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HIGHLY EFFECTIVE COATING SYSTEMS WITH SPECIAL CORROSION RESISTANCE REQUIREMENTS AS REPLACEMENTS FOR WASH PRIMER IN COATING SYSTEMS CONTAINING HEXAVALENT CHROMIUM

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Effective anticorrosion surface protection in environments with high corrosion rates and high climatic and chemical aggressiveness of the surrounding atmosphere and pollutants, through the use of paints and organic coatings with environmentally friendly and effective anticorrosion pigments, remains a challenge. One such example is the protection of metal surfaces of ground military equipment. Currently, surface protection in this area is still achieved, among other means, using epoxy resin-based coatings containing hexavalent chromium-based anticorrosion pigments, which are toxic and can cause health problems, including cancer. To date, coating systems containing hexavalent chromium are still permitted under exemptions in the field of ground military technology and materials. This paper deals with the formulation and testing of new coating systems in which the developed epoxy resin-based primers contain pigments based on chemically modified phosphates, while existing pigmented polyurethane-based topcoats are used. The aim of the work was to formulate highly effective corrosion protection using coating systems with high adhesion. A total of five coating systems with anticorrosion pigments based on modified phosphates and one coating system with a reactive base based on hexavalent chromium were prepared and tested. Corrosion resistance tests were conducted in a neutral salt spray environment. The results show that the MP-1 and MP-4 coating systems with anticorrosion pigments (Zinc Aluminum Orthophosphate Hydrate + Zinc-5-Nitroisophthalate) and (Zinc Aluminum Molybdenum Orthophosphate Hydrate) demonstrate high corrosion resistance comparable to that of a coating system with an anticorrosion pigment based on hexavalent chromium. These coating systems also show high adhesion, low corrosion from cuts, and compliance with the corrosion resistance requirements for coating systems for military use on ground military equipment and materials according to military standard ČOS 801001.

Keywords: organic coating, anticorrosion pigments, modified phosphates, hexavalent chromium, environmentally friendly coating systems

1. Introduction

The surface of ground military equipment consists of a number of metals, the most common of which is steel, which is subject to corrosion. Atmospheric corrosion of steel is an electrochemical process that requires the simultaneous presence of moisture and oxygen. Iron in steel oxidizes to form rust, which occupies approximately six times the volume of the original material. The rate at which the corrosion process progresses depends on a number of factors, but primarily on the "microclimate" surrounding the structure.

The main factors influencing the rate of atmospheric corrosion are:

- moisture exposure time,
- atmospheric pollution.

Wetting time is defined as the proportion of the total time during which the surface is wet (due to rain, condensation, etc.). It follows that corrosion will be minimal on unprotected metal surfaces in dry environments, such as inside heated buildings, because of the low availability of water.

The type and amount of contaminants (e.g., sulfates, chlorides, dust, etc.) are important factors in atmospheric pollution. Sulfates originate from sulfur dioxide produced during the combustion of fossil fuels, such as sulfur-containing oils and coal. Industrial environments

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are a main source of sulfur dioxide. Chlorides occur mainly in maritime environments, but military equipment may also come into contact with them when moving on salted roads. Both sulfates and chlorides increase the rate of corrosion. They react with the steel surface to form soluble iron salts, which can concentrate in pits and are themselves corrosive.

The process begins at anodic sites on the surface, where ferrous ions pass into solution. Electrons are released from the anode and move through the metal structure to adjacent cathodic sites on the surface, where they combine with oxygen and water to form hydroxyl ions. These ions react with ferrous ions from the anode to form ferrous hydroxide, which itself is further oxidized in air to form hydrated ferric oxide. The sum of these reactions can be represented by the following equation:

$$4Fe + 3O_2 + 2H_2O \rightarrow 2Fe_2O_3.H_2O \qquad (1).$$

After a certain period of time, however, polarization effects, such as the growth of corrosion products on the surface, cause the corrosion process to be suppressed. New reactive anodic sites may form, allowing further corrosion to occur. In this case, metal loss on the surface is reasonably uniform over a long period of time, which is usually described as "general uniform corrosion" [1]. A schematic representation of the corrosion mechanism is shown in *Figure 1*.

Uniform corrosion can cause large amounts of structural material to become unusable quickly.

In a local environment, the rate of corrosion can vary significantly due to the influence of shelter, prevailing winds, etc. The microclimate surrounding military equipment and materials determines the rate of corrosion. The data on the rate of corrosion cannot be generalized because of changes in atmospheric conditions.

