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ANODIC-MODIFIED ANTICORROSIVE COATINGS

M. Černý, J. Filípek

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Abstract

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Steel machine parts are exposed to electrochemical corrosion. This applies to many environments including atmosphere, soil, water, and even various fertilizers. High-carbon steel and low-alloyed steel are not stable (in terms of thermo-dynamics), do not feature effective passivation, and even the corrosion products do not form a stable protection layer. As a result, special anti-corrosion protection is critical. In heavy-corrosion environment, paint systems containing Zn have proven to be very effective.

Presented text describes verification of paint systems with high Zn content and compares them to galvanic Zn coatings. Steel samples with protective coatings have been tested in condensation chamber with neutral salt-spray. This way, corrosion resistance of Zn-rich paint systems and galvanic Zn coatings has been evaluated and compared. Galvanic Zn-coatings have shown complete decomposition during the chamber exposition. Thus, further testing was adopted for paint systems only with a special attention being paid to gradual degradation of anti-corrosion layer. Final part of the text lists reasons of coating degradation process and outlines possible solutions of the issue.

corrosion, protection against corrosion, zinc coating systems, galvanization

The intensity and development of material corrosion degradation within the complex of heterogeneous reactions are highly dependent on environment aggressivity, material structure and surface. Material surface disintegration is thus evoked by several factors, such as chemical, physical, and biological phenomena. Application of physical influences and impacting actions (such as rate of medium flow, rapid pressure changes, impact influences) is generally called as pseudo-corrosive damage, cavitation and abrasion.

The corrosion environments are of very different nature and origin. The most frequent environment is an earth's atmosphere. The other critically important media are soil and water environments. Following influences enhance corrosion activity: high content of acids, alkalis, salts, and organic chemicals of different concentrations. Corrosive impact is also increased in gas environments with changing pressure and temperature.

Corrosion degradation is often connected with material mass decrease and drop (not valid e.g. for intercrystalline corrosion and/or transcrystalline corrosion). Material loss and its structural degradation cause the changes in mechanical properties and visual changes.

The thermodynamic aspect of corrosion does not allow interaction of material with corrosive environment without creation of corrosive degradation. This fact applies to all construction materials.

The steel present in aggressive environment is affected by electro-chemical corrosion, because it is thermodynamically unstable, it does not have ability of effective passivation and the corrosion products do not create stable protective layer (Kraus, 2000).

The basic means of anti-corrosion protection are as follows: material selection, optimization of corrosive environment, optimised design, use of electro-chemical protection, application of protective layer (Mohyla, 1981). One of the several solutions how to control or decelerate the corrosion attack is the application of coating layers with zinc content.

Development in the field of coating applications is highly affected by ecological desirability. The extensive research in the area of non-toxic anti-corrosive pigments was started as a consequence of tendency of decreasing the content of volatile substances and reduction of lead and chromium-based anti-corrosive pigments. One of the important and perspective non-toxic anti-corrosive pigments is zinc in powder of lamellar form. In this case, the electro-chemical effect is used as a primary anti-corrosive protection (MM Průmyslové spektrum, 2002). The zinc coatings originally represented solely electro-chemical protection mean. The protection is realized through creation of galvanic cell, where the steel and zinc represent the electrodes, and the zinc serves as soluble anode (Hochmannová, 2007). The cathodic protection is active until the pores in the coating system are plugged. Consequently, the electro-chemical action changes into barrier one. The zinc reacts with moisture and atmospheric oxygen. The hydroxide zinc is created. This reaction induces increase of coating volume, which represents the barrier protection. The electro-chemical protection is active even after the damage of barrier layer.

The zinc is applied to the steel surface as a constituent of coating agent. According to the binding agent type, there are inorganic zinc-silicates and/or organic solvents.

The most frequent binding agents are alkyl(ethyl)-silicates and alkaline metal silicates. Since the alkyl-silicates are soluble in the organic solvents, they belong to soluble type. The alkaline metal silicates are used in inorganic water-based zinc coatings. Organic binding agents are represented by epoxids, polyurethanes (two-component or one-component and hardened by the air moisture), and other types of organic binders. The hardening is in case of inorganic zinc coatings realized through the reaction of binder and zinc.

