Comparison of anticorrosive coating systems' behaviour in laboratory tests and after 10 to 20 years of use on steel bridges

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Abstract

Correlation of laboratory and field tests of anticorrosion paint systems is usually done by comparing laboratory results with field ones after short time (for example 3–5 years) on the corrosion stations which simulate different macroclimates only. Our laboratory tests done according to ISO 20340 (Performance requirements for protective paint systems for offshore and related structures – cyclic test), ISO 9227 (Corrosion tests in artificial atmospheres – Salt spray tests) and EN-ISO 16474-3 (Methods of exposure to laboratory light sources – Part 3: Fluorescent UV lamps) are compared with the behavior of coating systems (various new generation epoxy-polyurethane systems) applied 12–17 years ago on steel bridges subjected to both micro- and macro- climates together with other hazardous factors.

All anticorrosive systems that have been used on the bridges still have retained relatively good protective properties. The most significant changes are visible on the topcoat, especially chalking, color shift and signs of binder degradation observed in FTIR spectra. The extend of changes observed in topcoats depends both on pigments and binder type used.

The establishment of new criteria for the optimal choice of anticorrosive coating systems for steel constructions is proposed.

Keywords: corrosion, corrosion protection, coating systems, testing

Introduction

The presented research results are part of a project carried out under the CORNET Initiative. The aim of the project is to develop the criteria and guidelines for the selection of coating systems for application on steel structures. They will be formulated based on the results of a research of coatings from existing structures and those obtained from accelerated laboratory test for the same coating systems, as those applied on selected bridges. The project also aims to help in the selection of appropriate and reliable research methods for the rapid evaluation of the properties of corrosion-resistant coatings.

An equally important objective of this research, for which, unfortunately, neither European nor state financing is possible, is the evaluation of the standard anti-corrosive epoxy-polyurethane systems used in highly corrosive environments (cat. C4 and C5) on large steel bridge structures, performed according to EN ISO 12944-5 [1] and according to the guidelines of the General Directorate of National Roads and Motorways in Poland [2]. The systems have been selected so as to include all types belonging to this group and found on bridge structures, and to make possible their evaluation. While evaluating the behaviour of the systems after some 15 years of operation, attention was also drawn to the causes of any defects found, i.e. coating degradation or improper application.

As far as accelerated tests of the protective properties of organic coatings are concerned, there are many methods which differ in terms of the test conditions (environment type, temperature, duration, constant/variable conditions, immersion, spraying, etc.) and evaluation of the results (visually, instrumentally) [3–12]. Due to the variety of coatings and factors influencing their effectiveness in corrosive environments, none of the existing accelerated testing methods is universal enough to be appropriate for use as a sole method for coating evaluation. Therefore it is essential to use several different methods to obtain the most realistic picture of the behaviour of coatings under natural conditions while testing their protective properties.

The most reliable results are obtained during field studies, in the actual environments in which the coatings are used. However due to their duration, such methods are unsuitable for the quick evaluation of coatings, especially in the case of coating systems for long-term corrosion protection. As a result, the evaluation of anti-corrosion properties is carried out via a series of laboratory methods (immersion, corrosion chambers, electrochemical tests). In addition, mechanical properties which also affect the protective properties of coatings (damage resistance, flexibility, hardness, etc.) are tested. The use of different research methods serves to better understand the usefulness of accelerated tests for the evaluation of coatings intended for long-term corrosion protection, and assists in the selection of the most appropriate ones.

A research procedure, which is a reversed version of the one widely applied in the selection of accelerated methods for the evaluation of the behaviour of coating systems under certain corrosive conditions was used – i.e. instead of verifying the reliability of laboratory methods in natural conditions, evaluation of coating systems that had been applied onto bridge structures many years ago and operated in cat. C4/C5I corrosive environments was carried out. Afterwards, the accelerated methods were chosen so as to achieve a similar degree of damage, as in the case of coatings evaluated on bridges.