Corrosion protection of steel in ground military equipment is usually achieved through permanent protection with organic coating systems containing anticorrosion pigments. Currently used pigments include those based on hexavalent chromium, which are found in a reactive base (wash primer), where a protective inhibitory coating is created by the reaction of chromate ions with metal ions on the surface of the protected metal to form metal oxide hydrates. Cr^{6+}-based pigments are among the most effective corrosion protection systems for a wide range of technically important metals and alloys. The protective mechanism of soluble chromate corrosion inhibitors consists primarily of inhibiting the anodic corrosion process. The chromate anion promotes the formation of a protective film consisting of iron and chromium oxides in oxidation state III on the surface of steel:

$$C_rO_4^{2-} + 5H_2O + 6e^- \rightarrow Cr_2O_3 + 10\,OH^- \qquad (2),$$

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^- \qquad (3).$$

The initial phase of chromate anion action on a metal surface can be characterized as physical adsorption, which then converts to chemisorption. The protective inhibitory coating is formed by the reaction of

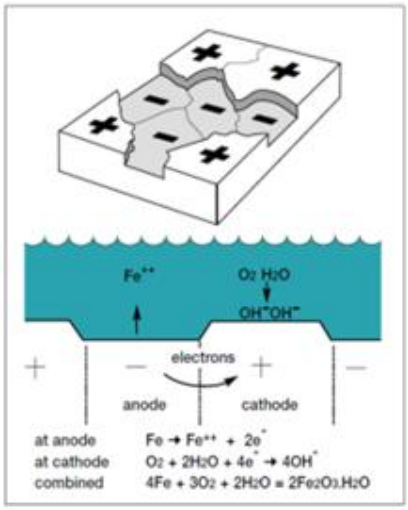


Figure 1: Schematic representation of the corrosion mechanism [1]

chromate ions with metal ions on the surface of the protected metal, resulting in the formation of metal oxide hydrates. The inhibitory properties of chromate pigments depend on the content of water-soluble chromate ions, the ratio of soluble chromate ions to corrosion-stimulating ions, and the active surface area of the chromate pigment particles. Anticorrosive chromate pigments provide effective protection for steel only in neutral, slightly acidic, and slightly alkaline environments. To suppress steel corrosion in acidic areas, a CrO_4^{2-} concentration of 0.01 mol L^{-1} is necessary, whereas in alkaline areas, a concentration of 0.001 mol L^{-1} is necessary. The chromate anion usually causes passivation on the steel surface even at a concentration of 0.0003 mol L^{-1}.

The inhibitory effect of chromate pigments depends on their solubility and on the CrO_4^{2-} content in the aqueous extract. Chromate corrosion inhibitors are very sensitive to the presence of chloride and sulfate anions. Chromates inhibit corrosion only in solutions containing less than 10 ppm SO_4^{2-}. Phosphate anions improve the inhibition effect [2],[3].

An overview of selected inhibitors considered as alternatives to Cr^{6+} is given in *Table 1*. The properties of the alternative inhibitors are compared with those of Cr^{6+} systems [4].

Inhibition systems containing hexavalent chromium exhibit certain properties that have not been found to a comparable degree in any substitute. These include, in particular, the ability to inhibit corrosion attack at coating defects, certain characteristics of inhibitor release from layers, and the excellent protective effects of layers formed by Cr^{6+} adsorption on the metal surface. Despite some good results achieved with alternative inhibitors, mostly in solutions, no full-fledged substitutes with comparable properties have yet been found for many applications of Cr^{6+} inhibitors [17]. It has been found that the release of Cr^{6+} from organic coatings is relatively rapid compared with that of other inhibitors [8], especially at the beginning of the process [18].