Important role plays the type (shape) of metallic grain (Kalenda *et al.*, 2003). The powder zinc is a grey powder, built of the spherical particles of metallic zinc (see Fig. 1a). It is produced by pressure distillation of zinc in inert atmosphere and vapor condensation in large condensation chambers and/or atomization of molten zinc. In order to eliminate the product contamination, the direct production (reduction of zinc ore) is substituted by indirect production, which is evaporation of regenerated metal at temperature of 900 °C. The lamellar (floccular) particles are less frequent in the coating layer in comparison with spherical particles of zinc. The floccular particles (see Fig. 1b) are produced by milling in fluid medium (petrol suspension) with addition of steatite or other surfactant, during which the dispersion of flakes in the form of paste is created.

Application of zinc-based coatings is defined by several standards:

ČSN EN ISO 10683 Spojovací součásti – Neelektrolyticky nanášené povlaky ze zinkových mikrolamel (2001) / Connective components – Non-electrolytically coated layers from zinc micro-lamellas.

ČSN EN 13858 Ochrana kovů proti korozi – Neelektrolyticky nanášené mikrolamelové povlaky zinku na součástech ze železa nebo oceli (2004) / Metal anti-corrosive protection – Non-electrolytically coated zinc micro-lamella layers on steel or iron components.

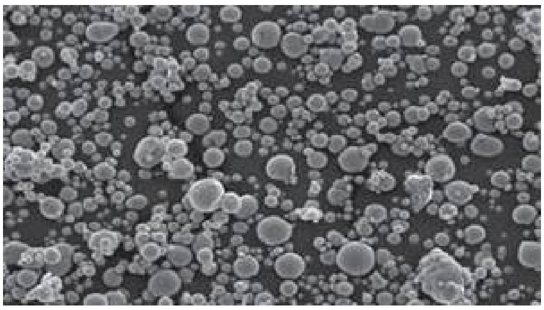
The military regulations are subjected to standard MIL-C-87115A Coating, Immersion Zinc Flake / Chromate Dispersion. There are also other standards such as VDA (The Society of German Automotive Industry). This surface treatment complies with EU 2000/53/EC, concerned with car production and recycling with regard to environment protection.

The mechanical testing of zinc coatings is generally performed by traditional methods (Horák *et al*, 2010) and/or newly developed methods such as nanoindentaion described e.g. in Severa *et al.* (2010a, 2010b).

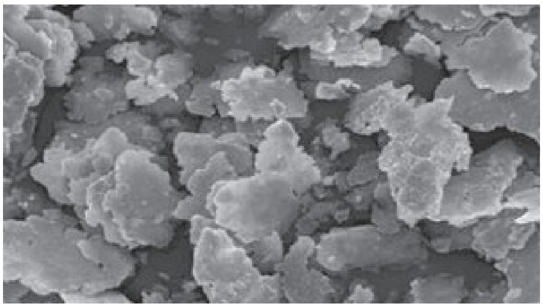
MATERIAL AND METHODS

Preparation of testing specimens

The laboratory corrosion tests were performed using the metal sheets made of steel according to ČSN 41 1375 (S235JRG2) and dimensions of 65 x 160 x 0.6 mm. The surface of the sheet was mechanically cleaned and degreased. All together, six types of coatings were tested (see Table I, Fig. 2).