Tested coating systems

Tests on actual bridge structures were carried out on bridges located in different corrosive conditions (Table 1). Coating systems, tested in laboratory and field conditions consisted of epoxy primers - differing in the type of hardener and anti-corrosive pigments, the epoxy interlayer and the polyurethane topcoat hardened with hexamethylene diisocyanate (HDI)- in most cases based on acrylic resin (Table 2). Those systems were selected for the studies as they have passed the tests required by the polish Road and Bridge Research Institute and by the General Directorate for National Roads and Motorways and due to the universality of their application in different sites in Poland [2,13].

Table 1. Characteristics of selected bridges

Location	Year	Category of corrosivity	Designation of coating system*
Bridge in Kośmin	2003	C4	A
Bridge in Tryńcza	2006	C4	B
Bridge in Góra Kalwaria	2000	C5I	C1
Gdański bridge in Warsaw	1999	C5I	C2
Kazimierz Wielki Bridge in Bydgoszcz	2000	C4	E
Fordon Bridge in Bydgoszcz	2001	C5I	F
Praski Bridge in Warsaw	2001	C4	G
* according to Table 2			

Table 2. Coating systems selected for testing

System	Coating type	Resin/hardener/ anticorrosive pigment	Average thickness, µm	
			on bridges	for laboratory tests
A	Primer	EP (HS)/amine adduct/Al (2 –4 wt.%)	207	273
	Interlayer	EP (HS)/polyamine/Al		
	Topcoat	PUR (acrylic)/HDI		
B	Primer	EP (HS)/polyaminoamide/Al (2 wt.%)	447	291
	Interlayer	EP (HS)/polyaminoamide/Al (2 wt.%)		
	Topcoat	PUR (acrylic)/HDI		
C	Primer	EP/polyamide/Zn (75 wt.% in a dry coating)	C1: 282 C2: 410	282
	Interlayer	EP/polyamide/Al (1-2.5 wt.%)		
	Topcoat	PUR (acrylic/polyester)/HDI		
D	Primer	EP (HB)/polyamine/–	–	303
	Interlayer	EP (HB)/polyamine/–		
	Topcoat	PUR (acrylic)/HDI		
E	Primer	EP/polyamidoamine/Zn (94 wt.% in a dry coating)	281	286
	Interlayer	EP/polyaminoamide/MIOX (58 wt.%)		
	Topcoat	PUR (acrylic)/HDI/MIOX (47 wt.%)		
F	Primer	EP/polyaminoamide/Al (10 wt.%)	281	290
	Interlayer	EP/polyamine/MIOX (12 wt.%), Al (10wt.%), Zn phosphate (5 wt.%)		
	Topcoat	PUR (acrylic)/HDI		
G	Primer	EP/polyaminoamide/Zn phosphate (10.6 wt.%)	188	276
	Interlayer	EP/polyaminoamide/MIOX (36.5 wt.%)		
	Topcoat	PUR (acrylic)/HDI		
HDI – hexamethyl diisocyanate				

Laboratory test methods

Physiomechanical properties of coatings

The following physical and mechanical properties of coatings have been tested:

− adhesion by the pull-off method acc. EN ISO 4624 [14],
− adhesion by the cross-cut method acc. EN ISO 16276-2 [15],
− impact resistance acc. EN ISO 6272-1 [16],
− hardness acc. EN ISO 1522 [17] (Persoz pendulum),
– cupping test acc. EN ISO 1520 [18].

Corrosion resistance of coatings

Resistance of coating systems to corrosive factors was examined acc. to EN ISO 9227 [19] and ISO 20340 [20]. Duration of a salt spray test was 1440 h acc. to EN ISO 12944-6 [21] for over 15 years' durability and a corrosivity category of C5I. The test was repeated three times (4320 h). A single 168 hour test cycle acc. to [20] included: 72 h exposure in a UV chamber (4 h, 60°C, UVA 340 lamp/4 h condensation, 50°C); 72 h salt spray exposure (salt mist, 35°C); 24 h in low temperature conditions (-20°C). The cycle was repeated 25 times (4200 h).