Table 1: Overview of selected inhibitors considered as alternatives to Cr^{6+}

Inhibitors	Advantages	Disadvantages
Molybdenates	In the protective layer in two oxidation states $Mo(4^+)$, $Mo(6^+)$ [5]-[7]. The layer is practically impermeable to chlorides [5,8,9], improving the barrier effect [8],[10]. Inhibition is not affected by the presence of chlorides. Structure of conversion coatings similar to Cr^{6+} layers [6].	Lower surface passivation ability (larger molecules, making accumulation at active sites more difficult) [5].
Vanadates	In the protective layer in two oxidation states V(4+), V(5+). Promising results in solution, suitable combination with other inhibitors [10]. Observed ability to protect metal at the site of damage [11].	Toxicity of V(5+). Currently ineffective in pigment form. Currently ineffective in pigment form.
Cerite salts	In the protective layer in two oxidation states Ce(3+), Ce(4+). Strong adsorption on metal [12]. In many cases, efficacy comparable to Cr^{6+} has been observed [9,13-15].	In many cases, no ability to protect the metal at the site of damage was observed [15].
Phosphates	On steel, comparable to Cr^{6+} [16].	Not very effective for zinc, aluminium, and their alloys.

Adequate corrosion protection with lower Cr^{6+} content is also possible by combining chromate and alternative inhibitors. Completely chromate-free inhibition systems are currently suitable only for a limited number of applications. The current application of several inhibitors appears promising, as their beneficial properties can be combined or a synergistic effect can be achieved, e.g., through the use of cerium salts with silicates [20] and molybdates [21], or vanadates with phosphates [22].

2. Experimental methods

2.1. Samples, anticorrosion pigments, and composition of coating systems

Anticorrosion pigments based on modified phosphates were selected for the experimental work, and the properties of the five proposed coating systems were compared in all subsequent tests with those of the previously tolerated coating system containing Cr^{6+} (see *Table 2*).

Composition of coating systems for samples MP-1 to MP-5: two-component epoxy anticorrosion primer with modified phosphates (Primer-1 to Primer-5) + two-component polyurethane matt topcoat + two-component polyurethane ultra-matt finishing coat. Composition of coating system for sample H-Cr: two-component reactive epoxy primer with hexavalent chromium (Primer-6) + two-component epoxy anticorrosion layer + two-component non-yellowing matt polyurethane topcoat.

Figure 2 shows the thicknesses of the coating layers in the MP-1 and H-Cr coating systems in cross-section.

Table 2: Identification of tested corrosion inhibitors in two-component epoxy anticorrosion primers

Sample designation	Primer designation	Identification of corrosion inhibitors
MP-1	Primer-1	Zinc Aluminium Orthophosphate Hydrate + Zinc-5-Nitroisophthalate
MP-2	Primer-2	Calcium Magnesium Orthophosphate
MP-3	Primer-3	Strontium Aluminium Polyphosphate Hydrate + Zinc-5-Nitroisophthalate
MP-4	Primer-4	Zinc Aluminium Molybdenum Orthophosphate Hydrate
MP-5	Primer-5	Zinc Calcium Strontium Aluminium Orthophosphate Silicate Hydrate + Zinc-5-Nitroisophthalate
H-Cr	Primer-6	Zinc Tetroxy Chromate

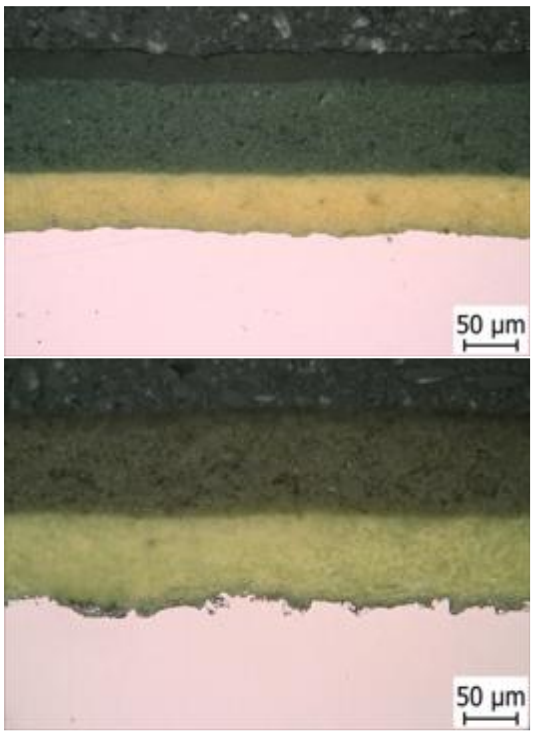


Figure 2: MP-1 and H-Cr in cross-section, viewed by optical microscopy

Table 3: Weight concentration [%] and type of anticorrosion pigment in epoxy primer

Corrosion inhibitors in samples designated by	Primer					
	1	2	3	4	5	6
MP-1	8	0	0	0	0	0
MP-2	0	8	0	0	0	0
MP-3	0	0	8	0	0	0
MP-4	0	0	0	8	0	0
MP-5	0	0	0	0	8	0
H-Cr	0	0	0	0	0	8.6

The weight concentrations of the anticorrosion pigments used in the primer are shown in *Table 3*.

