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Influence of Laboratory Ageing on the Preservation of Anti-graffiti Properties for Paint Systems Used in Rolling Stock

Marcin GARBACZ[1]

Summary
The article describes and presents the influence of selected ageing mechanisms of paint systems currently used in railways in Poland in the context of maintaining their original protective properties against graffiti. Six paint systems with different types of finish, which had anti-graffiti properties, were tested, and the characteristics of the surface of the paint system, such as gloss and colour, were determined after a series of painting and cleaning of graffiti (markers and sprays). The tested objects were subjected to artificial simulated ageing using laboratory solar radiation in a synergistic combination of temperature and humidity in accordance with PN-EN ISO 16474-2 and in accordance with the proprietary methodology described in DN 001/08/A2/16 section 4.1.8 using the UV-C radiation source (discrete spectrum). The tested samples were also subjected to a different type of ageing mechanism under strong corrosive conditions in the form of neutral salt spray according to the methodology described in PN-EN ISO 9227.

Keywords: ageing tests, xenon-arc radiation, UV-C radiation, neutral salt spray, paint systems, xenotest, gloss, colour, anti-graffiti protection, rolling stock

1. Introduction

Railway graffiti vandalism is a significant aesthetic and technical problem for owners and services responsible for the maintenance and upkeep of rolling stock vehicles. Although graffiti is now not as common a problem as it was at the turn of the current century, it nevertheless appears quite often on elements of rolling stock infrastructure, causing primarily material damage and large financial losses from cleaning and, in the worst cases, repainting trains. As people painting graffiti are mainly concerned with popularity or manifesting their views, in order to effectively counteract unwanted graffiti, the work must be quickly painted over in order to discourage vandals from carrying out similar practices in the future. It is often the case that the authors of such graffiti paintings sign their works with a pseudonym and upload the effects of their "creative" work to the Internet in the form of photos and videos [1].

The places where the artistic vision of graffiti painters is most often and most readily depicted include the most visible parts of the train, mainly the entrance areas (carriage body). The painting of undercarriages or roofs is occasional, due to the danger to the graffiti artist of, for example, electrocution, and above all because their work will be barely visible for others, which is the main objective of those carrying out this type of vandalism. For this reason, it is advocated that it is mandatory for carriage bodies to have permanent anti-graffiti protection, at least in the parts of the train most accessible to people painting graffiti. Unfortunately, it is most common for a vandal to paint over elements such as the train windows, the rubber seals around the windows and doors, or aluminium components, in addition to painting over the coating. Removing graffiti from such areas is also possible, but much more difficult and expensive. In addition, marks are left on such elements after cleaning [2].

The current types of paint systems used on new rolling stock have suitable and necessary anti-graffiti protection, most often in the form of a top layer of transparent paint, which additionally protects the coatings from harmful UV radiation, cleaning agents and other external factors. Old rolling stock, on the other hand, often cannot be cleaned, because when it is cleaned, the graffiti comes off together with the factory paint, and in such case, the only solution is to

[1] M.Sc. Eng.; Railway Research Institute, Materials & Structure Laboratory; e-mail: mgarbacz@ikolej.pl.

repaint the train. It can also happen that a single carriage may be repainted several times, so it is recommended to use long-lasting anti-graffiti systems and, in the worst-case scenario, to re-apply the top layer of worn paint. The anti-graffiti topcoat should also be of an appropriate thickness and be resistant to mechanical abrasion, as trains are increasingly being cleaned in automatic stations similar to those in car washes. Brushes used in car washes, depending on the hardness of the bristles, can cause scratches and wear on the abraded coating [2].

Materials & Structure Laboratory of the Railway Research Institute has been conducting research on the effectiveness of coatings used on Polish railways for many years. Tests are carried out on appropriately prepared test panels with paint systems (with the same coating performance parameters as those used on carriage bodies) according to ASTM D6578/D6578M-13 (2018) [3] and the detailed in-house procedure PB-LK-C15 [4], which specifies the method of evaluation. Field tests can also be carried out, but due to their low practicality, such tests are most often performed in the laboratory on a set of properly prepared samples. The aforementioned standard describes standard procedures when assessing the effectiveness of a coating resistance to graffiti, proposes markings as well as cleaning agents with increasing cleaning effectiveness. In order to make the test method proposed by the ASTM standard more realistic in the context of the problem of graffiti in railways, the Materials & Structure Laboratory modified and adopted a scale for assessing the effectiveness of protection against graffiti painting, as well as introduced only the means commonly used by people painting graffiti, i.e. permanent markers and sprays, into the tests. The laboratory uses specialist graffiti removers based on organic solvents, which are available on the market as liquids, gels or wipes soaked in the appropriate substance and which are recommended by the manufacturers of the paint systems concerned.

2. Test methodology, instruments and test material used

The test procedure consisted of painting over selected, commonly used on rolling stock, paint systems with anti-graffiti properties using a random selection of markings – 3 markers and 3 sprays. Paintings were carried out on surfaces divided by a suitable stencil on samples of the paint systems being assessed. The samples were 75 × 300 mm (the dimensions of each painting 75 × 30 mm), and the assessment was made by comparing the samples with an additional unpainted sample. Graffiti was left on the surface of the coating at room temperature (23°C ±2°C) for 24 h and then the graffiti was removed using the specified removers (AGS-221 gel and AGS-5). Subsequently, the resulting changes in the coating were assessed sequentially using corrected visual tests (after each painting and cleaning cycle) and instruments, e.g. spectrophotometer and glossmeter, to determine the exact change in colour or change in gloss value (evaluation using instruments after the 5th and 10th painting and cleaning cycles). The painting and cleaning process involved 10 complete cycles. The result of the tests in the visual evaluation showed the specific performance of the anti-graffiti coating in terms of the number of cycles in relation to the point at which, after the removal of the respective graffiti painting, a change appears on the surface of the coating for the first time (evaluation in relation to loss of gloss and colour change or even blistering).

The paint systems to be tested were prepared by the Principals cooperating with the Railway Research Institute. A detailed summary of the composition of the paint systems tested is shown in Table 1. The substrate was a variety of structural steels. The results are the average obtained for the three samples. The methodology, as well as the instruments used, is shown in Table 2.

The paint systems tested, including the graffiti topcoat, are tested in the Railway Research Institute laboratory on a day-to-day basis without taking into account the effects of harmful weather conditions, so the actual effectiveness of the coating protection under natural conditions may be much worse, especially with the passage of time. The effectiveness of the protection will be reduced when exposed to external ageing factors such as UV light, environmental conditions such as variable weather conditions, air pollution or specialist cleaning chemicals. Literature show that the ageing of samples significantly affects the results, which should also be taken into account when designing laboratory tests to check the quality of graffiti protection for a given topcoat/paint system [5, 6].

In this paper, comparative tests of aged and unaged samples were carried out to determine whether the effectiveness of the protection decreases dramatically due to progressive degradation under selected destructive factors.

The best correlation of laboratory test results for organic paint coatings with those obtained under natural conditions is achieved through different degradation mechanisms. When considering only the issues of the effects of radiation, temperature and humidity (including rain) to simulate these conditions in the laboratory, a number of test methods, including standardised ones, have been developed worldwide. One such method, the most widely used worldwide for testing paint products and which was used in the

Table 1

Summary of tested paint systems

System No.	Type of substrate (steel)	Full system composition	Type of surface protection
I	S235	• epoxy primer • polyester putty • acrylic filler primer • acrylic-polyurethane topcoat	acrylic-polyurethane topcoat paint
II	S235	• epoxy primer • polyester putty • acrylic filler primer • acrylic-polyurethane topcoat	acrylic-polyurethane topcoat paint
III	DC01	• epoxy primer • polyester putty • polyurethane filler primer • acrylic basecoat • polyurethane clearcoat	acrylic base paint + polyurethane clearcoat
IV	DC01	• epoxy primer • polyurethane topcoat	polyurethane topcoat paint
V	S235	• epoxy primer • polyester putty • acrylic filler primer • polyurethane basecoat • acrylic clearcoat 1 • acrylic clearcoat 2	polyurethane basecoat + acrylic clearcoat + acrylic clearcoat with improved properties
VI	S235	• epoxy primer • acrylic-polyurethane topcoat	acrylic-polyurethane topcoat paint

[own study].

ageing tests carried out, is PN-EN ISO 16474-2 [7]. This standard provides the most important information on how to carry out such tests in laboratories and how to control individual degradation factors during the test [8]. The total irradiance of the samples tested was 324 MJ/m^2, which theoretically corresponds to about 1.5 years under natural conditions in a temperate climate [9].

In addition, this paper presents analogous test results for simulated varying weather conditions in combination with UV radiation according to the procedure developed at Railway Research Institute and described in DN 001/08/A2/16 section 4.1.8 [10], which uses cyclic temperature tests (extreme above and sub-zero temperatures) and cyclic irradiation with a mercury-quartz lamp with filament (heating function) and a 400 W ultraviolet lamp (Q 400 Original Hanau) with a reflector made of painted aluminium sheet. The lamp used has no UV filter and emits a discrete spectrum (range from 238 nm), where the highest peak intensities are reached at 254 nm, 265 nm, 297 nm, 302 nm, 313 nm, 366 nm, 405/408 nm, 436 nm, 546 nm, 577/579 nm [11]. Details of the tests performed are presented in Table 2. The total ageing time using this method was 1,500 hours.

A different type of ageing is obtained in salt spray chambers, where the destructive agent is the electrolyte (sodium chloride), however, it was decided to also carry out such tests to determine the effect of neutral salt spray on the contribution to the worsening of the graffiti protection function. Tests were carried out according to PN-EN ISO 9227 [12] using neutral salt spray (this standard is the most widely used for continuous corrosion testing). The total ageing time using this method was 1,500 hours.

