Influence of conversion coatings on the resistance of adhesive joints to undercorrosion

Janoško E.[1], Guzanová A.[1], Szelag P.[2], Draganovská D.[1], Moro R.[1]
[1] Technical University of Košice, Faculty of Mechanical Engineering, Department of Technology, Materials and Computer Supported Production, Košice, Slovakia
[2] Pragochema, Prague, Czech Republic
E-mail: erik.janosko@tuke.sk

The paper deals with the application of conversion coatings for the preparation of surfaces before adhesive bonding of galvanized and non-galvanized steels. The morphology of the coatings was monitored by electron microscopy. The corrosion characteristics of the conversion coatings were determined by linear polarization. Steels treated with conversion coatings were used to form bonded joints using three structural adhesives. The resistance of the joints to undercorrosion was determined following the change in the load-bearing capacity of the joints after exposure in the climatic chamber.

INTRODUCTION

The most common way to protect steel against corrosion is to form organic coatings from liquid or powder materials. The basis of their effectiveness is to ensure the best possible adhesion to the base material [1]. Conversion coatings are used for this purpose. They are formed by the reaction of an active solution with a metal substrate which provides the ions needed to form a conversion coating and become part of it. The layers formed consist of insoluble inorganic compounds. Their main purpose is to reduce anodic and cathodic areas and to prevent the contact of reactive substances from the environment with the base metal [2]. The result is an increase in the slope of the anodic and cathode polarization curves, which results in a reduction in the corrosion rate of the base material.

Classical conversion coatings include phosphate coatings, chromate coatings, oxalate coatings or aluminium anodizing coatings [3]. For environmental reasons, chromate coatings are being replaced by more environmentally friendly variants without the content of toxic and carcinogenic sixvalent chromium [4]. Phosphate coatings require a higher bath temperature, which causes problems in their disposal and sediment processing, or in their sealing with chromic acid.

Surface passivation is also provided by zirconate or titanate preparations, which do not contain chromium compounds or other toxic and environmentally harmful substances [5,6]. They are formed from titanium or zirconium fluorocomplexes. The bath contains in particular H_2ZrF_6 and H_2TiF_6, various fluorides and may also contain a polymer which increases the corrosion resistance as well as the adhesion of the applied coating. The effect of the bath is to passivate microscopic pores or other inhomogeneities in the phosphate coating or base material. Zirconium absorbed in the surface layers occurs as ZrO_2. ZrO_2 coatings with a thickness of 20 to 30 nm provide higher protection against corrosion compared to conventional chromates and phosphates on low carbon steels. It is compatible with all types of organic coatings.

Another group of conversion layers are the so-called self-organized monomolecular layers. Coatings are formed by attracting polar compounds to the metal surface while the remainder of the organic chain aligns and faces away from the metal surface. On the opposite side of this organic molecule is a second suitable functional group promoting the adhesion of the applied organic coating. Suitable functional groups are those capable of being involved in the curing polymerization reactions of organic prepolymers. Examples are organosilanes which form a spatial network of silicate compounds linked by siloxane bonds. They contain epoxy organic functional groups which, through chemical bonds, are incorporated into the organic binder of the paint and significantly increase its adhesion [7-11].

The paper deals with the application of selected conversion layers for the preparation of substrates before adhesive bonding using epoxy and rubber-based adhesives. Some current construction adhesives are formulated on the same material basis as organic coatings – epoxy, polyurethane, etc. It is therefore interesting to find out whether conversion coatings also improve the

adhesion of adhesives and thus contribute to increasing the load-bearing capacity or corrosion resistance of adhesive joints. Iron phosphate and zinc phosphate, chromate-free zirconate passivation and an experimental adhesion promoter based on organosilanes are tested experimentally. The aim of the paper was to test the corrosion characteristics of conversion layers applied on galvanized and non-galvanized steel substrates, to create adhesive joints and to test their resistance to undercorrosion. At the same time, the aim was to determine whether the effect of increasing the adhesion by the application of organosilanes also works in the adhesive bonding.