2.2. Requirements for coating systems in the field of corrosion testing – corrosion test in salt spray

The NSS test is traditionally regarded as an accelerated test for comparing coating systems, particularly in terms of chloride resistance, susceptibility to subsurface corrosion, and the system's ability to limit the spread of corrosion from an artificial defect (cut). In this experiment, the samples were provided with one vertical cut in accordance with EN ISO 17872 prior to exposure, and the evaluation was carried out for up to 1,000 hours.

The requirements of ČOS 801001 for coating systems after exposure to salt spray in accordance with EN ISO 9227 NSS are described in *Table 4*.

2.3. Preparation of samples, testing, and evaluation methods

Test samples: steel test samples with dimensions of (100 × 150 × 1) mm, supplied with coating systems MP-1 to MP-5 and H-Cr. Cold-rolled steel plates in accordance with ČSN 11375 were used as the substrates for the coating systems of the test samples. The surface was prepared by blasting to Sa 2½.

Preparation of samples before testing: 21 days after applying the top polyurethane finishing coat by air spraying, the test samples were cut with a single-bladed hand cutting tool to produce a single vertical test cut with a length of 10 cm and a width of 0.5 mm (according to EN ISO 17872). After acclimatization under laboratory conditions, the samples were placed in a neutral salt spray corrosion test.

The used testing and evaluation methods are summarized in *Tables 5*.

Corrosion test mode:

- continuous
- temperature (35 ± 2) °C;
- 5% sodium chloride solution;
- de-mineralized water, conductivity max. 20 µS/cm;
- amount of fallout (mist) 1-2 ml/h on an area of 80 cm^2;
- precipitation pH 6.5–7.2;
- sample placement at an angle of 20° from the vertical;
- evaluation after 24, 48, 96, 168, 240, 504, 720, and 1,000 hours of testing.

3. Results and discussion

Evaluation of coating system thickness before salt spray exposure is shown in *Table 6.*

The performance of the coatings during exposure is shown in *Table A.1 in Appendix A.* The results of the visual assessments show that there was no surface corrosion (Ri 0) in any of the systems, and degradation was concentrated in the area of the artificial defect and in the form of blistering. The comparison was performed considering the following factors as decisive:

- blistering (EN ISO 4628-2 – size and density),
- spread of red corrosion from the cut (RC).

After 96 hours of salt spray exposure, red corrosion products were present in the cross-section of all test specimens. After 240 hours of exposure, unsatisfactory blister density and size were observed around the cut in sample MP-3; after 1,000 hours of exposure, this was also observed in samples MP-2 and MP-5.

Adhesion after exposure (EN ISO 2409), degree of delamination (EN ISO 4628-8), corrosion around the cut after coating removal, and corrosion of the base metal on the surface (EN ISO 4628-3) are described in *Table 7*.

Results after 1,000 hours and after system removal (EN ISO 4628-8 evaluation) show that the systems that

Table 4: Corrosion tests of dry coating systems – corrosion test in salt spray [1]

Evaluated quality characteristic	Test methodology	Test conditions		Required evaluation parameters
		Coating thickness [µm]	Exposure time [h]	Unacceptable changes: • visible defects; • corrosion on the surface; • degree of blistering according to EN ISO 4628-2: • blister size greater than 2; • blister density above 3; • adhesion after 24 hours above 1; • corrosion from the cut above 1.5 mm.
Corrosion test in salt spray	EN ISO 9227	Up to 70	336	
		71–130	720	
		Over 130	1000	