Two commonly used cleaning products, positively evaluated by railway operators and rolling stock manufacturers, were used for the tests. They were part of the AGS (Anti-Graffiti System) of the Swedish manufacturer Trion Tensid AB, used mainly by German, British and Swedish railways, but also increasingly by Polish ones:

- AGS 221 (gel) – designed to remove all types of spray paint and waterproof markers from the exterior walls of carriages. Allows 100% removal of graffiti, without damage to paint coating, seals,

Table 2

Test methodology and apparatus used

No.	Type of test	Reference document (method)	Instruments	Notes
				Ageing methods
1	**UV resistance (standardised method)**	ISO 16474-2 [7]	Weathering instrument, Atlas GmbH Xenotest 440, XENOSENSIV RC 34 BST	Methodology: EN ISO 16474-2, section 7.3, table 3, method A; filters simulating daylight with BST surface temperature control (65°C) and radiation control in the wavelength range (300 ÷ 400) nm; irradiance: 60W/m^2; temperature 38°C, relative humidity 50%, test periods: 102 min dry, 18 min rain; Total irradiation dose: 324 MJ/m^2 (approx. 1,500 h).
2	**UV resistance (own method)**	DN 001/08/A2/16 [10]	SECASI SI550C150F40H climatic chamber Famed-1 lamp, type L8/59 (UV-C)	Cyclic exposure to varying weather conditions: 1) T: + 60°C, RH: 95%, time 12 h; 2) T: - 20°C, time 6 h; 3) T: + 60°C, RH: 65%, time 6 h; 4) UV irradiation for 4 h every 48h (Famed-1 lamp, type L8/59). Test time: 1,500 h
3	**Resistance to neutral salt spray**	PN-EN ISO 9227 [12]	Ascott Premium CC1000IP salt spray chamber	T: (35 ± 2)°C; pH (collected solution): 6,5 ÷ 7,2; Concentration of sodium chloride (collected solution): (50 ± 5) g/l; Average spray collection rate for a horizontal collection area of 80 cm^2: (1.5 ± 0.5) ml/h; Test time: 1,500 h
				Methods of evaluation after ageing
4	**Evaluation of coating defects after ageing tests (visual evaluation)**	PN-EN ISO 4628-1 [13] PN-EN ISO 4628-2 [14] PN-EN ISO 4628-3 [15] PN-EN ISO 4628-4 [16] PN-EN ISO 4628-5 [17] PN-EN ISO 4628-6 [18]	not applicable	Evaluation with unaided eye. Rusting, cracking and flaking were not present.
5	**Evaluation of the effectiveness of graffiti protection (visual evaluation and evaluation using instruments)**	DN 001/08/A2/16 [10] ASTM D6578 / D6578M – 13(2018 [3]	Evaluation using instruments, points 6 and 7, Table 2	Cleaning agent used: AGS-221 gel and AGS-5; Markings: black marker (Molotow Marker 627HS 15mm Signal Black); pink marker (Molotow 620PP 15mm Fuchsia Pink); blue marker (Molotow Marker 627HS 15mm Shock Blue Middle); orange spray (Molotow – Premium Plus #602 lobster); green spray (Molotow – Premium Plus #609 juice green); silver spray (Molotow – Premium Plus #612 chrome). Modified evaluation scale according to standard: 0 – no change; 1 – not cleanable, shadow and gloss loss; 2 – not cleanable, heavy shadow; 3 – not cleanable, slight shadow; 4 – not cleanable, loss of gloss.
6	**Determination of gloss**	PN-EN ISO 2813 [19]	Rhopoint IQ-S glossmeter	The device simultaneously measures in three gloss geometries 20°, 60°, 85°. The results for the universal 60° geometry were analysed.
7	**Determination of colour coordinates**	PN-ISO 7724-1 [20] PN-ISO 7724-2 [21] PN-ISO 7724-3 [22]	Konica Minolta CM2600D, CCSII spectrophotometric standards Lucideon Ltd	D/8° sphere spectrophotometer with diffuse illumination; measurements were made with and without gloss trap (SCI/SCE), using D65 illuminant, 10˚ observer (measurement range (360 ÷ 740) nm, sampling every 10nm); colour coordinate results were determined using the CIELAB 1976 system for the parameters L* (brightness), a* (red-green), b* (yellow-blue) while colour differences were determined using the parameter ΔE*ab.

[own study].

glass or signs. Effective when used on the original polyurethane paint coating of the carriage. It does not require the surface to be treated with an anti-graffiti coating. The method of use is to apply the gel using a brush or atomiser (for the liquid version). After about 5–15 minutes, when the graffiti has softened, the surfaces should be wiped with a soft brush to loosen the paint. Dissolved paint is removed with a sweeper or warm water under moderate pressure (washer). Finally, the surfaces are cleaned with water and detergent and wiped dry. Composition: γ-butyrolactate 5–9%, ester (C9-C11) 5–10%, tensides, thickeners.

- AGS 5 (liquid) – designed to remove graffiti made with waterproof markers and spray paint, from external, smooth carriage surfaces such as laminates, glass, plastics. It is particularly suitable for removing waterproof markers. For spray paint, it is best to use the gel variety. It is also used on the outside of the carriages to remove residues of not loosened graffiti, after the first use of AGS 221. It also helps to remove glue and unwanted stickers. The method of use is similar to that described for the AGS-221. Composition: N-methylpyrrolidone 10–30%, glycol ether, tensides.

Graffiti removers can also be cloths soaked in a given preparation, where this form can be successfully used to remove small paintings on train carriages or in the laboratory (a very convenient form of application).

The market for available graffiti painting products for graffiti artists is huge, and it is not possible to test all types of markings used. The most commonly used are permanent markers and sprays. On the basis of the laboratory's experience, there can be large differences in the results obtained depending on the anti-graffiti coating, so to assess the effectiveness of the systems in question, tests should be carried out for the established markings that are the most common and available, as well as the most varied. It has been observed that for most coatings, an alcohol-based red marker usually leaves permanent marks that cannot be removed. Sprays with metallic additives are also difficult to remove. Markings in the form of markers and sprays from Molotow, a well-known and respected company for graffiti artists, were used in the study. The details are summarised in Table 2.

Pictures of the sample ageing test stands where the tests were carried out and an example of the graffiti painting are shown in Figures 1–4.

Fig. 1. Test stand for ageing samples according to ISO 16474-2 [7] (xenon weathering instrument, Atlas GmbH Xenotest 440) [Pic. M. Garbacz]

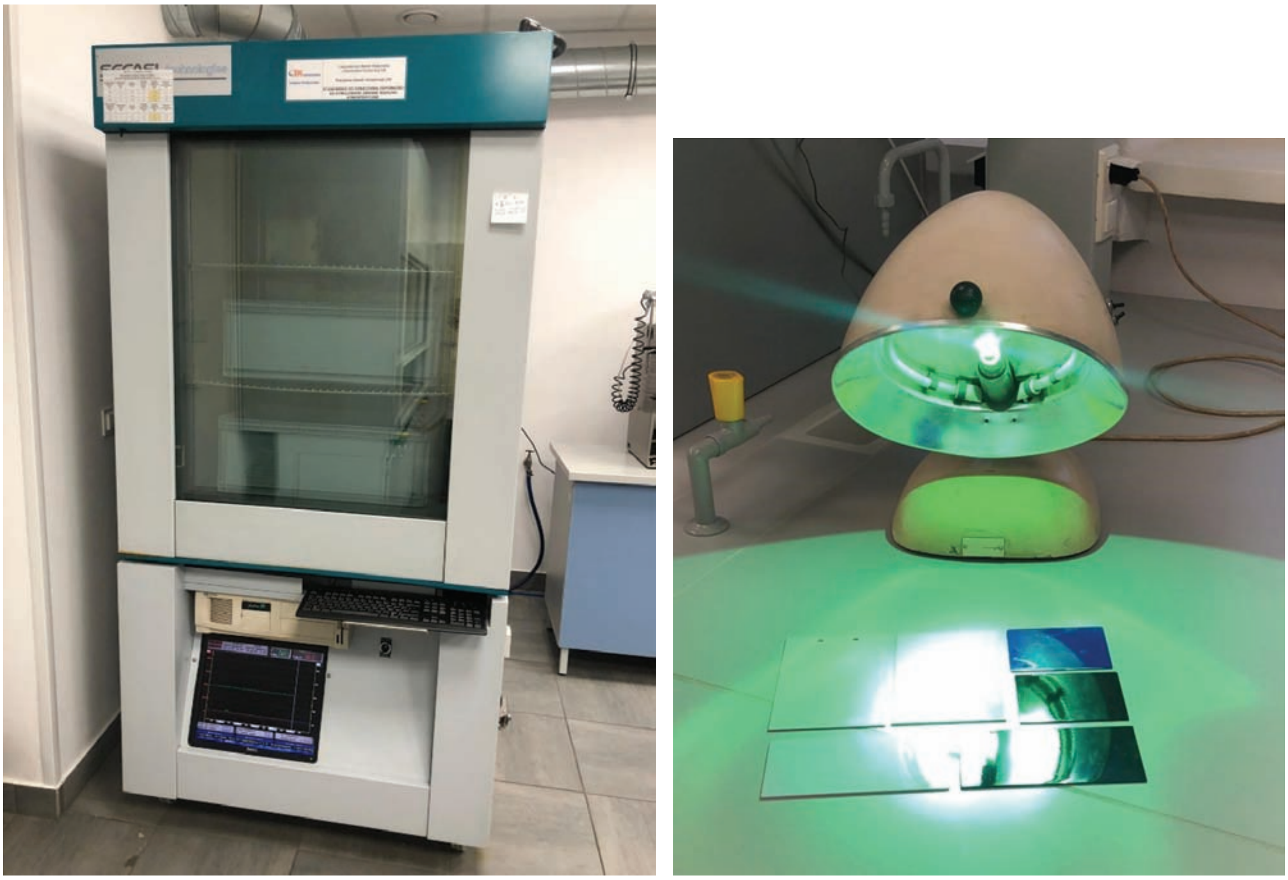

Fig. 2. Test stand for ageing samples according to DN 001/08/A2/16 [10] (SECASI SI550C150F40H climatic chamber and Famed-1 type L8/59 lamp) [Pic. M. Garbacz]