a – Powder zinc

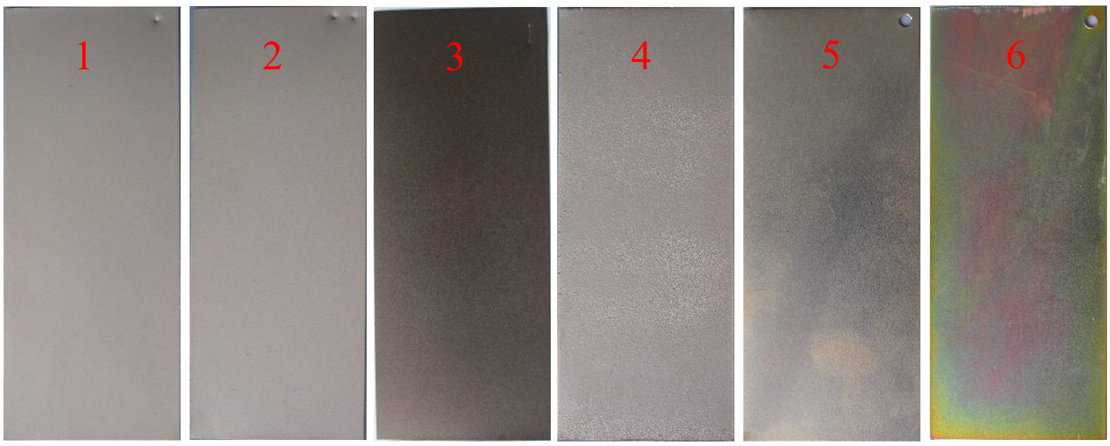


b – Lamellar zinc

1: *Zinc particle types*

I: *Protection coating specifications*

	Protection coating	Specifications
1	Delta-Protekt KL 100	Inorganic protective system based on zinc micro-lamellas. Inorganic primary system with cathodic protection of surface, so-called base-coat. Hardening is performed at 180–240 °C. It is recommended to combine it with top-coats Delta-Protekt VH 300, VH 301 GZ, and Delta-Seal.
2	Delta-Protekt KL 100 + Delta-Protekt VH 300	Delta-Protekt VH 300 is a coating material based on lithium-silicon-oxide polymer. After hardening it creates the transparent layer (with barrier effect even at small thin layers) on base coats DELTA PROTEKT KL 100 and/or DELTA TONE 9000. The mechanical properties, especially hardness, are improved.
3	Xylan	The coatings Xylan are purposely formulated (Technicoat, 2010). These materials combine the lubricants with low friction coefficients and highly thermally resistant organic polymers. Selected characteristics: low coefficient of friction (down to 0.02), wear resistance at high pressure, corrosion and chemical resistance, resistance against solar radiation, salt water, and operating fluids, high range of operation temperatures from −250 to +285 °C, flexible range of burning-in temperatures from 150 to 430 °C, adhesion to different base materials. Application by traditional methods – spraying, dip/spin (Holoubek, 2002) and other.
4	Würth Zinc in spray	Zinc is contained in a powder form. It is intended for protecting the ferrous metals, welds, and damaged surfaces. It provides the cathodic protection and it is weather proof and water proof up to the temperature of 500 °C.
5	Galvanizing	The reason for selection of this coating is following. The zinc coating producers often compare the resistance of their products with galvanic zinc.
6	Galvanizing + chromating	Chromated layers provide increased corrosion resistance due to passivating effect of chromium compounds and creating of physical barrier effect.



2: *Unexposed samples (etalons)*

Corrosion tests

The effectiveness of coatings was tested in condensation chamber (ČSN EN ISO 9227):

- temperature 35 °C, relative humidity 100 %, salt solution concentration 50 g/l, feeding of sprayed salt solution 0.5 l/h, inclination of specimens 20°
- duration of exposition in the condensation chamber 7, 14, and 28 days (168, 336, and 672 hours).

The evaluated parameters of the coatings

Before and during the corrosive exploitation, the following parameters were evaluated:

- thickness of the protective layer (ČSN EN ISO 2808),
- visual evaluation,
- cupping test (ČSN EN ISO 1520),
- tearing test of adhesion (ČSN EN ISO 4624),
- bending test on cylindrical bar (ČSN ISO 1519),
- cross-hatch test (ČSN ISO 2409).