Table 5: Testing and evaluation methods

Testing methods	
ČOS 801001, 6th Edition, Amendment 1	Requirements for coatings and coating systems for the protection of metal surfaces of ground military technology,
EN ISO 17872	Paints and varnishes – Guidelines for the introduction of scribe marks through coatings on metallic panels for corrosion testing,
EN ISO 9227	Corrosion tests in artificial atmospheres – Salt spray tests,
EN ISO 2808	Paints and varnishes – Determination of film thickness,
EN ISO 2409	Paints and varnishes – Cross-cut test,
Evaluation methods	
EN ISO 4628-1	Paints and varnishes - Evaluation of degradation of coatings - Designation of quantity and size of defects, and of intensity of uniform changes in appearance - Part 1: General introduction and designation system,
EN ISO 4628-2	Paints and varnishes - Evaluation of degradation of coatings - Designation of quantity and size of defects, and of intensity of uniform changes in appearance - Part 2: Assessment of degree of blistering,
EN ISO 4628-3	Paints and varnishes - Evaluation of quantity and size of defects, and of intensity of uniform changes in appearance - Part 3: Assessment of degree of rusting,
EN ISO 4628-8	Paints and varnishes - Evaluation of degradation of coatings - Designation of quantity and size of defects, and of intensity of uniform changes in appearance - Part 8: Assessment of degree of delamination and corrosion around a scribe or other artificial defect.

Table 6: Evaluation of coating system thickness before salt spray exposure

Sample designation	Minimum thickness [µm]	Maximum thickness [µm]	Average thickness [µm]	Standard deviation [µm]
MP-1	142	171	156.6	9.13
MP-2	141	163	151.8	8.00
MP-3	143	173	161.1	10.8
MP-4	134	159	150.0	8.87
MP-5	139	166	155.1	8.42
H-Cr	142	166	154.0	12.20

Notes: Average thickness determined from 20 measurements

were overall rated as satisfactory had the following characteristics:

- delamination around the cut is low to moderate (on the order of a few millimetres),
- corrosion around the cut after removal of the system is very low (tenths of a millimetre to a few millimetres),
- surface corrosion under the coating remains zero.

This supports the interpretation that the decisive factor is not the surface barrier, which is relatively good for all samples, but primarily the system's ability to "slow down" subsurface corrosion from a defect, a property in which chromate inhibitors traditionally excel. However, the test shows that certain phosphate-modified pigments (MP-1, MP-4) come very close to this property.

4. Conclusion

Results of the determination of the corrosion resistance of coating systems in a salt spray chamber by the NSS method in accordance with ČOS 801001, 6th Edition, Amendment 1 (*Table A.4, Item 1*) are shown in *Table 8*.

The results show that samples MP-1 and MP-4, coating systems with anticorrosion pigments (Zinc Aluminum Orthophosphate Hydrate + Zinc-5-Nitroisophthalate) and (Zinc Aluminum Molybdenum Orthophosphate Hydrate), complied with the requirements of ČOS 801001, 6th Edition, Amendment 1, for corrosion resistance in a salt spray chamber by the NSS method, as did the coating system with an anticorrosion pigment based on hexavalent chromium, which has been used in military environments for decades to protect metal parts of ground military technology. The results show clear selectivity among the phosphate-modified inhibitors. Samples MP-1 and MP-4 demonstrate high corrosion resistance in a salt spray chamber by the NSS method, as demonstrated by the following evaluations: visible defects, corrosion on the surface, corrosion from the cut, adhesion, degree of blistering (size and density), and degree of rusting. Samples MP-2, MP-3, and MP-5 show limiting factors, particularly in the area of blistering (unsatisfactory blister size or adhesion in the case of MP-5). This indicates that, in an NSS environment, one of the following may be critical for these formulations:

Table 7: Adhesion of the coating system to the steel surface after 1,000 hours of salt spray corrosion testing, delamination, corrosion at the cut, and appearance of the base metal after coating system removal