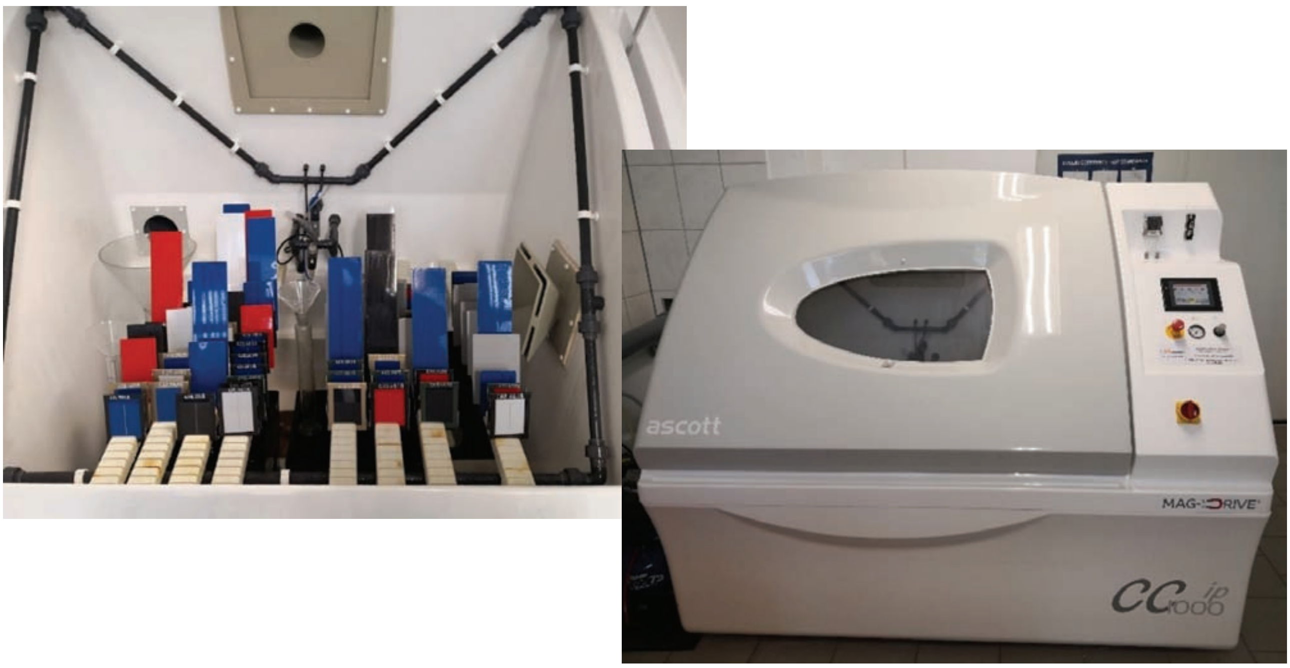

Fig. 3. Test stand for ageing samples according to PN-EN ISO 9227 [12] (Ascott CC1000IP salt spray chamber) [Pic. M. Garbacz]

Fig. 4. Test stand for determining graffiti resistance [Pic. M. Garbacz]

3. Test results and their interpretation

An evaluation of the results of the conducted tests is presented in sections 3.1÷3.3. Section 3.1 describes the resulting defects on the paint systems immediately after the ageing tests, which can also affect the final evaluation of the subsequent effectiveness of the graffiti protection. Section 3.2 describes the results for the visual evaluation of graffiti painting resistance as a function of the number of paints and cleaning, while Section 3.3 presents the evaluation using instruments performed with a glossmeter and spectrophotometer.

3.1. Evaluation of resulting defects on paint systems for selected ageing methods

Table 3 shows a summary of the test results of the resulting defects in the paint systems evaluated according to the PN-EN ISO 4628 series of standards after the ageing tests. The table only summarises the defects revealed in the form of blistering (PN-EN ISO 4628-2 [14]) and chalking (PN-EN ISO 4628-6 [18]), as rusting, cracking and flaking was not present and

Table 3

Summary of measurement results of all tested paint systems for the evaluation of coating deterioration according to the series of standards EN ISO 4628: Part 2 – blistering [14], Part 6 – chalking [18] for ongoing ageing tests

Type of ageing	PN-EN ISO 16474-2 [7]		DN 001/08/A2/16 [10]		PN-EN ISO 9227 [12]
System No.	Blistering[1] PN-EN ISO 4628-2 [14]	Chalking[2] PN-EN ISO 4628-6 [18]	Blistering[1] PN-EN ISO 4628-2 [14]	Chalking[2] PN-EN ISO 4628-6 [18]	Blistering[1] PN-EN ISO 4628-2 [14]
I	0(S0)	2	0(S0)	0 Faded coating, yellow stains/no chalking	0(S0)
II	0(S0)	2	0(S0)	0 Faded coating, yellow stains/no chalking	5(S2)
III	0(S0)	0	0(S0)	0 Visible local yellowing / no chalking	0(S0)
IV	0(S0)	0	0(S0)	0 Faded coating, yellow stains/no chalking	0(S0)
V	0(S0)	0	3(S2)	0	5(S3)
VI	0(S0)	0 Visible colour change and slight dulling / no chalking	0(S0)	0 Complete dulling of samples / no chalking	5(S2)

[1] 0(S0) – indicates no changes to the coating according to the terminology used in the standards; for example, a defect rating of 5(S3) would mean: density 5 (dense damage pattern), size 3 (up to 0.5 mm);
[2] degree determined according to the reference contained in the standard (6-grade scale, the higher the degree of chalking).

was omitted. The results obtained represent the average result for the 3 tested samples of each system. The specified expanded uncertainty of the resulting defect evaluation for all the ageing tests carried out at a confidence level of 95% and k = 2.0 is ± 1 scale of evaluation for the size and quantity of the resulting defect evaluated according to the PN-EN ISO 4628 series of standards [23, 24, 25].

For systems aged according to PN-EN ISO 16474-2 [7] for 1,500 h, none showed coating changes in the form of blistering, rusting, cracking or peeling. Systems I and II were chalking (they had the same topcoat) and already showed the first signs of chalking after 500 h of exposure. In the case of System VI, no chalking was observed (no chalking marks on the tape), but a very strong colour change (more intense shade) and a slight decrease in gloss was visible.

Chalking is a loose, brittle layer on the surface of a coating. Chalking is particularly common with paints that contain large amounts of titanium dioxide and fillers. Chalking is most common in epoxy coatings, but can be observed in almost all coatings left for a sufficiently long time to the conditions that cause it. High-quality paints may chalk slightly, but still maintain a “healthy” surface that does not crack and retains good moisture and weather resistance for many years.

The results for systems aged in a climatic chamber with cyclic quartz-mercury lamp irradiation according to DN 001/08/A2/16 [10] over a period of 1,500 h are different from those for systems aged according to PN-EN ISO 16474-2 [7]. Above all, System V (acrylic binder finish) showed blistering −3(S2), but no other defects of this system in the form of chalking or colour change of the coating such as yellowing or dulling became visible. It is likely that the blistering was influenced by high humidity and a cycle of alternating extreme above and sub-zero temperatures during ageing in the climatic chamber with a lower contribution of UV radiation to degradation. This resulted in the formation of micro-cracks and the formation of conductive paths to the substrate under the influence of mechanical fatigue (influence of higher internal stresses). In the other systems tested, sample changes in the form of yellowing or bleaching (unevenly across the surface, mainly polyurethanes) were visible. Increased chalking was not observed. System VI completely dulled (after only 500 h of ageing).

In the case of systems aged according to PN-EN ISO 9227 [12] for 1,500 h, intense blistering of the coating with high intensity, but small blister sizes was noted in half of the cases (systems II, V, VI). The other half of the systems surveyed showed no change.

In the presence of UV radiation, especially of high energy, polyurethanes undergo photodegradation with a gradual colour change. The exact mechanism of photodegradation of PU is uncertain. Photo-oxidation is thought to occur most easily in aromatic urethanes through the quinonoids. The urethane bridge oxidises to a quinone-imide structure. This structure is a strong chromophore, causing yellowing of urethanes [15]. The strength of the C=O bond present in the polyurethane structure is 500–700 kJ/mol, and this bond cannot be broken by solar radiation reaching the earth’s surface. The high-pressure quartz-mercury lamp used for irradiation in the ageing method according to DN 001/08/A2/16 [10] also emits radiation in the UV-C range with an emission peak at 254 nm, whose excitation energy is approximately 500 kJ/mol, thus providing the possibility of decomposing this bond [16]. However, the effect of UV radiation on acrylic topcoats is the decomposition of the polymer chains (photolysis) of the coating material and its intense oxidation. It is also possible that additional cross-linking may occur, which contributes to the generation of stresses in the structure of the coatings, resulting in the formation of various types of cracks.

In the case of the degradation of acrylates and methacrylates, when the alkyl side groups are short, in both types of polymers chain breaking predominates over cross-linking and no insoluble fractions are formed. Acrylates are much more reactive towards oxidation than methacrylates. When the aliphatic lateral ester groups are longer, the behaviour changes completely: the polymer undergoes rapid and extensive cross-linking with fragmentation [17]. Another issue is that the photo-oxidative stability of synthetic binders can be affected by the addition of pigments to the system, which may have a protective effect by absorbing and/or shielding UV light or may be photoactive and therefore catalyse or accelerate the photodegradation of the polymer. The mechanism by which pigments can act as photosensitisers is not well understood, and detailed data on the effect of inorganic pigments on the stability of synthetic paints is still unknown. In addition, synthetic paints contain other ingredients that can also contribute significantly to their UV degradation. Therefore, UV ageing tests of synthetic binders (the binders themselves) do not accurately reflect UV ageing of synthetic paints and the exact context of degradation remains unclear in many cases [18].

