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Evaluation of the Influence of Laboratory Weathering of Paint Systems used in Rolling Stock on Selected Mechanical Properties

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Abstract. This paper evaluates the results of selected mechanical properties of outdoor painting systems used in the railway industry and the influence of laboratory weathering (simulation of outdoor conditions) with sunlight, temperature, and moisture on the change of these properties. The impact of the above-mentioned weather parameters, particularly solar radiation, was briefly described on the degradation of coating systems of weathering on selected mechanical properties such as hardness, resistance to gradual deformation (cupping test), and adhesion (fracture strength) was evaluated. The tests were carried out at the Railway Institute, Materials and Construction Laboratory, using two weathering methods: ISO 16474-2 [1] and the in-house method described in DN 001/08/A2/16 paragraph 4.1.8 [2].

Introduction

The primary purpose of using organic coating systems in rail transport is to protect the metal from damaging factors such as rust, salt, and dirt and improve the vehicle's aesthetics. Multi-layer solvent-based products, increasingly replaced by water-based ones, are used to protect metal surfaces in rolling stock. This is dictated by the European Union regulations being established to reduce organic compound emissions caused by organic solvents [3].

The application of organic coatings in rolling stock can cover many areas, including car bodies, undercarriages, roofs, axles and wheels, and the interior of train equipment. Depending on the application site, different properties and requirements are expected from the paint system used. The most exposed to the negative effects of weathering are the external coating locations - mainly the car bodies. Such coatings are affected by several factors that cause their degradation over time, ranging from environmental pollution (chemical and biological), through aggressive media used in the form of cleaning agents (often incompetently and contrary to the recommendations of the agent manufacturers), to harmful solar radiation with high temperature and humidity, which are the leading cause of weakening the functional and decorative properties of the systems discussed. The radiation mainly affects the top layers of the applied protective system. Currently, polyurethane and acrylic products are used as the last layer of protection in rail transport. They are available in the form of a topcoat or base paint finish with a clear varnish, which provides the desired decorative properties, weather resistance, and protection against graffiti [4].

Degradation factor: UV radiation

The process of coatings degradation by solar radiation begins with photolysis. By absorbing ultraviolet (UV) radiation, the polymer enters an excitation state (to a higher energy state), which contributes to the breaking of covalent chemical bonds in its structure and the formation of reactive free radicals that initiate further chemical transformations. The ease with which the covalent bonds break depends on the energy of these bonds. The next step in the photochemical degradation of the polymer is self-oxidation, which occurs due to the reaction of free radicals with oxygen - with the simultaneous formation of peroxyl radicals. Further reactions follow the general scheme of free radical reactions. Peroxyl radicals react with the polymer molecules, attacking the hydrogen atoms in the polymer chains, resulting in the formation of hydroperoxides and other free radicals. The hydroperoxides (which are highly susceptible to photolysis) are broken down and the free radicals formed during the entire process of coating material destruction damage the polymer molecules. Free radicals can cause depolymerisation of macromolecular compounds, chain scission and oxidation of smaller molecules [5].

It should be emphasised that if a polymer does not absorb radiation, it does not degrade but may nevertheless be susceptible to attack by free radicals from the absorption and excitation of other film-forming materials (e.g. fillers). Aliphatic polymers are UV-resistant as they do not absorb ultraviolet radiation and are permeable. These polymers include acrylates, polyvinyl acetate and aliphatic polyurethanes. Aromatic organics such as epoxies and phenolic resins, on the other hand, have high UV absorption and are subject to photolysis and photo-oxidation. UV radiation can also "attack" the UV-sensitive layers beneath transparent topcoats. When using such transparent varnishes, care must be taken to ensure that light-sensitive primers and base surfaces are adequately protected from ultraviolet radiation [6].

Many methods can be used to protect paint systems against UV radiation. One of these, known as selective absorption, involves the appropriate modification of non-light-resistant top coats with pigments, other absorbers, or UV reflectors. Selective absorption of ultraviolet light by pigments protects the binder and increases the durability of the paint film. Materials such as zinc oxide, zinc sulfide, red iron oxide, carbon black and rutile titanium dioxide are effective absorbers of ultraviolet light and provide good protection for sensitive polymers. Other methods of radiation protection for coatings include:

– use of reflective pigments which act as a mirror and reflect light (e.g. aluminum flake pigments),
– use of luminescent pigments, which absorb the energy of near-ultraviolet radiation and re-emit it as a longer wavelength to produce colors with a much higher saturation or intensity in the red, orange, yellow and green wavelengths,
– the use of organic additives that selectively absorb ultraviolet light and are essentially similar to those used in suntan lotions. Like pigments, they absorb short-wave ultraviolet light and convert it into heat energy without degrading it when exposed to ultraviolet light [6].