Sample designation		Cross-cut test according to EN ISO 2409 [degree]	Delamination around the cut according to EN ISO 4628-8 [mm]	Corrosion around the cut after removing the coating system according to EN ISO 4628-8 [mm]	Corrosion of the base metal on the surface according to EN ISO 4628-3 [degree]
MP-1	1.1	0	0.8 mm	0.0 mm	Ri 0 (S0)
	1.2	0 to 1	1.6 mm	0.2 mm	Ri 0 (S0)
	1.3	1 to 2	0.7 mm	0.1 mm	Ri 0 (S0)
	1.4	0	1.1 mm	0.1 mm	Ri 0 (S0)
MP-2	2.1	1	0.8 mm	0.1 mm	Ri 0 (S0)
	2.2	2	1.1 mm	0.5 mm	Ri 0 (S0)
	2.3	1	1.3 mm	0.6 mm	Ri 0 (S0)
	2.4	1	0.7 mm	0.1 mm	Ri 0 (S0)
MP-3	3.1	1	1.7 mm	0.6 mm	Ri 0 (S0)
	3.2	1 to 2	1.2 mm	0.6 mm	Ri 0 (S0)
	3.3	1	1.7 mm	0.8 mm	Ri 0 (S0)
	3.4	1	1.2 mm	1.1 mm	Ri 0 (S0)
MP-4	4.1	1	0.6 mm	0.4 mm	Ri 0 (S0)
	4.2	0 to 1	0.5 mm	0.2 mm	Ri 0 (S0)
	4.3	1	0.4 mm	0.1 mm	Ri 0 (S0)
	4.4	1	0.6 mm	0.2 mm	Ri 0 (S0)
MP-5	5.1	1 to 2	1.0 mm	0.3 mm	Ri 0 (S0)
	5.2	1 to 2	0.6 mm	0.2 mm	Ri 0 (S0)
	5.3	2	0.6 mm	0.2 mm	Ri 0 (S0)
	5.4	2	0.5 mm	0.2 mm	Ri 0 (S0)
H-Cr	6.1	1	1.8 mm	0.8 mm	Ri 0 (S0)
	6.2	1	1.8 mm	1.5 mm	Ri 0 (S0)
	6.3	1	1.7 mm	1.1 mm	Ri 0 (S0)
	6.4	1	1.1 mm	1.3 mm	Ri 0 (S0)

Table 8: Results of determination of corrosion resistance of coating systems in a salt spray chamber by the NSS method

Sample designation	Requirement of ČOS 801001, 6th Edition, Amendment 1 (*Table A.4, Item 1*):
MP-1	complied
MP-2	did not comply – blister size greater than 2
MP-3	did not comply – blister size greater than 2
MP-4	complied
MP-5	did not comply with the quality criteria: • adhesion 24 hours after testing above 1 • blister size greater than 2
H-Cr	complied

- the speed/effectiveness of the inhibitory effect in the presence of chlorides,
- the barrier character and transport of water/ions through the film,
- the sensitivity of the interface to osmotic phenomena leading to blistering.

It is particularly interesting that some systems showed very low red corrosion at the beginning, but during the test, blistering appeared locally around the cut in selected samples. This corresponds to typical NSS degradation: an electrochemically active area is created at the site of the defect, where chlorides concentrate, alkalization/acidification occurs in microvolumes, and the risk of subsurface delamination or osmotic blistering increases.

Neutral salt spray (NSS) showed differences in inhibitor performance and in the system's ability to limit degradation from defects and blistering. It also appeared to be more critical for the metal-primer interface because chlorides promote subsurface corrosion around the defect and thus secondarily reduce adhesion and increase delamination.

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APPENDIX A

Table A.1: Visual assessment during exposure to salt spray

Evaluation time	Sample designation		Blisters in the area according to EN ISO 4628-2 *) [degree]	Rusting according to EN ISO 4628-3 **) [degree]	Rusting around the cut
After 24 hours	MP-1	1.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.2	0 (S0)	Ri 0 (S0)	Without RC
		1.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.4	0 (S0)	Ri 0 (S0)	Without RC
	MP-2	2.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-3	3.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		3.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		3.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		3.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-4	4.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		4.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		4.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		4.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-5	5.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		5.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		5.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		5.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	H-Cr	6.1	0 (S0)	Ri 0 (S0)	Weak RC
		6.2	0 (S0)	Ri 0 (S0)	Weak RC
		6.3	0 (S0)	Ri 0 (S0)	Weak RC
		6.4	0 (S0)	Ri 0 (S0)	Weak RC
After 48 hours	MP-1	1.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-2	2.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-3	3.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		3.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		3.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		3.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-4	4.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		4.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		4.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		4.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-5	5.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		5.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		5.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		5.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	H-Cr	6.1	0 (S0)	Ri 0 (S0)	Weak RC
		6.2	0 (S0)	Ri 0 (S0)	Weak RC
		6.3	0 (S0)	Ri 0 (S0)	Weak RC
		6.4	0 (S0)	Ri 0 (S0)	Weak RC

Table A.1: Visual assessment during exposure to salt spray (continued)