When the coating is exposed to aqueous sodium chloride solutions, as in the method implemented according to PN-EN ISO 9227 [12], the first stage of the destruction process is the formation of conductive path (capillaries), which allow direct access of chloride ions to the surface of the metal substrate. As a result of the accumulation of corrosive agents and the products of the processes they induce on the surface of the metal substrate, adhesion between the coating and the substrate is lost, resulting in detachment and blistering of the polymer coatings. The direct access of aggressive media to the substrate also allows various types of deep cracks and scratches to form in the coating. The diffusion rate of aggressive media in polymer coatings decreases as the number of layers increases. This is related to the fact that there is a low probability of contact between hydrophilic areas in successive layers of the coating system, which delays the formation of conductive paths. The capillaries in multilayer coatings have a complex shape which lengthens the path and decreases the rate of penetration of the media into the substrate protected by these coatings and delays the development of corrosion processes in the substrate. The impact of operational environmental factors has a significant effect on the energy level of polymer coatings. As a result of the adsorption of aggressive substances on the surface of the coating, its surface energy and associated mechanical strength decreases. In contrast, the absorption of aggressive media by polymer coatings contributes to their chemical degradation or swelling. Swelling of coatings can result in the development of micro-cracks, leading to cracking. The development of polymer cracking processes is significantly influenced by the simultaneous effects of the active environment and mechanical loads [30, 31].

3.2. Visual evaluation of graffiti resistance for unaged and aged paint systems using selected methods

The visual evaluation for the aged samples was carried out in comparison to the aged surface before the paint and cleaning cycles. In the case of samples where chalking occurred (system I and II – same type of surface protection), the photo-oxidation products were not removed before testing. The specified expanded uncertainty of the graffiti resistance test at a confidence level of 95% and k = 2.0 is ±1 painting cycle for changes occurring after removal of the graffiti in question [4] (uncertainty does not include uncertainty of the effect of ageing).

Based on the achieved test results shown in Table 4, as well as the observations made during the tests, it was concluded that:

- For the tested system, a high efficiency of anti-graffiti coating of the unaged samples was achieved. In most cases, the evaluation using corrected visual tests for unaged samples showed no changes on the coating in terms of gloss and colour for 10 paint and cleaning cycles for the markers and sprays used, manufactured by Molotow (Table 2). Significantly better results were achieved using AGS-221 (gel) than for AGS-5. In one case for System VI, it was observed that there was complete dulling of the coating for both graffiti removers used, also in the area outside the graffiti paintings, indicating that the removers reacted with the external paint coating and are unsuitable for this system.
- The ageing of the paint systems in the salt spray chamber according to PN-EN ISO 9227 [12] did not affect the effectiveness of the graffiti protection in any way and is comparable to the results obtained for unaged samples, indicating that the sodium chloride (corrosive agent) does not have a significant effect on the graffiti protection

Table 4

Summary of visual evaluation of the graffiti resistance test for unaged and aged paint systems by selected methods for the cleaning agents AGS 221-gel and AGS-5

Cleaning agent	AGS-221 gel				AGS-5	
Type of ageing	Non-aged samples	PN-EN ISO 16474-2 [7]	DN 001/08/ A2/16 [10]	PN-EN ISO 9227 [12]	Non-aged samples	DN 001/08/ A2/16 [10]
System No.	Number of cycles unchanged (coating appearance after graffiti removal according to scale) [1,2]					
I	10 (0)	5 (3)	10 (0)	10 (0)	7 (4)	6 (3)
II	10 (0)	4 (3)	10 (0)	10 (0)	8 (4)	4 (3)
III	10 (0)	10 (0)	10 (0)	9 (3)	10 (0)	7 (4)
IV	10 (0)	10 (0)	3 (1)	10 (0)	6 (4)	3 (1)
V	8 (4)	10 (0)	4 (4)	10 (0)	6 (4)	4 (4)
VI	0 (4)	5 (4)	0 (2)	0 (4)	1 (2)	2 (4)
Mean	8 (–)	7 (–)	6 (–)	8 (–)	6 (–)	4 (–)

[1] Modified evaluation scale according to ASTM D6578 / D6578M – 13(2018) [3]: 0 – no change; 1 – not cleanable, shadow and gloss loss; 2 – not cleanable, heavy shadow; 3 – not cleanable, slight shadow; 4 – not cleanable, loss of gloss.

[2] Number of cycles without change: average for the 6 different markings used in this study (markings are summarised in Table 2) when evaluating the appearance of the coating after removal of the graffiti paint – the most common change.

properties, even when there are intensive changes in the form of blistering (systems II, V, VI).

- The ageing of the systems with UV radiation with the synergistic combination of temperature and humidity for ageing methods carried out according to PN-EN ISO 16474-2 [7] and the procedure described in DN 001/08/A2/16 [10], in some cases, resulted in a slight decrease in the coating's resistance to graffiti. Interestingly, the changes varied and were dependent on the ageing method used.
- The ageing according to PN-EN ISO 16474-2 [7] with daylight filters applied in the Xenotest instrument was not as severely destructive and did not result in a significant decrease in the coating's resistance to graffiti painting. In the case of Systems I and II, where chalking was observed, the systems partially retained their graffiti protection function. An increase in gloss values was also observed with successive painting and cleaning cycles, most likely due to the removal of photo-oxidation products by graffiti removers (polishing of the coating). For System VI, where there was an intensive change in colour and a slight decrease in gloss while chalking was absent, an increase in the system's resistance to graffiti painting was observed, which is a positive thing (evaluation in relation to the changed surface after the ageing test).
- The greatest decrease in graffiti resistance was observed for samples aged in the climatic chamber according to procedure DN 001/08/A2/16 [10], which involves tests at extreme above and subzero temperatures with additional irradiation using a quartz-mercury lamp (4 hours of irradiation, every 48 hours of testing). The results may have been significantly influenced by the source of radiation in the short-wave UV-C range, which does not occur naturally due to the filtering of this type of radiation by the ozone layer present in the Earth's atmosphere. On the other hand, the systems I and II, which chalked when tested using the ageing method according to PN-EN ISO 16474-2 [7], did not show any changes when this ageing method was used and their graffiti resistance is comparable to that of the unaged samples, while systems IV and V, which again did not show any changes in the graffiti resistance evaluation after ageing according to PN-EN ISO 16474-2 [7], in this case lost their graffiti resistance function. System IV with the polyurethane topcoat most likely contained significant amounts of aromatic urethanes in its composition (indicated by the visible local yellowing of the coating – Table 3), which, due to the high energy of radiation, caused structural changes to the polymer and a decrease in resistance to graffiti painting. In the case of System V, in which two types of acrylic clearcoats and a polyurethane paint base were used externally, it is possible that the base was exposed to UV radiation due to its high aromatic content and the free radicals generated in this way also weakened the outermost acrylic structures (the yellowing was not visible to the unaided eye, as the colour of the coating made it difficult to see the changes, but measurements with a spectrophotometer showed an intense change in the b* parameter of about 5.0, indicating a shift towards a more yellow colour). For this ageing method, it was also observed that AGS-221 (gel) was more effective in removing graffiti than AGS-5, however, during testing, local formation of microcraters were observed on various systems (I, II and VI) for AGS-221 (mainly at the edges of graffiti, where the graffiti painting did not protect against contact between the cleaning agent and the coating), which was more aggressive than for AGS-5, indicating that the ageing of the coatings using this method significantly decreased the effectiveness of coatings against external aggressive attack.
- No increased difficulty in removing the markings was found depending on the type of carrier used, i.e. marker or spray, also depending on the graffiti remover used (AGS-221 and AGS-5).
- The visual evaluation was mostly in line with the evaluation using instruments (results presented in section 3.3).

3.3. Change in gloss and colour after graffiti resistance testing for unaged and aged paint systems using selected methods

Before ageing, the average gloss and colour values of the tested paint systems were determined. The results are summarised in Table 5.

The estimated expanded uncertainties for a confidence level of 95% and k=2 are: for gloss measurements ±4 [GU] for all 3 measurement geometries, while for colour measurements: for achromatic samples: ±0.64 for L*, ±0.19 for a*, ±0.32 for b* and ±0.43 for ΔE*; for chromatic samples: ±0.80 for L*, ±0.80 for a*, ±0.89 for b* and ±0.83 for ΔE* (the uncertainties relate to the measurements using instruments only, and do not include the uncertainty of ageing and the graffiti protection evaluation test). The specified expanded uncertainty for the ageing test method using xenon lamp light and climatic chamber at a confidence level of 95% and k = 2.0 is 8% [23, 24] while for salt spray tests it is 25% [25].