RESULTS AND DISCUSSION

The thickness of the surface layer

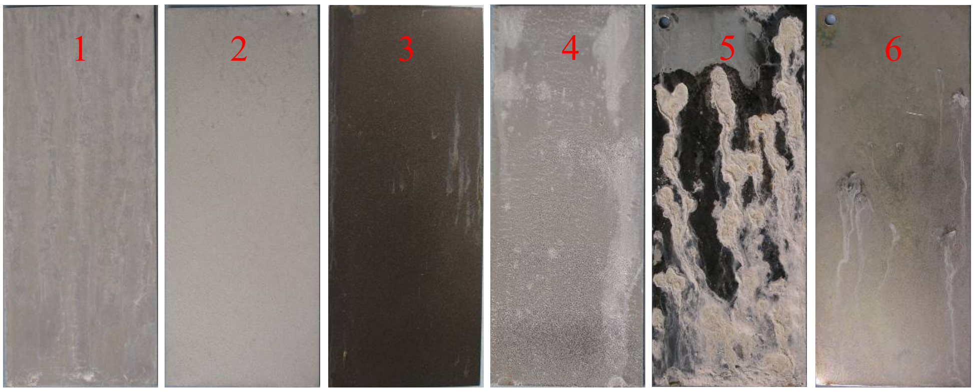
The thickness of the surface layers was measured by the equipment Permascope. Measured values are listed in Table II.

Visual evaluation

According to standard ČSN EN ISO 9227, the specimens were removed from the salt chamber in the interval of 7, 14, and 28 days. During each removal, the level of degradation was visually evaluated (see Fig. 3).

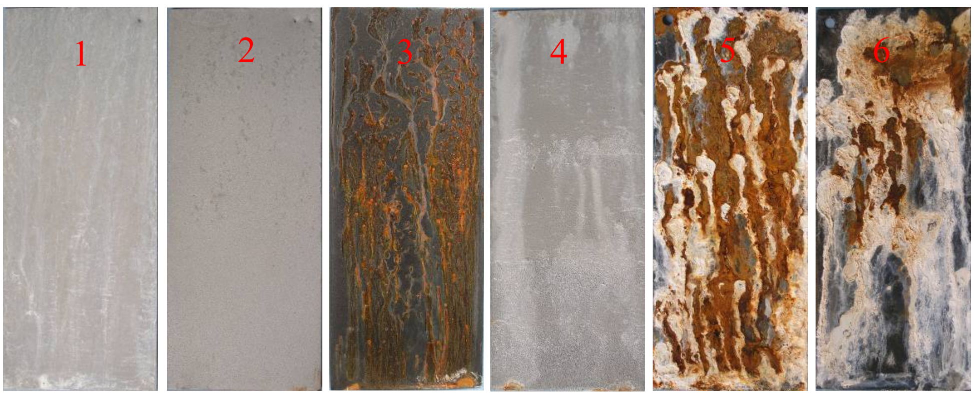
II: *Protection layer thickness values*

	Protection system	Thickness of the layer [μm]						Average thickness	Coefficient of variation
1	Delta-Protekt KL 100	5.5	7.7	4.5	6.3	4.7	5.3	5.67	0.191
2	Delta Protekt KL 100 + Delta-Protekt WH 300	8.2	7.9	7.3	9.8	5.8	8.4	7.90	0.153
3	Xylan	5.7	4.6	6.3	3.5	4.6	3.8	4.75	0.207
4	Würth	63	61	65	67	66	70	65.33	0.044
5	Galvanizing	4.5	3.5	2.7	4.1	3.7	3.1	3.60	0.166
6	Galvanizing + chromating	5.2	4.3	3.6	4.9	3.9	3.6	4.25	0.146



a: 7 days of exposition

b: 14 days of exposition



c: 28 days of exposition

3: *Development of coating corrosion damage*

Durability of the surface protective systems in the salt solution is highly variable. The surface layers No. 5 (galvanized) and No. 6 (galvanized and chromated) were totally degradated after 28 day exposition and thus they were excluded from the following tests.