Coating resistance to accelerated aging

Accelerated testing of resistance to atmospheric conditions (UV, moisture) was conducted in a Q-Panel QUV chamber acc. EN ISO 16474-3:2014-02 [22]. UVB 313 lamps and the following cycle were employed: 4 h UV/60ºC + 4 h condensation/40ºC. Exposure time: 1000 h. The test conditions were adopted from EN 13523-10 [23].

After 1000 h exposure in a UV chamber, the change in gloss and colour were determined. The gloss was measured using a TRIGLOSS multi-angle glossmeter by Byk, acc. to EN 2813 [24], and the colour via SP 62, X-Rite, with a measurement geometry d/8, using a method that takes into account gloss (SPIN), and illuminate/observer/10° − acc. to ISO 7724-2 [25]. The colour measurements were given in the CIELAB system (L*a*b*).

Preparation of samples for laboratory tests

Mechanical properties (impact resistance, hardness and cupping) and the resistance to accelerated aging were examined for coatings applied on standardized panels, not subjected to abrasive blasting (150 mm x 70 mm x 0.8 mm).

Corrosion resistance tests were carried out using panels measuring 150 mm x 100 mm x 4 mm and T-shaped samples, for coatings applied on substrates blasted prior to application to reach Sa 2½ grade.

Field test results

Coatings on bridges were evaluated visually for chalking, blistering, peeling, cracks and corrosion according to EN ISO 4628 [26]. The adhesion of the coatings was determined with the cross-cut method, whereas the barrier properties with electrochemical impedance spectroscopy (EIS). Ionic contamination in selected hazard zones on bridges was also evaluated. The locations of measurements were selected depending on the design of the bridge; exemplary locations are shown in Figure 1. The guiding principle behind the selection was to make sure that the locations included areas with the highest corrosion risk (lower flange or places where debris falls from a lane, sheltered areas inside the structure and locations of different exposure to solar radiation from both sides of the bridge on the webs or top flanges). The test results are presented in Table 3.

It was expected that in places with the greatest corrosive risk, the coatings would bear the most damage, which can be assessed both visually and by examining the adhesion as well as by EIS method. Also, it was expected that there would be a diversification of damage depending on the type of system and on the differences in the total thickness of the coating systems (falling however within the recommendations of the standard [1]).

Table 3. Test results of coating systems applied on bridges

System	Average thickness, µm	Adhesion, degree	Destruction, degree	Average logIZI at 0.1 Hz	Average ionic contamination, mg/m² *
A	207	0	no damage	8.0	1560
B	447	0–2	chalking 2 corrosion Ri1 corrosion in crevices	9.1	34
C1	252	2	chalking 2	8.2	142
C2	410	2–3	chalking 1, on the lower flange 2 corrosion Ri1	8.6	186
E	281	2	chalking 3	8.7	215
F	365	0	chalking 1 corrosion in crevices	9	103
G	188	1	chalking 1 corrosion on sheet stacks and on the surface of the lower flange	7.7	414

* the concentration of ionic contamination provided here is not an average of multiple measurements and is given only for informational purposes. It tells us about the levels of ionic impurities on bridge structures in Poland

Results of the EIS tests prove that after over a dozen years of service on bridges, coatings still show very good barrier properties (a detailed EIS interpretation of the results of the field and laboratory tests will be carried out in the second part of the project and will be the subject of a separate publication). On all bridges tested, the log IZI value at 0.1 Hz was in most cases above 8 (Table 3) – reduced barrier properties were observed only locally, as can be seen in the case of the bridge in Góra Kalwaria (Fig. 1, Table 4). No link was found connecting reduced coating resistance with the location of coating exposure on bridges, or with the type of the system used. However, a slight reduction of the protective properties of coatings of a thickness below 250 µm was observed. Varying degrees of chalking of the topcoat were observed for different coating systems.