Tab. 1. Mechanical properties and surface condition on delivery

	DC	TL
Yield strength [MPa]	197	220
Tensile strength [MPa]	327	320
Elongation [%]	39	28
Weight of Zn coating [g m^{-2}]	–	100, i.e. 14 µm thick Zn coating on both side
Surface condition	matt	minimized spangle
Oiled [g m^{-2}]	0.5-2.5	0.6-2.5

MATERIALS AND METHODS

Materials

Cold-rolled low-carbon deep-drawn steel DC 04 (hereinafter referred to as DC) with a thickness of 0.8 mm and structural hot-dip galvanized high-strength low-alloy steel TL 1550-200+Z (hereinafter referred to as TL) with a thickness of 0.8 mm were used in the experiment. Mechanical properties of the materials and their chemical composition are given in Tab. 1 and 2.

Surface preparation

The following types of surface treatments were chosen for the experiments – iron phosphating, zinc phosphating, chromate-free zirconate passivation and surface treatment with organosilane. The technological procedure of individual surface treatments for both used substrates is given in Tab. 3.

EDX analysis of conversion coatings

The morphology and chemical composition of the coatings were analyzed using an electron microscope by EDX analysis.

Tab. 2. Chemical composition of base materials (wt. %)

	C	Mn	P	S	Si	Al	Ti	Nb	Cu
DC	0.04	0.25	0.009	0.008	–	–	–	–	–
TL	0.1	1	0.08	0.03	0.5	0.015	0.15	0.1	0.2

Tab. 3. Procedure of individual surface treatments

<table>
<tr><th colspan="2">Iron phosphating</th><th colspan="2">Zinc phosphating</th><th>Chroman-free zirconate passivation</th><th>Organosilane -based passivation</th></tr>
<tr><td colspan="2">substrate</td><td colspan="2">substrate</td><td colspan="2">substrate</td></tr>
<tr><th>DC</th><th>TL</th><th>DC</th><th>TL</th><th>DC+TL</th><th>DC+TL</th></tr>
<tr><td colspan="6">Degreasing, 5 % Pragolod 57N, 60 °C, 8 min</td></tr>
<tr><td colspan="6">Water rinsing</td></tr>
<tr><td rowspan="2">phosphating, Pragofos 2051 A, 60 °C, 3 min</td><td rowspan="2">phosphating, Pragofos 2051 A + + Pragofos 1502, 60 °C, 3 min</td><td colspan="2">Surface activation, 0.3 % Pragofos 1007 A, RT, 3 min, constantly stirring the bath</td><td rowspan="2">zirconate passivation, Pragokor BP, RT, 3 min</td><td rowspan="2">organosilane passivation, RT, 10 min</td></tr>
<tr><td>phosphating, Pragofos 1501, 60 °C, 5 min</td><td>phosphating, Pragofos 1501 + + Pragofos 1502, 60 °C, 5 min</td></tr>
<tr><td colspan="6">Water rinsing</td></tr>
<tr><td colspan="6">Rinsing with demineralized water</td></tr>
<tr><td colspan="6">Hot air drying</td></tr>
</table>

Accelerated corrosion test

The BioLogic SP-150 was used to perform accelerated corrosion tests. The measurement was performed using a three-electrode circuit: a working electrode – substrate with a particular conversion coating, reference electrode – saturated calomel electrode, counter platinum electrode. The solution used was 3.5 % aqueous NaCl solution. The experiment consisted of the following steps:

- OCP (Open Circuit Potential) was measured for 1 hour.
- LP (Linear Polarization) test was carried out with a scan rate of 0.5 mV/s in the range of -200 to 200 mV.

The EC-Lab V11.30 program was used to analyze the results. Rp was calculated from a linear polarization in range ± 20 mV from Ecorr.

Application of conversion coatings as surface preparation under adhesive joints

The following adhesives were used to form the joints:

- One-component adhesive Epoxy/PVC-Polymerblend with glass beads. The tensile strength of the adhesive is 13.5 MPa. Shear strength according to DIN EN 1465 at 23 °C is at least 12 MPa.
- Structural rubber one component adhesive, heat curing, solvent free. The minimum tensile strength of the adhesive is 12 MPa and the minimum shear strength according to DIN EN 1465 at 23°C is 15 MPa.
- Heat curing solvent-free one-component high crash resistant structural adhesive based on toughened epoxy resin. The minimum tensile strength of the adhesive is 35 MPa, the minimum shear strength according to DIN EN 1465 at 23 ° C is 30 MPa.