Cupping test

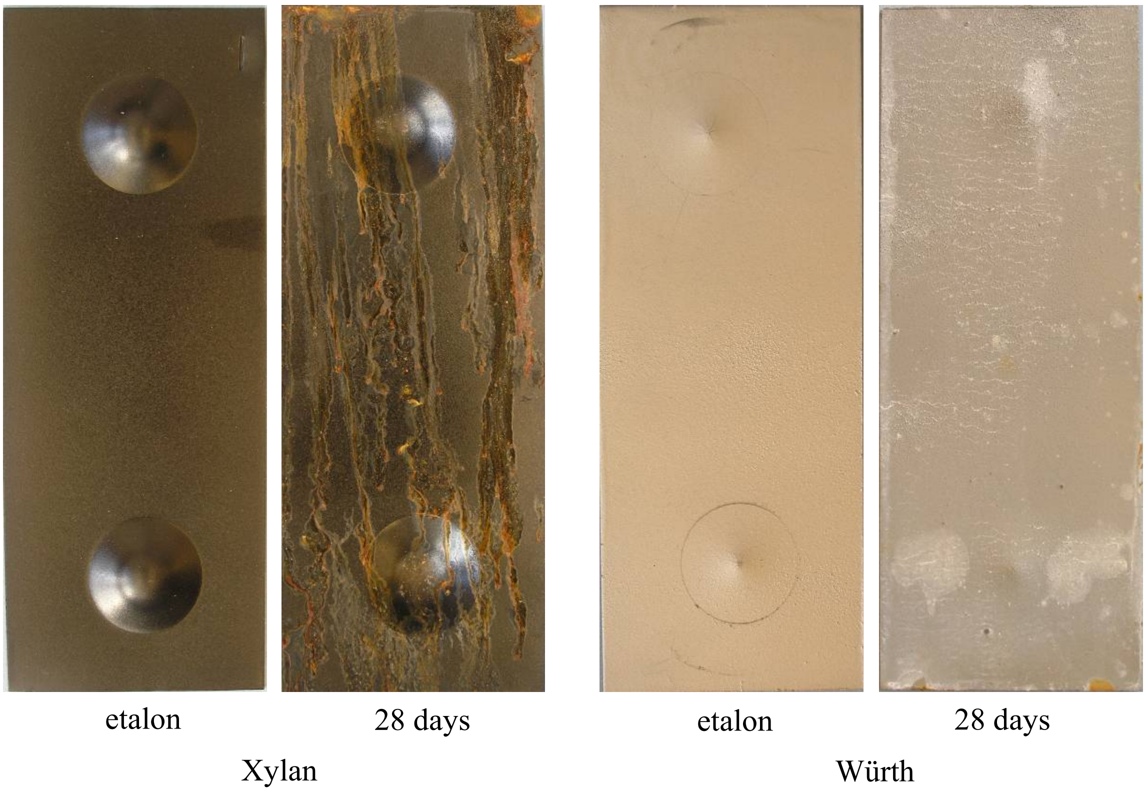
This test evaluates resistance of the surface against cracking or separating from the metallic base after having been gradually strained. The results of the test (Table III, Fig. 4) show on good resistance of Xylan layer and the worst resistance of Würth layer.

Cross-hatch test

According to the results listed in Table IV and shown in Fig. 5, it is clear that the best adherence of the layer to the base was received in case of specimen No. 3 (Xylan). The specimen No. 1 (Delta-Protekt KL 100) was evaluated as a second best. Good adherence is in this case given by only one application layer. The complete system MKS-DELTA