Tables 6 and 7 show, respectively, the changes in gloss values in the universal measuring geometry 60° according to EN ISO 2813 [19] and the changes in colour value for the parameter ΔE* – CIELAB 1976 according to EN ISO 7724-1,2,3 [20, 21, 22] for the tested

Table 5

Gloss values (20°, 60°, 85°) and colour coordinates (CIELAB 1976) determined prior to testing (reference values) for a given paint system prior to the anti-graffiti paint system evaluation tests

System No.	Average specified gloss values (EN ISO 2813) [19]				Average specified colour coordinates CIELAB 1976 (EN ISO 7724-2 [21])						
	Type of coating	20° [3] [GU]	60° [3] [GU]	85° [3] [GU]	Colour	SCI[1]			SCE[2]		
						L*[4]	a*[4]	b*[4]	L*[4]	a*[4]	b*[4]
I	glossy	89	93	98	blue	37.9	–5.3	–28.3	28.6	–7.9	–35.4
II	glossy	87	92	98	blue	38.0	–5.6	–28.0	28.8	–8.4	–35.1
III	glossy	89	94	97	light grey	82.2	–1.1	–2.8	79.6	–1.2	–2.7
IV	glossy	89	92	100	dark grey	30.1	–0.2	–2.0	15.5	–0.4	–3.1
V	glossy	85	91	97	blue	37.0	–3.8	–27.7	27.5	–5.8	–35.0
VI	glossy	74	86	95	red	44.4	49.1	29.3	38.0	57.6	47.7

[1] SCI (Specular Component Included) – takes into account the gloss of the sample;
[2] SCE (Specular Component Excluded) – does not take into account the gloss of the sample;
[3] Refers to the measuring geometry at which the measurement is performed (incident beam axis and optical axis of the receiver perpendicular to the tested surface);
[4] The colour system co-ordinates L*, a*, b* mathematically describe a given colour in the CIELAB 1976 colour space. The scales of the a-axis (green to magenta) and b-axis (blue to yellow) extend between –150 and +100 and –100 and +150 values, while the L* axis describes the brightness of the colour within the 0 to 100 value [own elaboration].

Table 6

Summary of mean changes in gloss values for measurement geometry 60° according to EN ISO 2813 [19] for tested paint systems with anti-graffiti protection

Cleaning agent		AGS-221 gel				AGS-5	
Type of ageing		Non-aged samples	PN-EN ISO 16474-2 [7]	DN 001/08/ A2/16 [10]	PN-EN ISO 9227 [12]	Non-aged samples	DN 001/08/ A2/16 [10]
System No.	Number of cycles	Δ60° [difference before testing]					
I	0[1]	–	–84	–12	–2	–	–2
	5	–4	–46	–12	–7	–8	–28
	10	–6	–40	–23	–6	–14	–25
II	0[1]	–	–81	–3	–4	–	–3
	5	–5	–45	–8	–6	–5	–24
	10	–6	–45	–26	–8	–12	–24
III	0[1]	–	0	–2	0	–	–2
	5	–4	–3	–8	–3	–17	–26
	10	–9	–11	–18	–2	–16	–34
IV	0[1]	–	1	–1	1	–	–5
	5	–4	–2	–16	–1	–24	–19
	10	–5	–5	–18	0	–23	–24
V	0[1]	–	–6	1	0	–	2
	5	–2	–2	–9	–6	–9	–25
	10	–10	–1	–13	–5	–16	–14
VI	0[1]	–	–17	–77	–2	–	–78
	5	–7	–26	–55	–10	–11	–53
	10	–8	–27	–53	–11	–11	–50

[1] Values determined after selected ageing methods prior to the start of the graffiti resistance tests related to the values of unaged samples (relative to the results summarised in Table 5) [own study].

Table 7

Summary of mean colour changes for ΔE* - CIELAB 1976 according to PN-EN ISO 7724-1,2,3 [20, 21, 22] for tested paint systems with anti-graffiti protection

		Cleaning agent: AGS-221 gel								Cleaning agent: AGS-5			
Type of ageing		Non-aged samples		PN-EN ISO 16474-2 [7]		DN 001/08/A2/16 [10]		PN-EN ISO 9227 [12]		Non-aged samples		DN 001/08/A2/16 [10]	
System No.	Number of cycles	$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$, where: ΔL^*, Δa^*, Δb^* the difference of the measured colorimetric indices before and after the test											
		SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE
I	0[1]	–	–	1.9	12.8	4.6	6.8	0.6	0.9	–	–	3.3	6.8
	5	0.5	0.7	1.5	7.9	2.8	4.4	0.8	0.9	0.6	0.7	1.5	5.1
	10	0.5	0.4	1.8	7.4	2.3	4.2	0.2	0.5	0.7	1.7	1.1	4.9
II	0[1]	–	–	1.7	12.5	3.4	4.6	0.4	0.9	–	–	3.6	4.8
	5	0.8	0.6	1.4	8.0	2.6	3.6	0.7	0.7	0.6	0.9	1.3	5.0
	10	0.5	0.4	1.6	7.4	2.1	4.0	0.4	1.0	0.6	1.4	1.2	4.5
III	0[1]	–	–	1.0	1.1	4.5	4.7	0.5	0.6	–	–	6.1	6.4
	5	0.6	0.5	1.1	1.1	3.5	3.4	0.4	0.3	0.4	0.6	4.1	3.8
	10	0.7	0.5	1.0	0.7	3.1	2.8	0.4	0.4	0.9	0.5	3.5	3.3
IV	0[1]	–	–	0.3	0.2	0.6	2.6	0.2	0.5	–	–	0.6	2.6
	5	0.1	0.6	0.1	0.2	0.2	4.5	0.2	0.2	0.6	4.7	0.2	5.0
	10	0.1	1.4	0.1	0.7	0.8	5.2	0.2	0.3	0.2	4.7	0.8	5.2
V	0[1]	–	–	1.3	1.4	5.4	6.2	0.4	0.5	–	–	4.8	5.8
	5	0.4	0.4	1.3	1.5	3.7	5.0	0.4	0.6	0.2	1.7	4.0	6.6
	10	1.0	1.0	1.3	1.5	3.1	4.6	0.3	0.6	1.0	2.3	2.6	4.4
VI	0[1]	–	–	6.7	18.8	4.0	21.9	0.3	0.5	–	–	5.0	22.5
	5	0.5	2.9	4.5	15.4	1.0	17.1	1.1	1.8	0.8	4.7	2.0	16.6
	10	0.4	2.6	4.6	16.2	0.8	16.9	0.7	3.0	1.2	2.9	1.8	15.4

[1] Refers to the instrumental evaluation of the colour difference of aged samples for the selected methods in relation to unaged samples, i.e. the values before testing collected in Table 5 (not yet subjected to the graffiti protection evaluation test). In the case of samples where chalking occurred (e.g. system I and II – same type of surface protection), the photo-oxidation products were not removed prior to the evaluation test for graffiti resistance.

paint systems with anti-graffiti protection for unaged and aged samples as a function of the number of painting/cleaning operations (i.e. after 5 and 10 cycles).

Figures 5–8 show the changes in the measured gloss values for the 60˚ geometry, depending on the type of ageing method used and the graffiti remover, while Figures 9–14 show the changes in the measured colour values for ΔE* – CIELAB 1976, depending on the type of ageing method used and the graffiti remover, measured using a sphere spectrophotometer with two measurement modes (with the specular component included and excluded). The results shown in Tables 6 and 7 and in the graphs (Figures 5–14) are the average for the 6 different markings used in the tests carried out (the markings are summarised in Table 2).

Based on the test results shown in Table 6 and Figures 5–8, it is concluded that:

- A high effectiveness of the anti-graffiti coating protection of the unaged samples for the tested systems and proper gloss retention was achieved. Similar results were obtained after 5 and 10 cycles of painting and cleaning (retention of the effectiveness of the anti-graffiti coating with respect to the number of paintings and cleaning), with the cleaning agent AGS-221 (gel) performing significantly better. The AGS-5 agent was ineffective and left visible streaks that slightly affected the gloss of the tested systems. In the case of gloss evaluation according to PN-EN ISO 2813 [19], the decreases in gloss values in the 60 geometry averaged −4 [GU] (5 cycles), −7 [GU] (10 cycles) for the cleaning agent AGS-221 (gel), and −12 [GU] (5 cycles) and −15 [GU] (10 cycles) for the cleaning agent AGS-5.

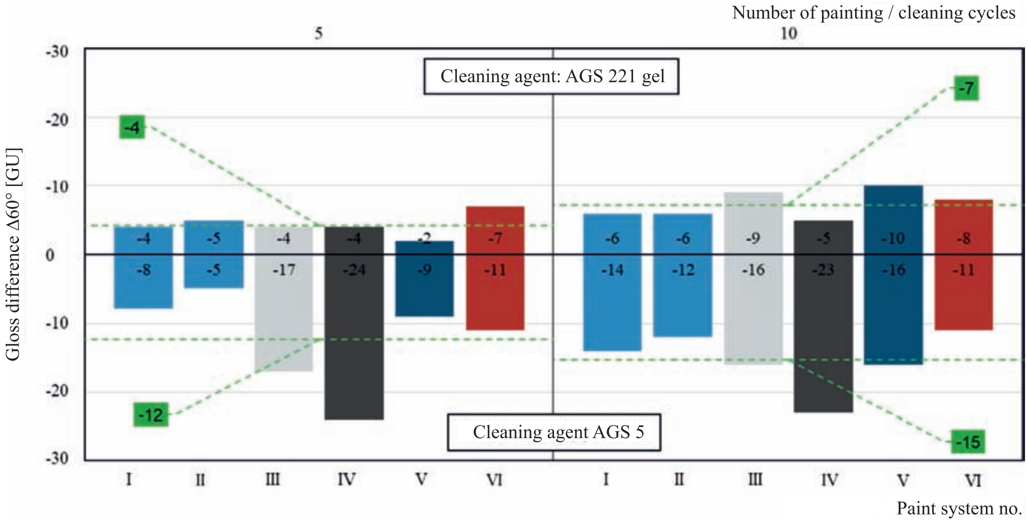

Fig. 5. Change in gloss value in 60° geometry after graffiti resistance test after 5 and 10 cycles of painting and cleaning for unaged samples (AGS-221 and AGS-5 remover) [own study]