Fig. 1. Bridge in Góra Kalwaria: a) general view, b) arrangement of measuring vessels

Table 4. Impedance modulus at frequency 0.1 Hz as a function of the measurement location on the bridge in Góra Kalwaria

Measuring vessel	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
log $Z_{0,1}$ po 2h $\Omega\cdot cm^2$	8.35	8.44	8.80	5.89	6.67	9.04	9.32	9.04	8.55	8.61	8.54	9.65	8.68	8.70	9.79
log $Z_{0,1}$ po 24 h, $\Omega\cdot cm^2$	8.09	8.19	8.67	6.00	5.71	8.28	9.02	7.97	8.43	8.44	8.35	8.90	8.85	9.03	8.56

Laboratory test results

Physiomechanical properties

All coating systems selected from the ones applied on bridges are characterized by very good adhesion to the substrate and by good impact resistance (weight dropped from 100 cm) (Table 5). The pull-off force for most of the tested systems is 8-9 MPa - a cohesive tear occurs in the topcoat or in the interlayer. No separation of the coating system from the substrate was observed.

Hardness and cupping are strongly related to each other, and depend on respective type of paint in the coating system.Low cupping was characteristic for hard coatings and as hardness of the coating decreased the cupping increased.

Table 5. Physiomechanical properties of coatings

System	Average adhesion		Impact resistance, drop height	Hardness, s	Cupping in mm
	Pull-off method, MPa	Cross-cut method, degree			
A	8.51 D	0	100	237	0.7
B	9.35 D	0	100	220	0.6
C	9.6 D	0	100	151	1,7
D	8.55 C	0	50	171	1.3
E	8.95 D	0	100	111	1.1
F	5.14 D	0	100	81	1.8
G	9.1 C	0	100	95	6.1

Resistance of coatings to corrosive factors

There was no blistering or corrosion on all of the un-scratched coatings (panels and T-profiles) after 4320 h (3 cycles of 1440 h each) of exposure to salt spray and after 25 cycles (4200 h) of tests in variable conditions (UV/salt mist/temp. -20°C acc. [20]) (Table 6). Blisters and corrosion appeared only on the scratched panels. Under continuous exposure to corrosion at a constant temperature (5% NaCl spray, temp. 35°C) there was less damage in the scratch than in variable corrosive conditions. The least damage was observed on coating systems E and F, with primers containing Al and Zn pigmented flakes. Coating systems B and C, in which Al and Zn pigmented primers were also used, were more damaged around the scratch marks. This can be explained by the greater metal flake content in the primer and by the presence of micaceous iron oxide in the interlayer of coating systems E and F.

Generally it can be concluded that for similar test duration, greater damage, both in terms of corrosion and blistering around the scratch mark, is observed in the tests involving variable cycles and where the changes in the subsequent cycles are not significant.

Table 6. Resistance of coatings to salt spray and changing conditions

System	Sample type	Blistering				Corrosion, width from scratch			
		Salt spray		Variable conditions		Salt spray		Variable conditions	
		1440 h	3 x 1440 h (4320 h)	8 cycles (1344 h)	25 cycles (4200 h)	1440 h	3 x 1440 h (4320 h)	8 cycles (1344 h)	25 cycles (4200 h)
A	no scratch	no change	no change	no change	no change	no change	no change	no change	no change
	with scratch	single S2–S3 around the scratch mark	single S4 around the scratch mark	3(S2)–3(S3) around the scratch mark	4(S3)–4(S4) around the scratch mark	1–3 mm	3–4 mm	3–4 mm	up to 7 mm
	T-shape	no change	no change	no change	no change	no change	no change	no change	no change
B	no scratch	no change	no change	no change	no change	no change	no change	no change	no change
	with scratch	no change	single S(3)–S(4) around the scratch mark	(S2)–4(S3) around the scratch mark	4(S3)–4(S5) around the scratch mark	no change	up to 1 mm	3–6 mm	5–8 mm
	T-shape	no change	no change	no change	no change	no change	no change	no change	no change
C	No scratch	no change	no change	no change	no change	no change	no change	no change	no change
	with scratch	no change	no change	2(S3) – 4(S4) around the scratch mark	5(S4) around the scratch mark	no change	up to 1 mm	5.5–8 mm	9–16 mm
	T-shape	no change	no change	no change	no change	no change	no change	no change	no change
D	no scratch	no change	no change	no change	no change	no change	no change	no change	no change
	with scratch	no change	no change	2(S2)–3(S3) around the scratch mark	4(S4) around the scratch mark	2–4 mm	up to 9 mm	up to 3 mm	up to 6 mm
	T-shape	no change	no change	no change	no change	no change	no change	no change	no change
E	no scratch	no change	no change	no change	no change	no change	no change	no change	no change
	with scratch	no change	no change	no change	do 3(S3) around the scratch mark	no change	up to 2 mm	no change	up to 6 mm
	T-shape	no change	no change	no change	no change	no change	no change	no change	no change