III: *The results of cupping test*

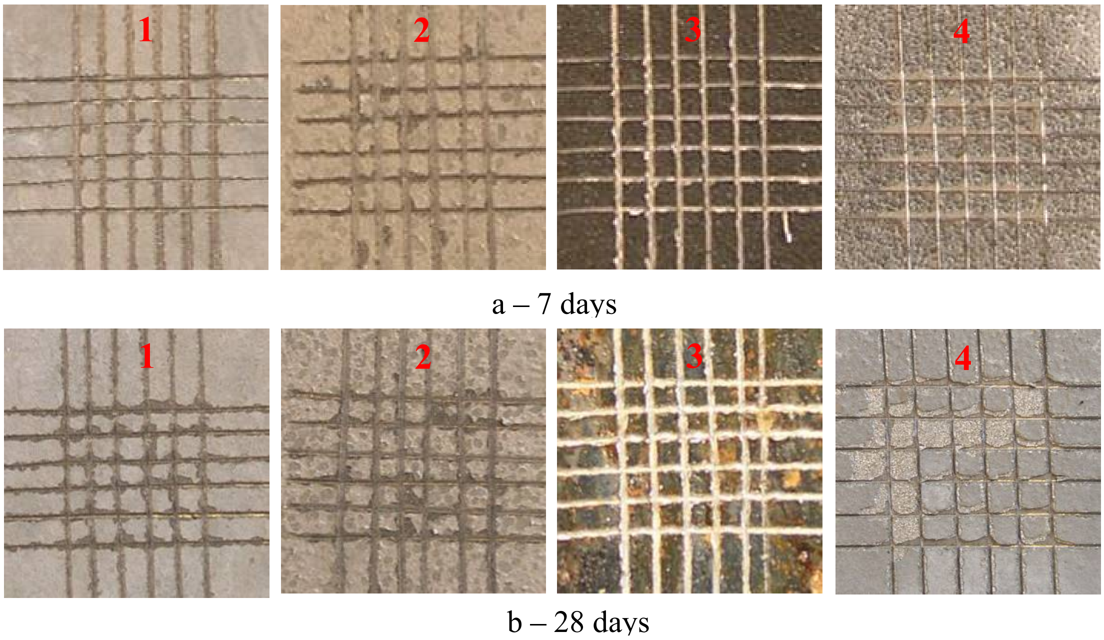
	Protection system	Duration of exposition (days)			
		etalon	7	14	28
1	Delta-Protekt KL 100	> 6	> 6	2.4	1.3
2	Delta Protekt KL 100 + Delta-Protekt WH 300	5.5	3.68	1.92	0.91
3	Xylan	> 6	> 6	> 6	> 6
4	Würth	2.06	1.93	1.18	0.99



4: *Cupping test*

IV: *Cross-hatch test evaluated according to ČSN ISO 2409*

	Protection system	Duration of exposition (days)			
		etalon	7	14	28
1	Delta-Protekt KL 100	0	1	1	2
2	Delta Protekt KL 100 + Delta-Protekt WH 300	1	2	3	3
3	Xylan	0	0	0	0
4	Würth	0	2	2	4



5: *Cross-hatch test applied to coatings exposed in salt chamber*

(specimen No. 2) is composed of two layers. Its adherence is worse than in the case of two previous systems. The system Würth has shown the signs of decreased adhesion immediately beginning of degradation (influenced by mechanical properties of the layer).

Bending test on cylindrical bar (Table V, Fig. 6)

The systems DELTA MKS and Xylan were found to be resistant against bending and non of the specimens cracked. The bending test damaged the zinc in spray Würth, the surface was cracked even on the bars of large diameter.

Tearing test of adhesion (Table VI and Fig. 7)

According to the results listed in Table VI it is obvious that biggest resistance was found in case of coating Xylan.