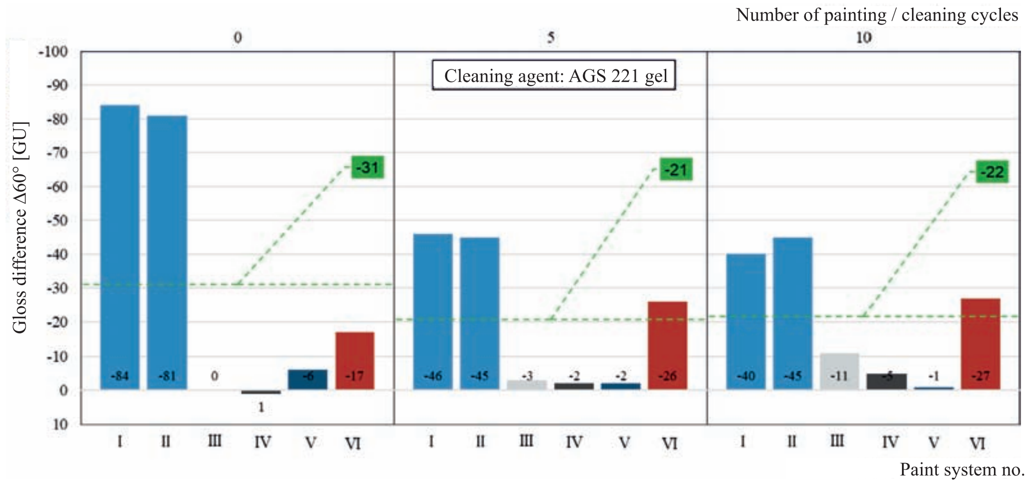

Fig. 6. Change in gloss value in 60° geometry before and after graffiti resistance test after 5 and 10 cycles of painting and cleaning for samples aged according to PN-EN ISO 16474-2 [7] (AGS-221 remover) [own study]

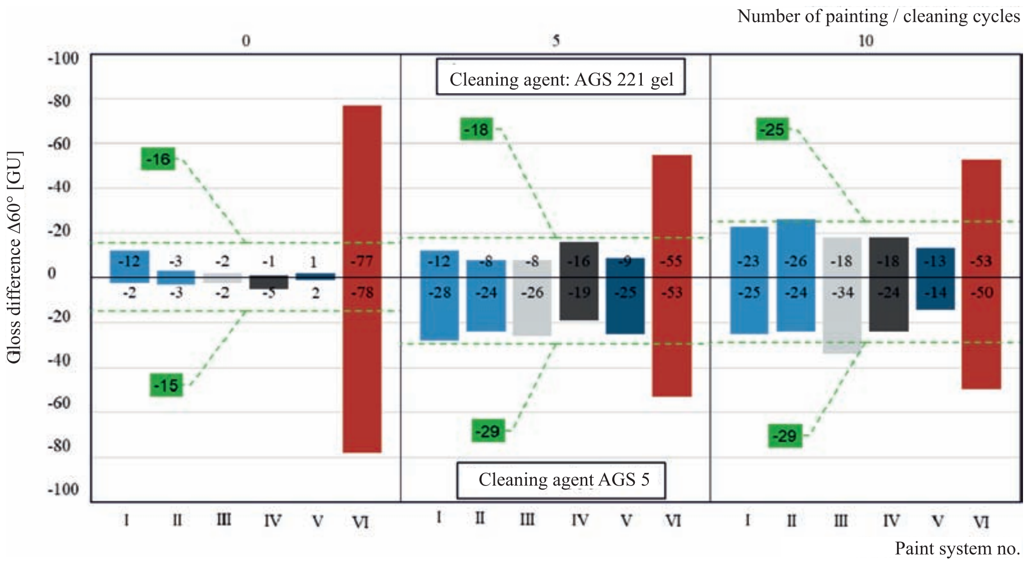

Fig. 7. Change in gloss value in 60° geometry before painting and after graffiti resistance test after 5 and 10 cycles of painting and cleaning for samples aged according to DN 001/08/A2/16 [10] (AGS-221 and AGS-5 remover) [own study]

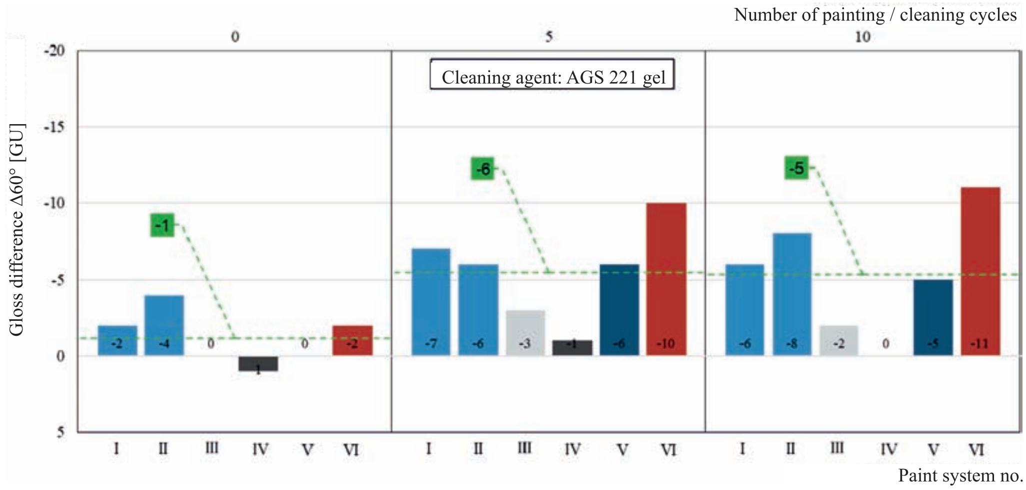

Fig. 8. Change in gloss value in 60° geometry before and after graffiti resistance test after 5 and 10 cycles of painting and cleaning for samples aged according to PN-EN ISO 9227 [12] (AGS-221 remover) [own study]

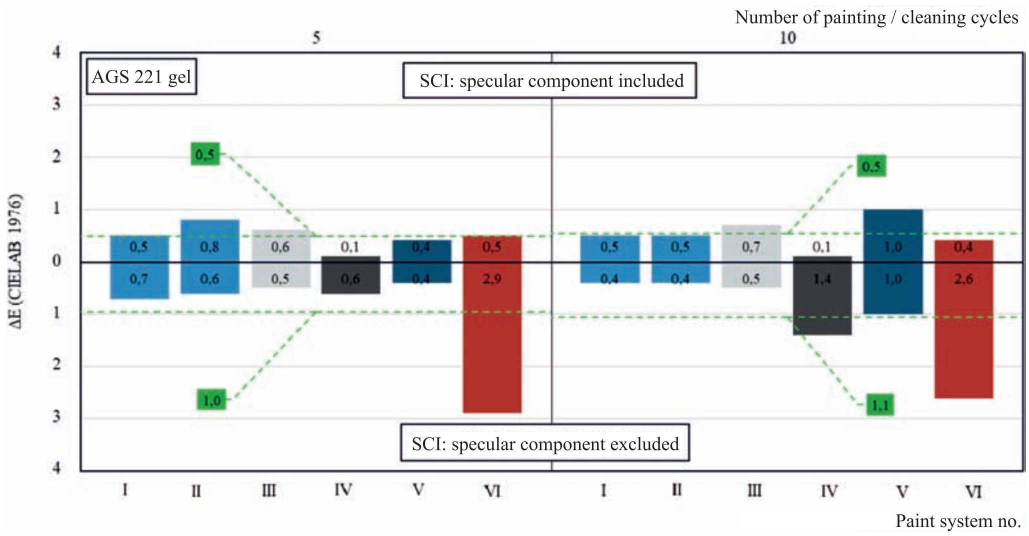

Fig. 9. Change in colour value for ΔE* – CIELAB 1976 after graffiti resistance test after 5 and 10 cycles of painting and cleaning for unaged samples (AGS-221 remover with the specular component included and excluded) [own study]

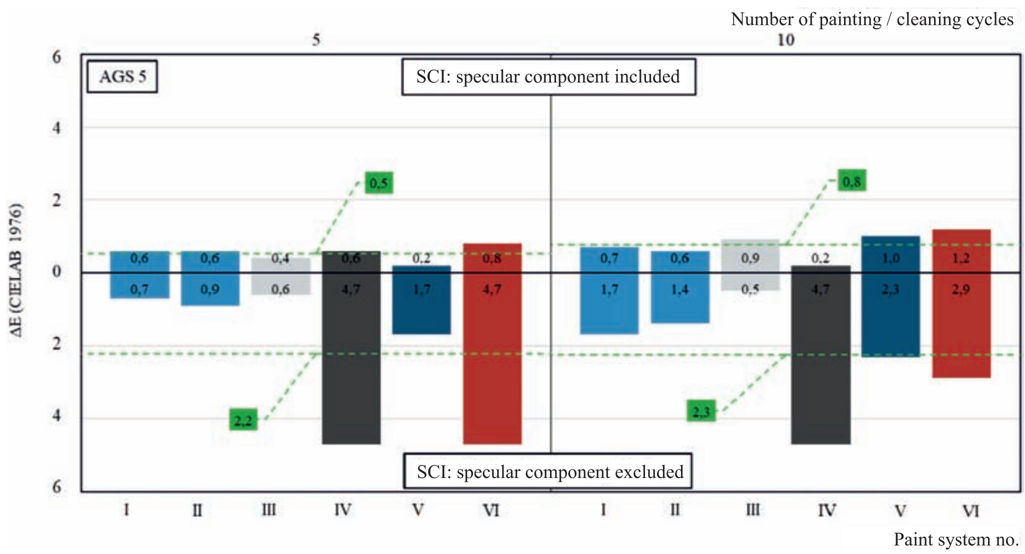

Fig. 10. Change in colour value for ΔE* – CIELAB 1976 after graffiti resistance test after 5 and 10 cycles of painting and cleaning for unaged samples (AGS-5 remover with the specular component included and excluded) [own study]