Evaluation time	Sample designation		Blisters in the area according to EN ISO 4628-2 *) [degree]	Rusting according to EN ISO 4628-3 **) [degree]	Rusting around the cut
After 96 hours	MP-1	1.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-2	2.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-3	3.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		3.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		3.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		3.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-4	4.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		4.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		4.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		4.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-5	5.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		5.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		5.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		5.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	H-Cr	6.1	0 (S0)	Ri 0 (S0)	Weak RC
		6.2	0 (S0)	Ri 0 (S0)	Weak RC
		6.3	0 (S0)	Ri 0 (S0)	Weak RC
		6.4	0 (S0)	Ri 0 (S0)	Weak RC
After 168 hours	MP-1	1.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		1.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-2	2.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
		2.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width
	MP-3	3.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width, 10-20 P (S2)
		3.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width, 5-10 P (S2)
		3.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width, 3-5 P (S2)
		3.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width, 5-10 P (S2)
	MP-4	4.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-5	5.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		5.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		5.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		5.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	H-Cr	6.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		6.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		6.3	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		6.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width

Table A.1: Visual assessment during exposure to salt spray (continued)

Evaluation time	Sample designation		Blisters in the area according to EN ISO 4628-2 *) [degree]	Rusting according to EN ISO 4628-3 **) [degree]	Rusting around the cut
After 240 hours	MP-1	1.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		1.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		1.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		1.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-2	2.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		2.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		2.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 1 P (S2)
		2.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-3	3.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width, 15-20 P (S2)
		3.2	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width, 5-10 P (S2)
		3.3	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width, 3-5 P (S2)
		3.4	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width, 5-10 P (S2)
	MP-4	4.1	0 (S0)	Ri 0 (S0)	RC of 0 to 1 mm width, 1 P (S2)
		4.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-5	5.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		5.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		5.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		5.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	H-Cr	6.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		6.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		6.3	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		6.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
After 504 hours	MP-1	1.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		1.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 2 P (S2)
		1.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		1.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-2	2.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 1 P (S3)
		2.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 1 P (S2)
		2.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 1 P (S3)
		2.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-3	3.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 15-20 P (S2)
		3.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 10 P (S2)
		3.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 5 P (S2)
		3.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 5-10 P (S2)
	MP-4	4.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-5	5.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		5.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		5.3	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		5.4	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
	H-Cr	6.1	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		6.2	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		6.3	0 (S0)	Ri 0 (S0)	RC of 2 mm width
		6.4	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width

Table A.1: Visual assessment during exposure to salt spray (continued)

Evaluation time	Sample designation		Blisters in the area according to EN ISO 4628-2 *) [degree]	Rusting according to EN ISO 4628-3 **) [degree]	Rusting around the cut
After 720 hours	MP-1	1.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		1.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 2 P (S2)
		1.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		1.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-2	2.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		2.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 1 P (S2)
		2.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 1 P (S3)
		2.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-3	3.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 20 P (S2)
		3.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 10 P (S2)
		3.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 5 P (S2)
		3.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 10 P (S2)
	MP-4	4.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		4.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width
	MP-5	5.1	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 1 P (S2)
		5.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width
		5.3	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		5.4	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
	H-Cr	6.1	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		6.2	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		6.3	0 (S0)	Ri 0 (S0)	RC of 2 mm width
		6.4	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
After 1000 hours	MP-1	1.1	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		1.2	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width, 2 P (S2)
		1.3	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		1.4	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
	MP-2	2.1	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		2.2	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width, 1 P (S2) + 1 P S3)
		2.3	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width, 1 P (S3)
		2.4	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
	MP-3	3.1	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width, 20 P (S2)
		3.2	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 10 P (S2)
		3.3	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 3 P (S2) + 2 P (S3)
		3.4	0 (S0)	Ri 0 (S0)	RC of 1 mm width, 7 P (S2) + 3P (S3)
	MP-4	4.1	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width, 2 P (S2)
		4.2	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		4.3	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		4.4	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width, 1 P (S2)
	MP-5	5.1	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width, 1 P (S3)
		5.2	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width, 1P (S2)
		5.3	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width, 2P (S2)
		5.4	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width, 1 P (S3)
	H-Cr	6.1	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		6.2	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width
		6.3	0 (S0)	Ri 0 (S0)	RC of 2 mm width
		6.4	0 (S0)	Ri 0 (S0)	RC of 1 to 2 mm width

Notes: *) – grade 0 (S0) – no blister, **) – grade Ri 0 (S0) – no corrosion, xP – number of blisters, Sx – size of blister, RC – red corrosion