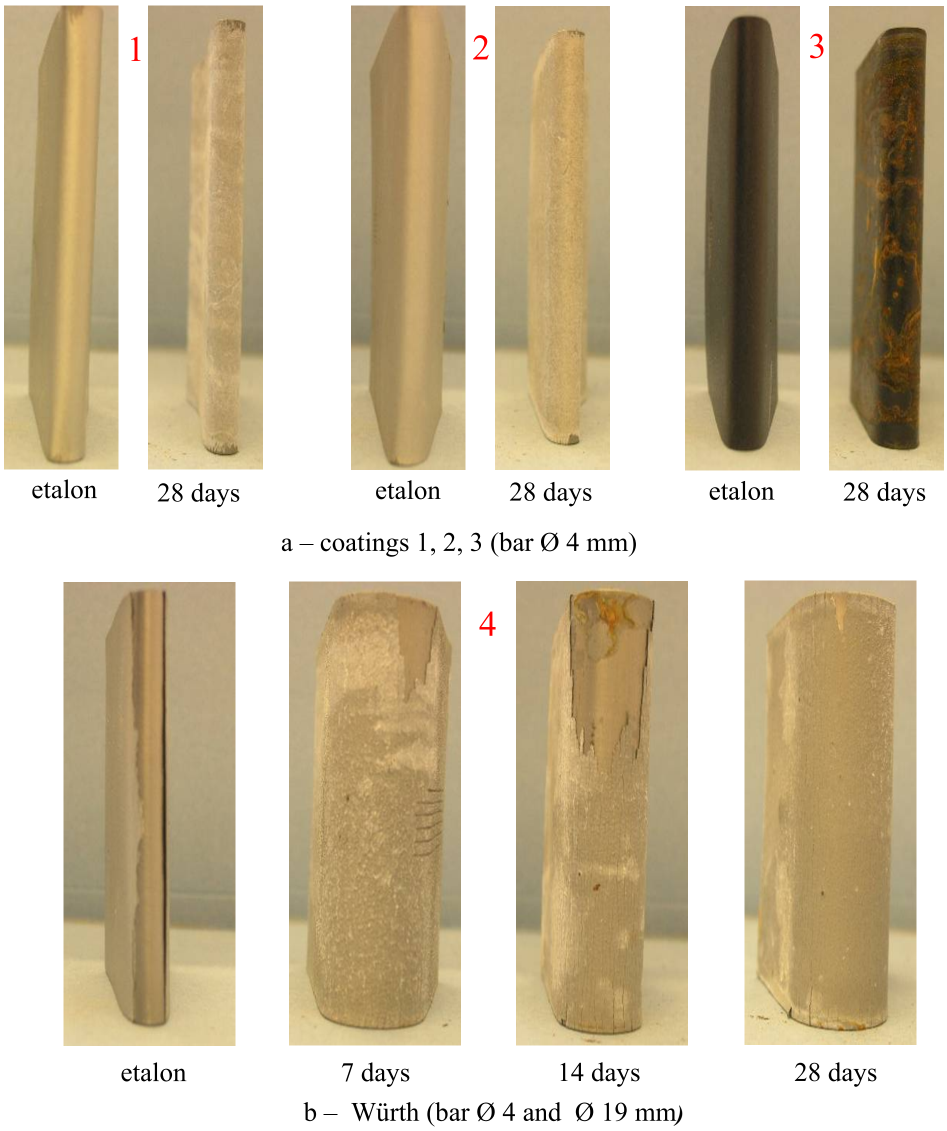
The visual evaluation clearly proven the quality of zinc coatings Delta-Protekt KL 100, Delta-Protekt VH 300 and Würth. These coatings show a high resistance even after 28 days of exposition in a salt chamber. Surprisingly, rather fast degradation was found in case of Xylan. Addition of Zn lamellas was relevant, concerning resistance against corrosion, in case of Delta-Protekt KL 100, Delta-Protekt VH 300 and Würth (powder zinc particles in case of this coating). Compared coating created by standard galvanizing was completely inadequate after 7