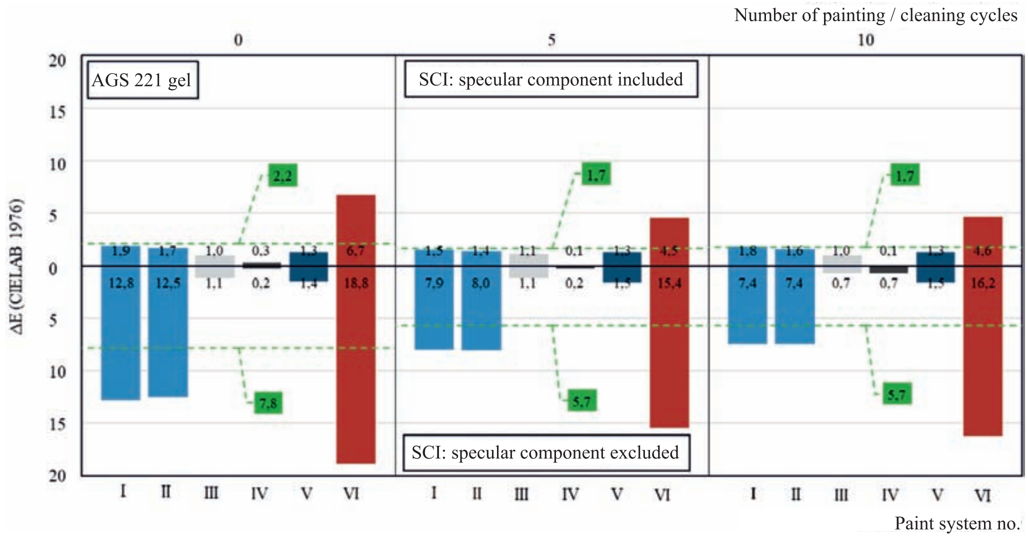

Fig. 11. Change in colour value for ΔE* – CIELAB 1976 after graffiti resistance test before painting and after graffiti resistance test after 5 and 10 cycles of painting and cleaning for samples aged according to PN-EN ISO 16474-2 [7] (AGS-221 remover with the specular component included and excluded) [own study]

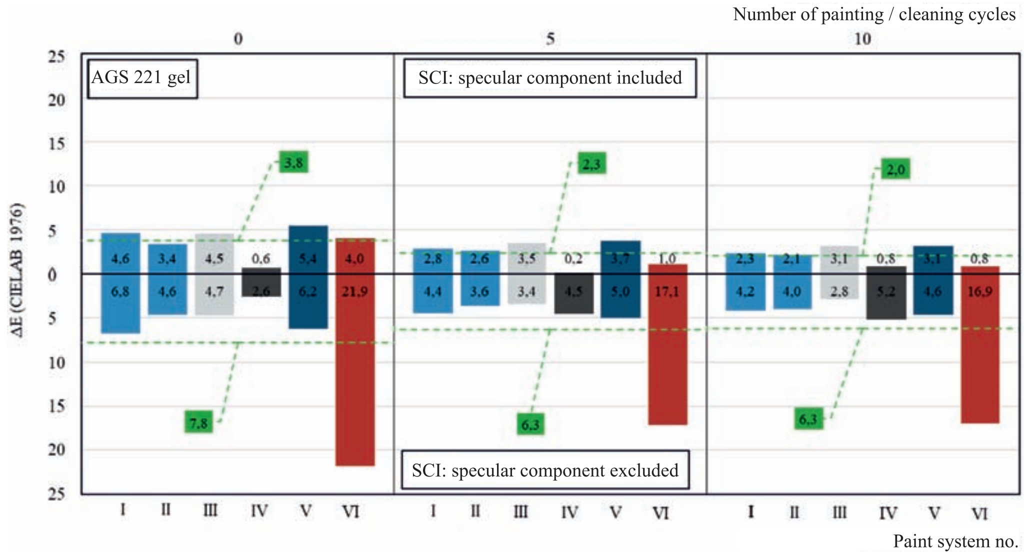

Fig. 12. Change in colour value for ΔE* – CIELAB 1976 after graffiti resistance test before painting and after graffiti resistance test after 5 and 10 cycles of painting and cleaning for samples aged according to DN 001/08/A2/16 [10] (AGS-221 remover with the specular component included and excluded) [own study]

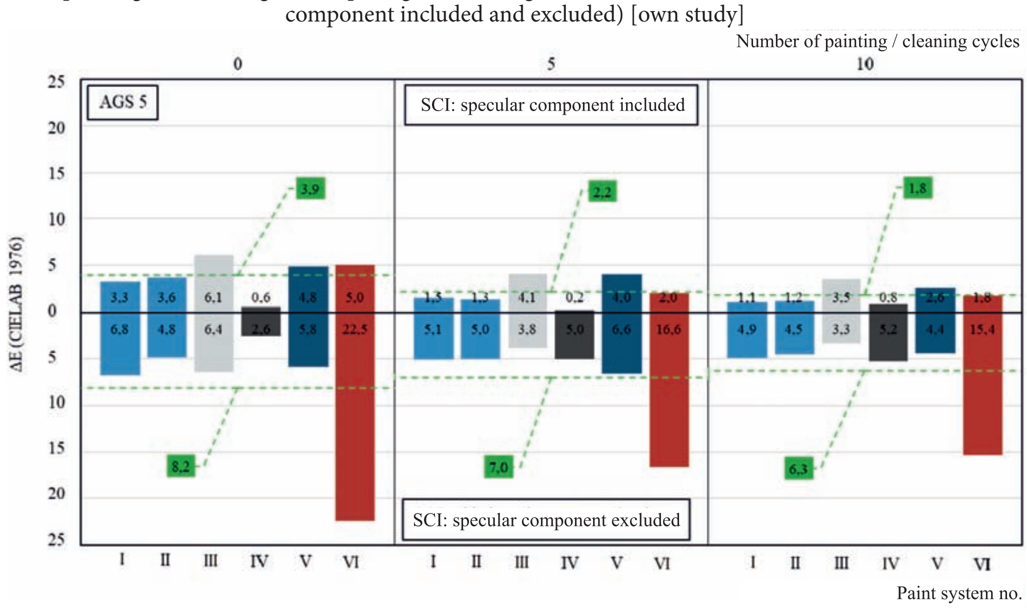

Fig. 13. Change in colour value for ΔE* – CIELAB 1976 after graffiti resistance test before painting and after graffiti resistance test after 5 and 10 cycles of painting and cleaning for samples aged according to DN 001/08/A2/16 [10] (AGS-5 remover with the specular component included and excluded) [own study]

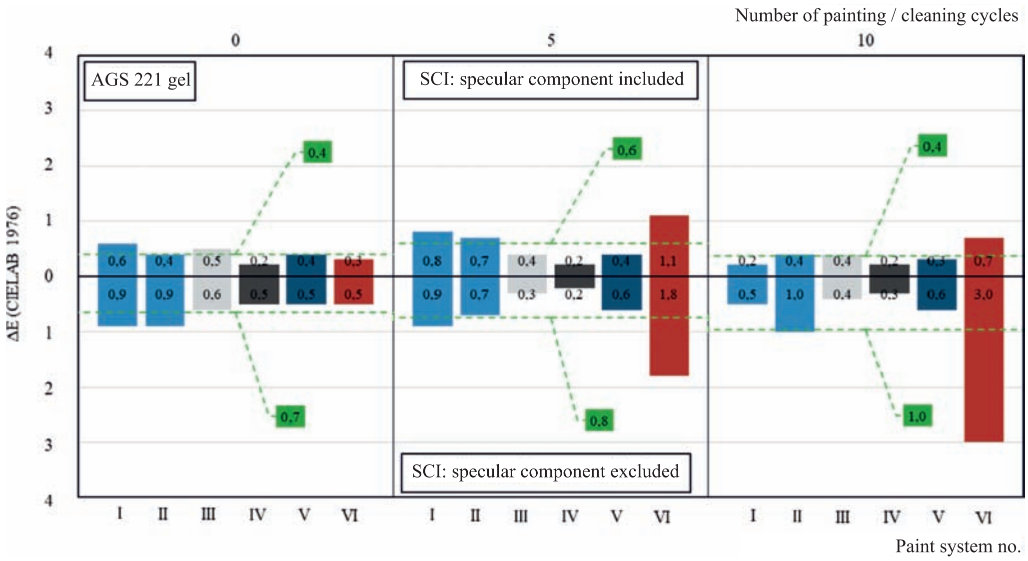

Fig. 14. Change in colour value for ΔE* – CIELAB 1976 after graffiti resistance test before painting and after graffiti resistance test after 5 and 10 cycles of painting and cleaning for samples aged according to PN-EN ISO 9227 [12] (AGS-221 remover with the specular component included and excluded) [own study]