cont. Table 6. Resistance of coatings to salt spray and changing conditions

F	no scratch	no change	no change	no change	no change	no change	no change	no change	no change
	with scratch	single S3–S4 around the scratch mark	single S4–S5 around the scratch mark	2(S2) around the scratch mark	up to 2(S3) around the scratch mark	1–2 mm	up to 2.5 mm	up to 2 mm	up to 5 mm
	T-shape	no change	no change	no change	no change	no change	no change	no change	no change
G	no scratch	no change	no change	no change	no change	no change	no change	no change	no change
	with scratch	no change	single S4 around the scratch mark	2(S2)–(S3) around the scratch mark	3(S4)–4(S4) around the scratch mark	1–3 mm	to 4 mm	4–6 mm	6–7 mm
	T-shape	no change	no change	no change	no change	no change	no change	no change	no change

The resistance of coatings to accelerated aging

There were nearly no changes in the colour of the coatings B and G after 1000 h of exposure in the UV chamber; a ΔE below 1 is visually undetectable (Table 7). The most significant change in colour was observed for coating F (ΔE = 5.84), as a result of its intensive sheen. The colour difference of the remaining coatings does not exceed 5, which is a very good result in the case of such extended exposure to UV radiation emitted by UVB 313 lamps. The gloss value did not undergo significant change either.

Following changes in gloss and colour permitted by standard [27] (depending on the resistance category) are acceptable:

– colour – 3 (category R_{uv2}) or 5 (category R_{uv3}),

– gloss – 30% (category R_{uv2}) or 60% (category R_{uv3}),

Therefore, the change in gloss and colour in the majority of the tested coatings falls within the ranges provided by the standard.

Table 7. Properties of coatings after 1000 h of exposure in a UV chamber

System	Gloss 60°, %			Colour change ΔE	Chalking*, degree
	initial	after exposure	Gloss change, %		
A	89	83	-7	3.32	0 (0)
B	89	74	-17	0.69	0 (2)
C	73	67**	-8	2.98	1 (1–2)
D	87	75**	-14	4.36	4 (–)
E	6	5	-17	4.35	0 (3)
F	7	11	+43	5.84	0 (1)
G	75	64	-15	0.36	0 (1)

* in brackets – chalking degree in natural conditions

** after removal of the chalked layer

From all of the topcoats selected among the ones applied on bridges, the smallest changes were observed in the case of coatings A, B and G. Following the exposure, all of these coatings possessed bands originating from the binder which was not exposed to UV radiation (Fig. 2).

