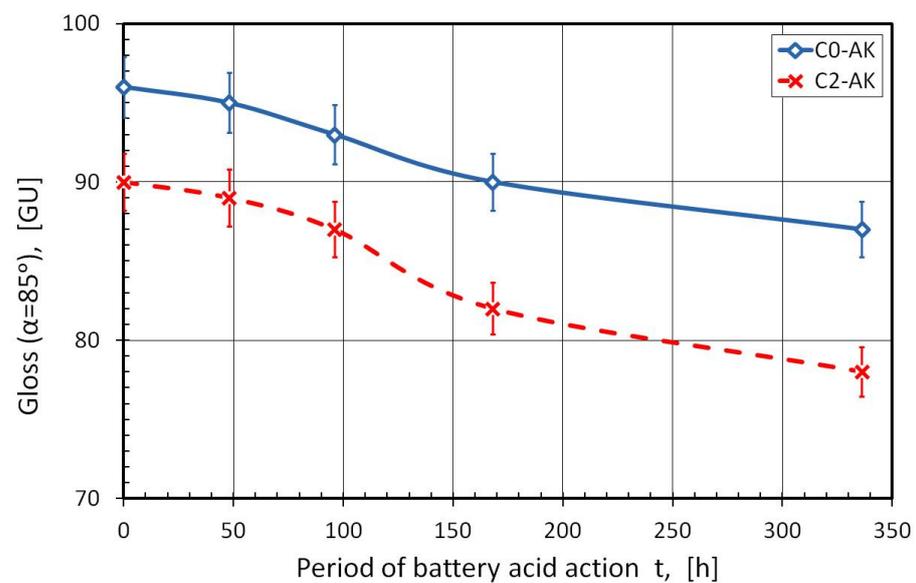


Figure 10. Influence of ageing with battery acid on the gloss of acrylic topcoats at $\alpha = 85^\circ$.

Table 11. Trend line equations and the values of the determination coefficient R^2 of acrylic topcoat gloss at $\alpha = 20^\circ$.

Symbol of the Coating	Mathematical Model of Gloss Characteristics at $\alpha = 20^\circ$	Determination Coefficient R^2
C0-AK	$y = 6 \times 10^{-5} x^2 - 0.0519 x + 91.171$	0.9972
C2-AK	$y = 8 \times 10^{-5} x^2 - 0.0664 x + 71.426$	0.9928

Table 12. Trend line equations and the values of the determination coefficient R^2 of acrylic topcoat gloss at $\alpha = 60^\circ$.

Symbol of the Coating	Mathematical Model of Gloss Characteristics at $\alpha = 60^\circ$	Determination Coefficient R^2
C0-AK	$y = -10^{-6} \cdot x^3 + 0.0008 x^2 - 0.1905 x + 94.886$	0.9987
C2-AK	$y = -9 \times 10^{-5} x^2 - 0.0326 x + 79.918$	0.9999

Table 13. Trend line equations and the values of the determination coefficient R^2 of acrylic topcoat gloss at $\alpha = 85^\circ$.

Symbol of the Coating	Mathematical Model of Gloss Characteristics at $\alpha = 85^\circ$	Determination Coefficient R^2
C0-AK	$y = 4 \times 10^{-5} x^2 - 0.0423 x + 96.406$	0.9862
C2-AK	$y = 4 \times 10^{-5} x^2 - 0.0523 x + 90.712$	0.9699

3.8. Assessment of the Colour of Acrylic Coatings

The degree of colour change of acrylic coatings was assessed according to criterion ΔE with the help of a Konica Minolta CM-700d apparatus, which is commonly used for this purpose in scientific research. ΔE is a standard measurement, created by the International Commission on Illumination (ICI), that quantifies the difference between two colours. The measurements showed substantial colour changes (visible even with unaided eye) as the colour parameter ΔE reached a value over 5 (Table 14).

Table 14. Parameters ΔE of the acrylic coatings aged with battery acid.

Symbol of the Coating	Period of Battery Acid Action (h)	ΔE
C0-AK	336	5.29
C2-AK	336	5.74

The reason for the colour change was the fading of the pigment (iron red) under the influence of battery acid. Previous two-year climatic ageing caused colour fading, primarily as a result of the sun's ultraviolet radiation.

4. Conclusions

The results of the examinations presented in this paper enable the following statements about the influence of two-year climatic ageing and battery acid action for a period of 336 h on acrylic coatings' properties:

1. Climatic ageing of acrylic coatings for a period of 2 years caused their oxidation, which was documented by spectroscopic IR investigations. SEM examination of the surface condition of the acrylic coatings showed that, as the ageing period increases, the destruction degree of the surface increases too (Table 1a–d). As observed, climatic ageing leads to the chipping of filler and pigment particles from the surface of the coatings and to microcracks, craters, and the appearance of etchings on the surface. The microcracks, which had a shape of parallel bands, probably formed areas of silver cracks, which arose because of the destructive influence of UV.
2. Battery acid action for 336 h caused an increase in oxidation intensity in the acrylic material, which was documented by the results of the DSC examinations. The development of oxidation processes in the acrylic material contributed to the decrease of its Buchholz hardness. The rate of hardness loss of acrylic coatings (previously climatically aged for 2 years) in the course of ageing with battery acid was higher than that of climatically unaged ones.
3. A slight increase in thickness of both kinds of coatings (non-aged and aged climatically) was also observed. The reasons for this phenomenon could be seen in the coating swelling as a result of soaking with battery acid. The tendency of acrylic coatings to absorb battery acid increases with ageing time progression. This was also confirmed by the contact angle θ_C decrease in the case of water drops by a dozen percentage points for the coatings aged climatically. Therefore, the susceptibility to blistering of the coating aged with battery acid increased.
4. Ageing of the coatings also contributed to a degradation increase of their chemical structure. This was indicated by an increase in the free surface energy (SFE) of the coatings. Acrylic coatings after ageing with battery acid demonstrated a polar component higher by 40%, which proved greater chemical degradation of these coatings, compared to non-aged coatings. Conversely, in the case of the coatings previously aged climatically, an increase of the polar component was higher and equal to 58%.
5. The contact angle decreased by over 16% in the case of water. Therefore, the susceptibility to water absorption of coatings aged with battery acid increased, which caused blistering.
6. The influence of ageing factors on the coatings contributed to their surface roughness increase. The coatings previously climatically aged for 2 years presented higher values of surface roughness parameters than the non-aged coatings. This was associated with a higher susceptibility of the climatically aged coatings to chipping. It was caused by a higher oxidation degree of acrylic resin due to climatic ageing. Spectroscopic IR investigations proved an increased content of carbonyl groups in the climatically aged coatings compared with the non-aged coatings.

7. There was a substantial decrease of the gloss of coatings, which was caused by the increase in the surface roughness due to coating material chipping. The roughness increased with the lengthening of the period of battery acid action. It should be stressed that acrylic coatings previously aged climatically for 2 years showed greater gloss loss than the non-aged coatings.
8. Substantial changes of coating colour were assessed according to the accepted criterion ΔE . The colour parameter ΔE of each examined coating reached a value over five. Colour changes were also visible with an unaided eye.
9. As general results from the above conclusions, battery acid action caused destruction (blistering, surface roughness increase, gloss loss, and colour change) of the examined coatings. The destruction increased in the case of the coatings previously aged climatically.

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