- The salt spray test according to PN-EN ISO 9227 [12] did not significantly deteriorate the protective function of the paint systems against graffiti and is comparable with the results obtained for unaged samples in the evaluation of the change in gloss properties of the coatings. This indicates that the corrosive agent of sodium chloride does not significantly affect the gloss parameter of the coating, even when intense changes in the form of blistering occur (systems II, V, VI). In the case of gloss evaluation according to PN-EN ISO 2813 [19], the decreases in gloss values in the 60° geometry averaged –6 [GU] (5 cycles) and –5 [GU] (10 cycles) for the cleaning agent AGS-221 in gel form.
- Ageing according to PN-EN ISO 16474-2 [7] did not result in a significant decrease in the coating's resistance to graffiti in the context of the evaluation of the gloss parameter for those paint systems for which no changes were observed after ageing alone (system III, IV and V) – an average gloss decrease of –2 [GU] (5th cycle) and –6 [GU] (10th cycle). In the case of systems I and II (same topcoat), where chalking (total loss of gloss) was observed, a steady increase in gloss values was observed after 5 and 10 cycles compared to the values before the start of the evaluation test for the effectiveness of graffiti resistance. The increase in gloss value was half that of the gloss value of the unaged samples and was caused by the removal of footoxidation products with graffiti remover (chalk layer). For System VI, where, after ageing, there was an intensive change in colour and a slight decrease in gloss with the absence of chalking signs, a decrease in graffiti resistance was observed in the context of the evaluation of the gloss parameter, which still decreased by an average of around 10 [GU] (5/10 cycle) in relation to the value before the start of the evaluation test for the effectiveness of graffiti resistance for the washing agent AGS-221 (gel).
- Ageing according to DN 001/08/A2/16 [10], with the exception of case VI (complete dulling), had practically no effect on the initial gloss value compared to the pre-ageing value, however, a slightly greater decrease in resistance to graffiti painting was observed after the 5th and 10th cycle. This indicates a slight weakening of the protective function of the tested systems against graffiti. In the case of the gloss evaluation according to PN-EN ISO 2813 [19], the average drops in gloss values in the 60° geometry were –18 [GU] (5 cycles), –25 [GU] (10 cycles) for the cleaning agent AGS-221 (gel) and –29 [GU] (5 and 10 cycles) for the cleaning agent AGS-5. In the case of system VI, which had completely dulled after ageing, a slight increase in gloss value of about 30 [GU] was observed after the graffiti resistance test, probably due to the removal of some of the photo-oxidation products as well as the polishing of the surface as a result of the paint removal.

A spherical spectrophotometer (spherical measuring geometry d/8°) was used to observe the change in the colour parameter ΔE* – CIELAB 1976 after graffiti painting for samples that had not been aged and had been aged using selected methods, which uses the so-called Ulbricht sphere and which allows measurements to be made including the specular component (SCI) or excluding it (SCE).

The spherical measuring geometry used in the SCI mode (i.e. with the specular component included) focuses on the pigmentation of the measured sample. In this measurement mode, a beam of light directed into a sphere is perfectly scattered by an inner surface with a very high reflectance and uniformly illuminates the surface of the measured sample. Regardless of how the surface scatters the reflected light, it is completely collected from all sides inside the sphere and measured with the sensor, which is angled at 8°to the perpendicular axis. Because gloss is completely included in the measurement, the spherical instrument ignores differences in appearance and ‚sees' the same colour on a shiny, matt or any other textured sample.

The Ulbricht sphere in the spectrophotometer used for the measurements also has a hole called a light trap, which allows gloss to be eliminated from the measurement. In this so-called SCE mode (i.e. with the specular component excluded), the sphere instrument imitates the directional geometry quite well (colour, gloss, texture included). In practice, it is first necessary to determine the difference between two samples (in this case, measurements before and after graffiti painting) by evaluating their measurements made in SCE mode. Then, by checking the SCI data, it can be determined whether the deviation is caused by differences due to pigment changes (caused, for example, by the under-cleaning of the graffiti agents used) or whether its main source is differences in surface structures (e.g. increased roughness) caused by the graffiti paintings and/or the cleaning agent [2, 32]. Based on the test results shown in Table 7 and Figures 9–14, it is concluded that:

- High effectiveness of the anti-graffiti coating of the unaged samples for the tested systems and the retention of colour properties were obtained. Similar results were obtained after 5 and 10 cycles of painting and cleaning (retention of the effectiveness of the anti-graffiti coating with respect to the number of paintings and cleaning). In one case for system VI, where a loss of gloss and indirectly of colour was visually observed, the spectrophotometer measurement also showed dulling with a slight colour change for both cleaning agents. This change had a strong character of a change in the surface texture of the coating, indicating that the cleaning agents used are simply unsuitable for this system (the same changes were also visible outside the edges of the removed paintings). For system V, AGS-5, which is theoretically much weaker and less aggressive than AGS-221 (gel), did not perform well in removing the paintings. In this case, visible white streaks were observed, which may indicate a hindered removal of the agent from the surface of the coatings (the same changes were also visible outside the edges of the removed paintings). In the case of colour evaluation for the parameter ΔE* – CIELAB 1976 according to PN-EN ISO 7724-3 [22], the average changes in ΔE* were: 0.5 / 1.0 (SCI / SCE – 5th cycle), 0.5 / 1.1 (SCI / SCE – 10th cycle) for the cleaning agent AGS-221 (gel) and 0.5 / 2.2 (SCI / SCE – 5th cycle), 0.8 / 2.3 (SCI / SCE – 10th cycle) for the cleaning agent AGS-5.
- The salt spray test according to PN-EN ISO 9227 [12] did not significantly deteriorate the protective function of the paint systems against graffiti and is comparable with the results obtained for unaged samples in the evaluation of the change in the colour parameters of the coatings. This indicates that the corrosive agent, which is sodium chloride, does not significantly affect the colour parameter of the coating, even when intense changes in the form of blistering occur (systems II, V, VI). In the case of the colour evaluation for the parameter ΔE* – CIELAB 1976 according to PN-EN ISO 7724-3 [22], the average changes in ΔE* were: 0.6 / 0.8 (SCI / SCE – 5th cycle), 0.4 / 1.0 (SCI / SCE – 10th cycle) for the cleaning agent AGS-221 (gel).
- Ageing according to PN-EN ISO 16474-2 [7] significantly influenced the colour change in half of the cases tested (system I, II and VI), while in the other half practically no significant changes were observed. In the first case for systems I, II, VI, when evaluating the resistance to graffiti painting after ageing, in each case an increase in resistance to graffiti painting was observed (lower ΔE* value in relation to the initial value before ageing) as a result of the removal of some of the photo-oxidation products formed during the ageing of the systems, and the greatest change was observed for systems I and II (removal of the chalk layer). Although the changes after ageing were strongly evident, the systems partially retained their protective properties against graffiti. For the cases where no changes after ageing were observed, the graffiti resistance was similar for the case of samples that had not been aged. In the case of the colour evaluation for the parameter ΔE* – CIELAB 1976 according to PN-EN ISO 7724-3 [22], the average changes in ΔE* were: 1.7 / 5.7 (SCI / SCE – for both the 5th and 10th cycle) of the cleaning agent AGS-221 (gel).
- Ageing according to DN 001/08/A2/16 [10] significantly affected the colour change in each case compared to the value determined before ageing (mean value for SCI mode for cycle 0: ΔE* = 3.9, while mean value for SCE mode for cycle 0: ΔE* = 8.0). In the case of the graffiti resistance evaluation after such ageing, an increase in graffiti resistance was observed in each case (lower ΔE* value compared to the initial value before ageing) due to the removal of some of the photo-oxidation products formed during the ageing of the systems and the greatest change was observed for system VI. In the case of

the colour evaluation for the parameter ΔE*– CIELAB 1976 according to PN-EN ISO 7724-3 [22], the average changes in ΔE* were: 2.3 / 6.3 (SCI / SCE – 5th cycle), 2.0 / 6.3 (SCI / SCE – 10th cycle) for the cleaning agent AGS-221 (gel) and 2.2 / 7.0 (SCI / SCE – 5th cycle), 1.8 / 6.3 (SCI / SCE – 10th cycle) for the cleaning agent AGS-5.

4. Summary and conclusions

Tests have shown that the contribution of UV radiation has a significant effect on the performance of the coating and its subsequent protection against graffiti. In addition, an aged coating may be more susceptible to an aggressive cleaning agent. For the ageing tests carried out according to EN ISO 16474-2 [7], for coatings that chalked or underwent intensive colour/gloss changes, significant decreases in graffiti protection were achieved, whereas for coating systems that retained their original decorative properties after ageing tests, similar graffiti protection values to those for unaged samples were achieved. Testing in a climatic chamber with periodic exposure to a quartz-mercury lamp according to procedure DN 001/08/A2/16 [10] resulted in unnatural changes to the coating and a reduction in the protective properties against graffiti in each case. Salt spray chamber ageing according to EN ISO 9227 [12] did not result in a deterioration of the anti-graffiti properties of the tested systems, where the aged samples showed almost the same properties as the unaged samples. The results for the newly prepared (unaged) samples selected for testing showed very high protection against graffiti paint in terms of retaining their decorative properties in the form of gloss or colour – these are commonly used paint systems in the Polish railway industry.

Durable anti-graffiti coating systems appear to be one of the best possible solutions for protecting railway carriages from vandalism. The design of anti-graffiti coating systems should be carried out with the remover in mind, in order to study the interaction between coating, graffiti and solvent in detail. Before any new, previously untested graffiti removers are used, tests should first be carried out to check the reaction of the product with the coating, as the graffiti remover can permanently damage such a coating.

On the basis of the data obtained and many years of experience in conducting laboratory tests, it seems reasonable to carry out comprehensive tests of entire finished paint systems applied to carriage bodies. The anti-corrosion and anti-graffiti capabilities of the systems should be determined. At the same time, they should also be laboratory tested after performing ageing tests in order to better assess their properties and the decrease of their effectiveness and to translate these results into their long-term use and exposure to natural ageing factors.

Visual measurements coincided with those made using instruments, but in many cases it is difficult to distinguish between certain features of the coating, e.g. whether there has been a change in colour or a decrease in gloss, due to the very subjective nature of the evaluation. Therefore, it is advisable to supplement the visual evaluation with an evaluation using instruments, which provides precise information on the intensity and nature of the changes occurring in the paint coating. A sphere spectrophotometer, with a geometry of d:8°, was also shown to be a valuable device for determining the changes occurring on the coating. The question is whether the changes are a type of pigmentation change (e.g. under-cleaning of the markings) or whether the changes are influenced by a change in the geometric structure of the surface (e.g. smoothness) caused by the markings/cleaning agent, which has a significant impact on the final decorative properties of the coating.

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