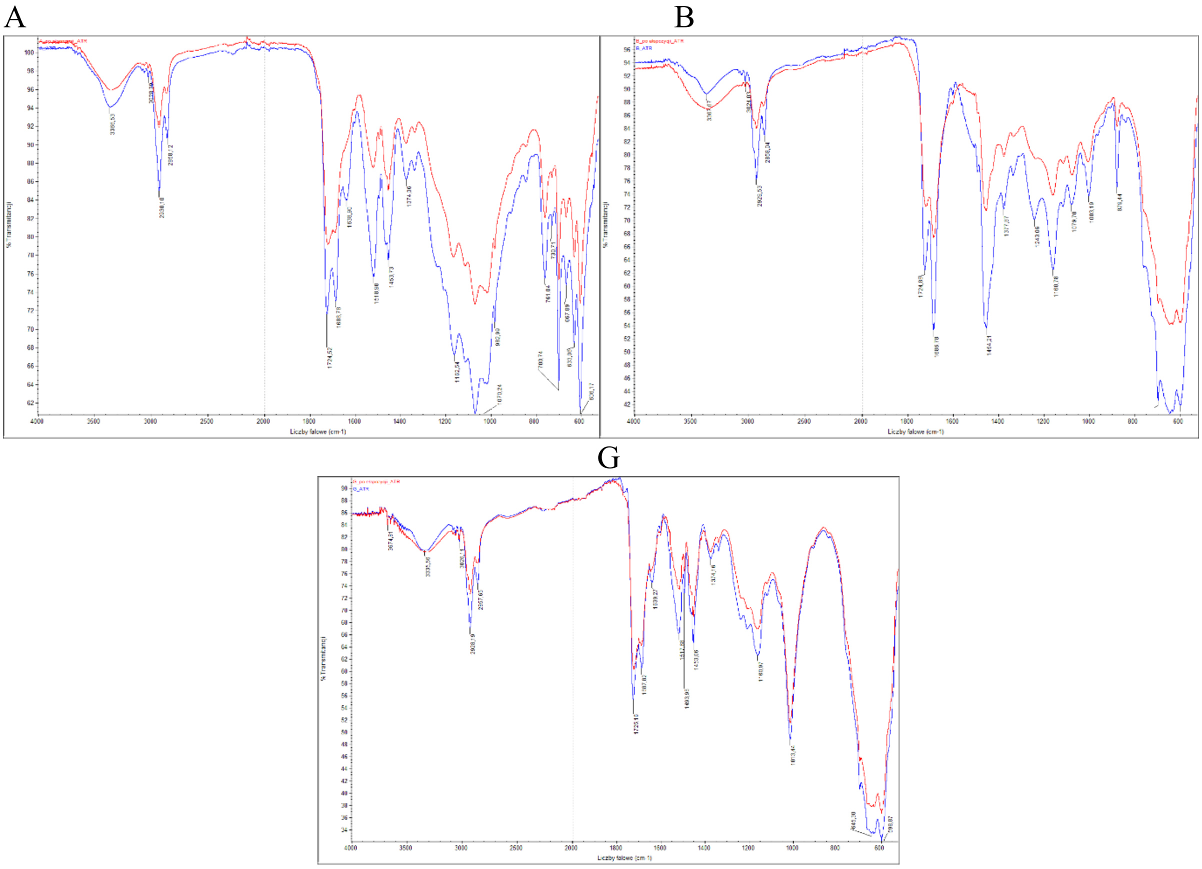

Fig. 2. Spectra of topcoats in systems A, B and G: blue line – before exposure, red line – after 1000 h of exposure in a UV chamber

In case of coatings C, D, E and F, an almost complete disappearance of NH- (ca. 3300), CH−, CH_2− (2930, 2860, 1452, 1336), C=O (1725, 1687, 1638), C−N, N−H urethane (1517) and C−O−C acrylic (1161) bands is observed, which is clearly visible for coating D (Fig. 3).