Degradation factor: temperature and humidity

In addition to destructive radiation, a factor contributing to the destruction of the polymer is the effect of thermal radiation, known as thermal degradation. The temperature of the material is influenced by many factors: air temperature (depending on latitude, prevailing climatic conditions, and season), the dose of infrared radiation, airflow within the specimen (thermal exchange of the material with the environment) and the properties of the material itself (color and thermal conductivity coefficient). The absorption of radiation is closely correlated with the color of the material exposed. Lighter materials reflect more radiation than darker ones, which absorb it. Also, in this case, the surface and structure of the material (e.g. its polishing) are of great importance. The actual temperature of a material is often up to 30°C higher than the measured ambient temperature. It is important to realize that temperature significantly affects the properties of a material by increasing the rate and number of chemical and photochemical reactions in the material caused by UV radiation. It also increases the rate of diffusion of fillers (e.g. stabilizers, plasticizers) as well as additional components in the form of impurities from the atmosphere. Rapid temperature changes (cooling and heating) result in shrinkage and stretching of the material, with consequent cracking and peeling. The degradation of the material can be further increased by water absorption and desorption (hydrolytic degradation), so these two elements must be considered as a parameter that together increases the degradation of the material. In addition, rainwater can provide pollutants from the atmosphere and thus accelerate material degradation [7].

Other degradation factors
In addition to the factors mentioned above, factors contributing to the degradation of paint systems are mechanical degradation (under mechanical stress), oxidative degradation (under the influence of oxygen), hydrolytic degradation under the influence of an agent other than water, such as acids and alkalis, and biological degradation. In nature, we most often deal with a synergic correlation of all factors [8].

The above-mentioned degradation processes occurring in the polymer deteriorate the coating's physical, chemical, and mechanical properties, which in particular leads to a decrease in corrosion resistance and susceptibility to stretching and bending, while abrasion and scratch resistance (hardness) brittleness increase. Exploitation factors affecting the paint coating mainly increase the roughness of its surface and consequently its decorative properties, causing it to deteriorate, e.g. by loss of gloss, color change, fading, or local discoloration. External factors, coming into contact with polymeric coatings, generate their physical degradation in the form of silver cracks (their name derives from the characteristic silvery reflections visible in the reflected light of a microscope), etching and craters, blistering, inter-layer delamination, loss of adhesion between the coating and the substrate. There is also an increase in the roughness of the surface and a decrease in the resistance to chemicals used for cleaning or the effectiveness of anti-graffiti protection due to an increase in the adhesion of the coating. Consequently, the coating material degradation leads to a reduction in its service life [5,8].

Research methodology and research material:
The performance of a paint system under natural conditions can and should be checked by conducting accelerated laboratory tests simulating sunlight and other laboratory weather conditions such as temperature and humidity. Accelerated laboratory tests should simulate and approximate the conditions under which the materials are used as closely as possible. A large body of scientific literature on organic coatings shows that the best correlation between laboratory test results and results obtained under natural conditions is obtained by combining different degradation mechanisms. When only the effects of radiation, temperature, and humidity (including rain) are considered to simulate these conditions in the laboratory, many test methods have been developed worldwide, including standardized ones. One of such methods, which is the most commonly used globally for testing paints and varnishes, is the series of standards PN-EN ISO 16474, which collects (contains) the basic and most important information on carrying out such tests in laboratories [7].

Weathering tests in IK were carried out according to the second part of the standard mentioned above, which assumes the use of apparatuses equipped with xenon arc lamps for this purpose. The total irradiance was 324 MJ/m^2, theoretically about 1.5 years under natural conditions for a temperate latitude climate [9].

In addition, this paper presents similar test results for simulated varying atmospheric conditions according to the procedure developed at IK in which cyclic irradiation is used with a table lamp with a filament (heating function) and an ultraviolet radiator of 400W with a reflector made of varnished aluminum sheet. The light used has no UV filter and emits a discrete spectrum (range

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from 238 nm). Short wavelengths transmit higher energy, which can be the initiator of photochemical reactions and thus lead to faster destruction of coatings. Weathering in the climatic chamber has a different degradation mechanism than that carried out in chambers with xenon lamps; namely, high positive and negative temperatures and their rapid changes are simulated in the climatic chamber. Under the influence of the temperature shock, coatings undergo shrinkage and stretching of the material, which consequently causes cracks and peeling and a decrease in selected physical properties of the coating, such as elasticity or adhesion.

The exact weathering methodologies and assessment methods after aging and information on the testing apparatus used are shown in Table 1.