The working range of the adhesives lies between –40 and 90 °C. Simple lap joints were made according to DIN EN 1465, with an overlap area of 25 × 12.5 mm, adhesive thickness 0.2 mm. Curing of the adhesive occurred in an electric oven at 175 °C, 25 min. The resistance of the joints to undercorrosion was tested by the PV1200 climate test. The determination of the shear strength of the adhesive joints by tension loading was performed in the as-bonded state as well as after the exposure in the climatic chamber. The test in the climate chamber consisted of 10 cycles. The course of temperature and relative humidity during one cycle is shown in Figure 1. Subsequently, the maximum force at joint failure was recorded at loading rate 10 mm·min^{-1} on tensile machine, Figure 2.

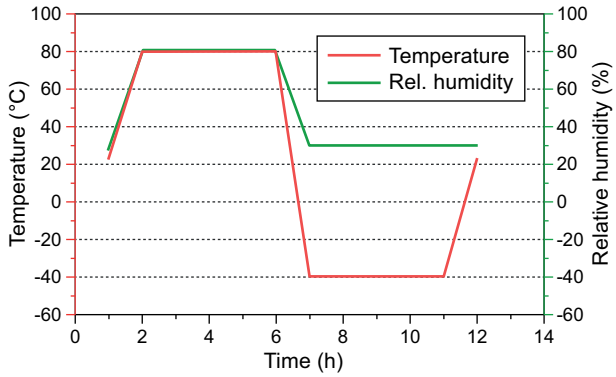


Fig. 1. Time course of temperature and relative humidity in one climatic cycle

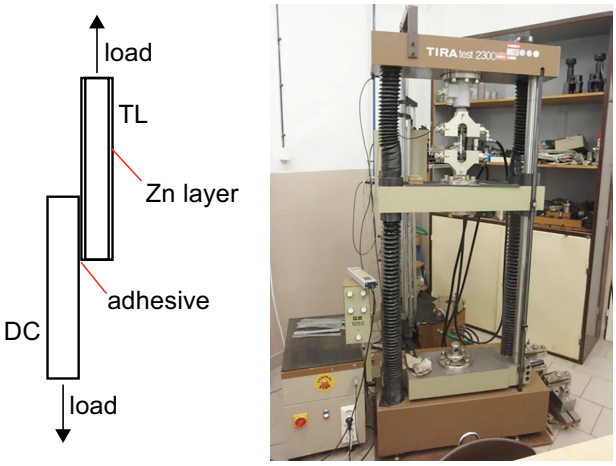


Fig. 2. Loading scheme of adhesive assemblies (left), tensile test machine TIRAtest 2300 (right)