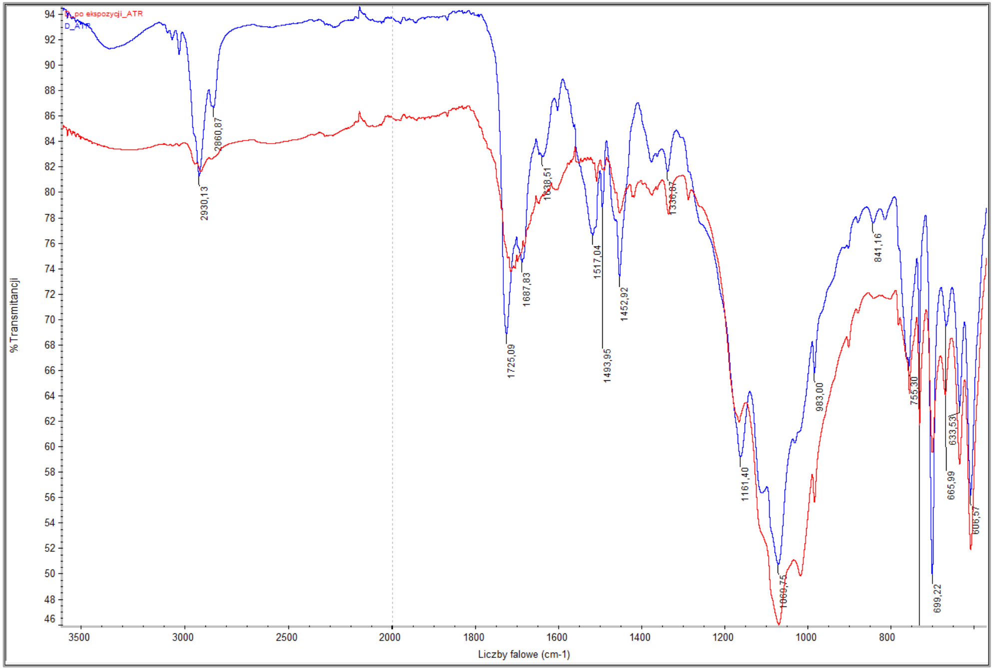

Fig. 3. Spectra of topcoat in system D: blue line – before exposure, red line – after 1000 h of exposure in a UV chamber

After over a dozen years of service, the coatings on bridges behave similarly to the coatings submitted to 1000 h exposure in a QUV chamber. The bands generated by coatings exposed to natural atmospheric conditions on bridges remain the same or disappear in the same way as in the laboratory conditions (Fig. 4). The degree of chalking defined for coatings applied on bridges does not always overlap with the degree defined in the laboratory for the respective systems. The degree of chalking is greater in natural conditions than it is in the test chamber (Table 7).

Fig. 4. Spectra of topcoats in system C: green line – non-aged coating, blue line – coating aged in the natural environment (removed from the bridge), red line – coating aged in laboratory conditions (1000 h of exposure in a UV chamber)

Conclusions

All coating systems applied on bridges retained their protective properties. Corrosion was reported on some bridges in critical areas, especially in crevices or in areas where apparent application errors were made. Similar results were achieved when the same coating systems were tested in laboratory conditions. In accelerated test conditions, damage was only reported on scratched coatings. It was also noted that greater blistering and corrosion around the scratch marks was observed on coatings exposed, for the same amount of time, to variable, rather than constant (5% NaCl at constant temperature), corrosive conditions.

Test in simulated atmospheric conditions, in a UV chamber, also revealed a similar mechanism of degradation as in the case of coating systems exposed to natural conditions. IR spectra of the coatings removed from bridges and of laboratory samples show that bands characteristic for polyurethane binders either disappear or remain in place. Certain differences occurred in terms of the intensification of the chalking phenomenon.

The coatings tested in laboratory conditions in most cases demonstrated very good adhesion to the substrate and resistance to mechanical factors while maintaining their colour and gloss.

On the basis of the field studies conducted on bridge structures located in areas of strong corrosion risk (taking into account areas of the most intensive corrosion risk on the bridges themselves, i.e. areas which accumulate road salt) it is concluded that there are no differences in coating degradation depending on the system used (provided the thickness of the system is as recommended in standard [1]). This indicates that the coatings are of very high quality and have met the requirements of the Technical Recommendations document, i.e. a document in which paints are approved for use on bridges. This fact suggests that the use of more economical systems should be considered and emphasis should be placed on the precise supervision of certified inspectors for the duration of the works.

On the basis of the conducted tests it can be assumed that the results of the laboratory tests obtained so far, correspond to a large degree to the actual behaviour of coatings after a dozen or so years of service in a natural environment characterised by cat. C4-C5 corrosivity. Moreover it may be noticed, that the requirements found in ISO 20340 [20] are too restrictive, whereas the ones in EN ISO 129444 are too weak for durability category H and corrosivity category C5. Rising the maximum durability period from over 15 years to over 25 years should also be considered.

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