The research material consisted of exterior painting systems commonly used on Poland's railway car bodies and roofs. The tested systems were composed of two-component and multi-component systems, depending on their application place, while the base was different grades of structural steel. The compositions of the systems numbered IV, VI, and XI, which include train roofs as their primary application place, consisted of epoxy primers and polyurethane and acrylic topcoats or their mixtures. The remaining systems consisted of epoxy primers, epoxy or polyester putties, polyurethane, acrylic, and mixed filling primers and finishing coats of the topcoat type (systems I, II, IV, VI, VII, XI) or basecoat + clearcoat type (systems III, V, VIII, IX, X), also based on polyurethane, acrylic resins and their mixtures. The average thickness of the tested multi-component systems was within the range of (200 ÷ 300) µm, except for system number III (a thick putty layer was used here, and the average thickness was about 700 µm). In contrast, the average thickness of the two-component systems was about 150 µm.

Table 1. *Research methodology along with the apparatus used for this purpose.*

No.	Type of test	Reference document (method)	Apparatus	Remarks:
Weathering methods:				
1	Resistance to UV radiation (standardized method)	ISO 16474-2 [1]	Light test chamber, Atlas GmbH Xenotest 440, XENOSENSIV RC 34 BST	methodology: PN-EN ISO 16474-2, point 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; chamber temperature 38°C, relative humidity 50%, test periods: 102 min dry, 18 min rain; total irradiation dose: 324 MJ/m^2 (approx.. 1500h).
2	Resistance to UV radiation (in-house method)	DN 001/08/A2/16 [2]	Climatic chamber SECASI SI550C150F40H lamp Famed-1 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 48 h (Famed-1 lamp type L8/59). Testing time: 1500 h.
Assessment methods after aging:				
3	Determination of hardness	ISO 1522 [10]	TQC Sheen TI SP 0500	König's pendulum was used for the measurements; the measured hardness was related to the hardness against the glass (calibration)

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4	Determination of resistance to indentation	ISO 1520 [11]	Erichsen 202 EM	minimum depth of indentation to cause failure to be determined (steady rate 0,2 mm/s); to be assessed with the normal corrected vision
5	Determination of adhesion/cohesion (fracture strength - Cross-cut test or X-cut test)	ISO 2409 [12] ISO 16276-2 [13]	Hand-held multi-blade cutting tool by Erichsen (type B, C) or cutter with a rigid blade by Erichsen van Laar (with a V-shaped cutting edge)	method dependent on coating thickness, above 250 µm an X-shaped cut was used; Tesa tape used with adhesion strength according to the standard

Evaluation of results and conclusions

Table 2. *Summary of results of adhesion, indentation, and hardness measurements before and after weathering test according to ISO 16474-2 [1] and DN 001/08/A2/16 [2].*

System* No.	**Fracture strength – ISO 2409 [12] / 16276-2 [13], [degree of adhesion]. (P=95%, k=2, ± 1 s.p.)**			**Indentation – ISO 1520 [11], [mm]. (P=95%, k=2, ± 0,4 mm)**			**Hardness – ISO 1522 [10] [absolute value related to the hardness of the glass]. König (P=95%, k=2, ± 0,04)**		
	unaged material	ISO 16474-2	DN 001/08/A2/16	unaged material	ISO 16474-2	DN 001/08/A2/16	unaged material	ISO 16474-2	DN 001/08/A2/16
I	1	2	2	11.4	3.7	5.3	0.33	0.44	0.43
II	1	2	2	9.0	1.1	1.0	0.35	0.45	0.48
III	1	1	1	0.8	0.4	0.7	0.33	0.58	0.72
IV	1	2	1	7.6	2.3	1.7	0.51	0.73	0.80
V	0	0	0	8.7	1.9	2.0	0.26	0.59	0.62
VI	0	0	1	10.0	7.8	7.9	0.41	0.48	0.55
VII	0	0	0	6.6	5.7	5.3	0.08	0.12	0.12
VIII	1	1	1	7.2	6.5	6.0	0.07	0.08	0.11
IX	1	2	-	-	-	-	0.17	0.35	-
X	1	1	-	-	-	-	0.41	0.53	-
XI	1	0	-	-	-	-	0.52	0.53	-

* bold indicates systems with topcoat: basecoat + clearcoat, all other cases topcoat.

The adhesion test carried out using the cross-cut method or X-cut method (depending on the thickness of the system) did not show any significant deterioration of this parameter after the aging tests. The most significant difference achieved in pre-aging and post-aging results for both aging methods was, in each case, only 1 degree of adhesion. In each case, only a decrease in adhesion was observed between the layers of the system (no delamination from the base).

In the case of tests on resistance to indentation, in most cases, relatively large drops of this parameter after aging were observed; however, some of the systems tested retained their properties at a satisfactory level (systems VI, VII, VIII). Also, in this case, similar results were obtained for both aging methods used, where the average drops in adhesion for all tested systems were 4.0 mm for the ISO 16474-2 method [1] and 3.9 mm for the method according to DN 001/08/A2/16 [2], respectively.