V: *Bending test results (bar diameter 4/19mm)*

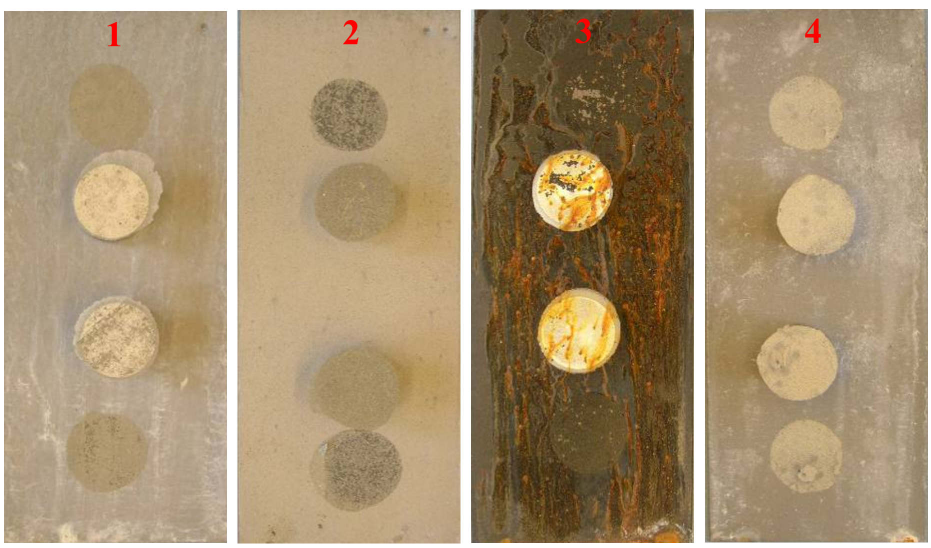
	Protection system	Duration of exposition (days)			
		etalon	7	14	28
1	Delta-Protekt KL 100	unfaulted			
2	Delta Protekt KL 100 + Delta-Protekt WH 300	unfaulted			
3	Xylan	unfaulted			
4	Würth	Ø 4	Ø 19	Ø 19	Ø 19

VI: *Tearing test of adhesion, ČSN EN ISO 4624 [MPa]*

Duration of exposition (days)	Protection system			
	Xylan	Delta-Protekt KL 100	Delta-Protekt KL 100 + Delta-Protekt VH 300	Würth
Etalon	adhesive	0.5	1	0.5
7	adhesive	0.5	1	0.5
14	adhesive	0.5	1	0.5
28	1	0.5	1	0.5



6: *Bending test on a cylindrical bar*



7: *Tearing test of adhesion (28 days of exposition)* days of exposition and inadequate after 14 days of exposition in case of galvanizing + chromating.

Mechanical testing revealed the weak results of zinc coatings loaded mechanically. The high content of filler replacing binding material results in decrease of resistance against bending and adhesion in case of cross-hatch as well as tearing test. The only exception is Xylan, where the normal as well as tangential strength of anti-corrosive layer is increased due to content of slip particles and higher ratio of polymer binder.

The coating Würth is especially convenient for temporary protections lasting about 12 months. Its extreme softness creates a layer, which is not resistant to mechanical loading, but its adhesive strength is satisfying for quick and cheap cathodic protection. Powder form of zinc particles is probably more convenient, when considering adhesive-cohesive behaviour of coating. But not even the high formability is able to absorb the large deformations of base material.

Generally, the concept of cathodic protection of tested coatings under the influence of high content of zinc can be pronounced as relevantly positive and increasing the anti-corrosion protection. The percentage content of zinc particles in relation to content of binder still remains questionable. Finding the optimum balance between these two constituents should be carefully considered by the producers.

SUMMARY

Presented text compares anti-corrosion Zn-rich paint systems and traditional Zn-coating created using traditional galvanic method. The results have been based on visual evaluation of the tested samples. The testing included exposition in neutral-salt-spray chamber for 7, 14, and 28 days. Further evaluation has been performed in accordance with function/protection quality parameters. As galvanic Zn-coatings have shown complete degradation during the chamber exposition, only Zn-rich paint systems have been taken into account.

The test results are as follows:

- Delta-Protekt KL 100, Delta-Protekt VH 300, and Würth coatings have shown the highest level of anti-corrosion resistance.
- Galvanic Zn-coatings can not withstand the salt chamber environment.
- Mechanical tests (grid test, detachment test, deepening test, on-spike bend test) have proven significant influence of Zn-components in the paint system filler.
- The filler/matrix ratio seems to be important as well. Over-dosed composition leads to decrease of paint system mechanical properties. This impacts overall paint system quality level.
- Higher Zn-particle content contributes to cathodic protection. It is crucial to consider a specific coating application conditions.

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Address

doc. Ing. Michal Černý, CSc., doc. Ing. Josef Filípek, CSc., Ústav techniky a automobilové dopravy, Mendelova univerzita v Brně, Zemědělská 1, 613 00 Brno, Česká republika, e-mail: michalc@mendelu.cz, filipek@mendelu.cz