When evaluating hardness, an increase in this parameter was observed in every specimen tested. A more significant increase was observed in the case of aging according to an in-house aging method.

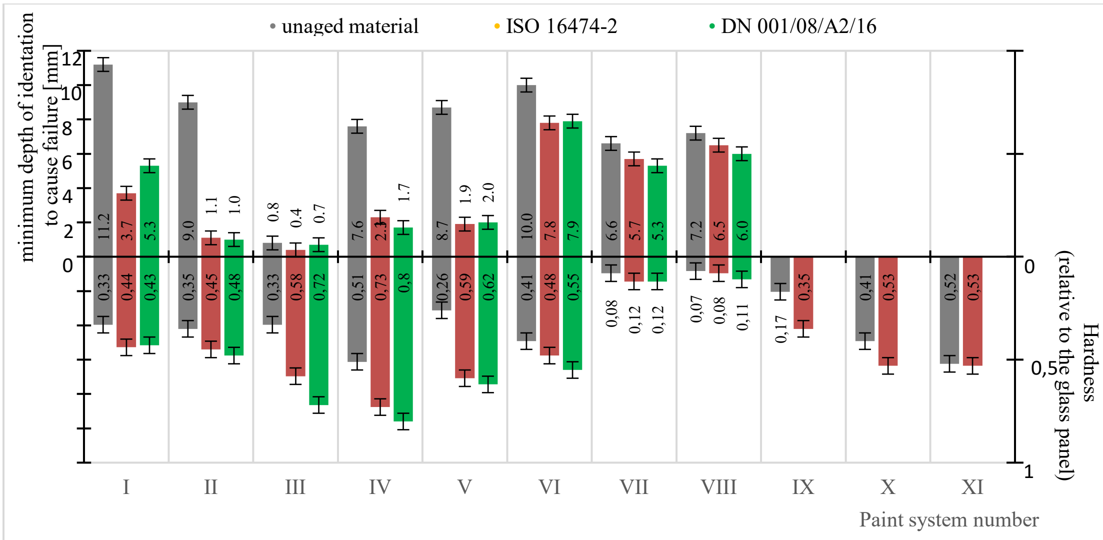

Fig. 1. *Graphical summary of the minimum indentation depth causing damage to the coating [mm] according to ISO 1520 [11] and hardness (about the glass constant) determined by the König pendulum damping method according to ISO 1522 [10] for selected tested paint systems.*

There is noticeable a certain correlation between an increase in hardness (and therefore brittleness) and a decrease in such parameters as adhesion or resistance to indentation – the more significant the increase in hardness, the greater the negative change in such parameters as adhesion or resistance to indentation. A high hardness value is a recommended parameter due to the increase of, among others, scratch resistance. However, other properties of coatings related to their elastic properties to be complete cannot be neglected – as in every case, a compromise solution has to be found.

Summary

As a result of selected mechanical tests carried out for complete paint systems used in rolling stock, it is concluded that, as a result of environmental tests conducted in the laboratory with a synergistic combination of light radiation, temperature, and moisture, there is a significant deterioration of mechanical properties such as resistance to indentation and, to a lesser extent, a decrease in the adhesion of the paint system (interlayer), while the hardness (brittleness) of the paint systems increases.

Although two different aging methods were used to evaluate the selected mechanical properties, differing primarily in the type of radiation (full light spectrum for the xenon UV-VIS-IR lamps consistent with natural light vs. UV including UV-C in the form of discrete radiation for the table lamp for the own method) and the different cycles of varying temperature and humidity, the similar character of changes were obtained and the results in specific cases were practically convergent, which allows the conclusion that the intensity of the contribution of individual aging factors on the mechanical properties is of secondary importance here and it is only essential that each of these factors is taken into account in the chosen aging method (interconnection of degradation mechanisms).

When evaluating the selected mechanical parameters of the painting systems, no clear advantage of the paint systems in the combination of base paint + clear coat over the surface paint finish was found. Based on the conducted research, it can be concluded that the paint systems used in the railway industry are characterized by high mechanical properties, which, however, deteriorate considerably as a result of environmental stress. The average decrease in adhesion for all 11 tested paint systems was approximately 0.3 adhesion units. In contrast, the reduction in resistance to indentation reached the value of a 50% decrease (the results were the same for both aging methods and referred to the average values determined before aging). The average increase in hardness was 42% for the aging method according to ISO 16474-2 [1], while for the aging method described in DN 001/08/A2/16 [2], the hardness increase was 54%. Considering the above data, it is reasonable to consider conducting selected tests of coatings after aging tests to fully assess their quality, allowing to estimate the time of their satisfactory use until the required repainting. In the railway industry, this is quite important because the downtime of trains in painting shops and the renovation of the system itself incur high financial expenses.

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