RESULTS AND DISCUSSION

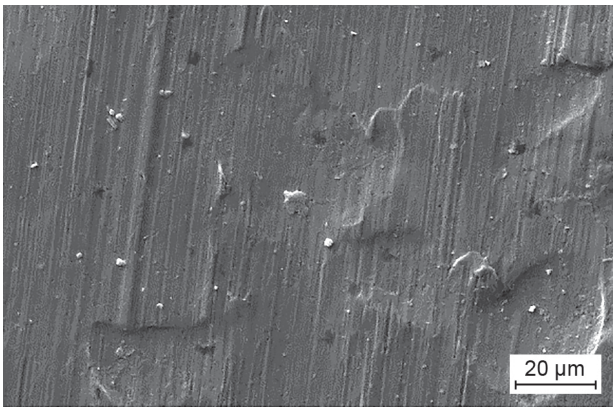
EDX analysis of coatings

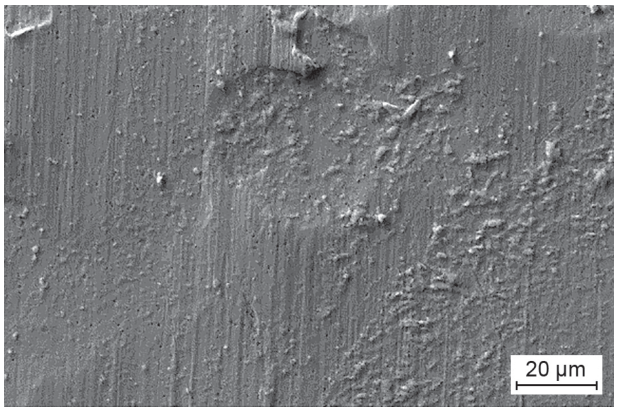
The appearance of the surfaces with individual conversion coatings and corresponding EDX spectra are shown in Figure 3.

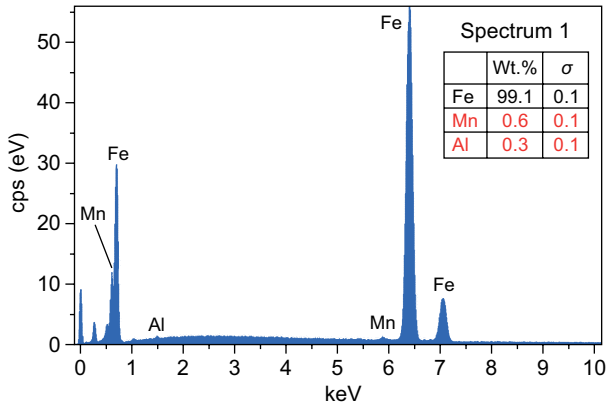
From Figure 3, it can be seen that the chromate-free zirconate passivator and the iron phosphate form a thin amorphous layer, or, in the case of the organosilane sol-gel layer, which does not change the character and appearance of the original morphology of the substrates. Their presence cannot be detected visually, only by EDX analysis, which confirms the presence of characteristic elements in these coatings. Only zinc phosphate overlaps the original surface morphology with a system of in-soluble phosphate crystals.

EDX analysis of the unmodified surface of DC steel corresponds to the chemical composition of simple carbon steel, in the analysis of TL material, zinc and aluminum dominate, which corresponds to the hot-dipped zinc layer on microalloyed steel.

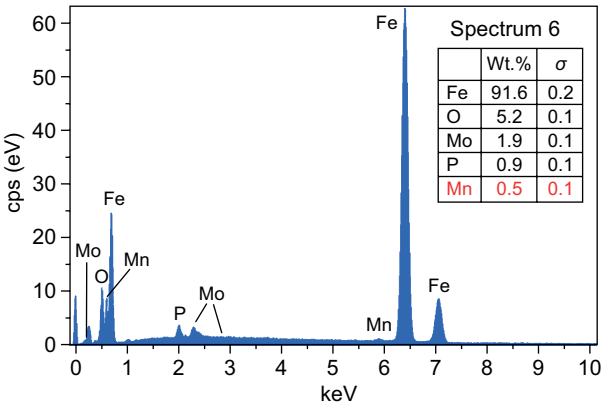
According to [2, 12-13], the iron phosphate coating consists mainly of vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$ and a smaller amount of γ-Fe_2O_3, or Fe_3O_4, $FePO_4 \cdot 2H_2O$ and $Fe(OH)_3$.



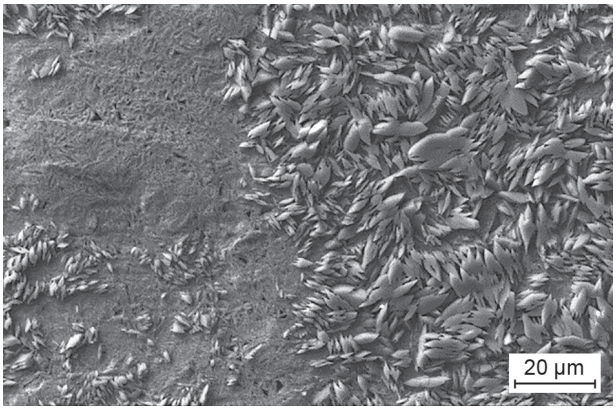


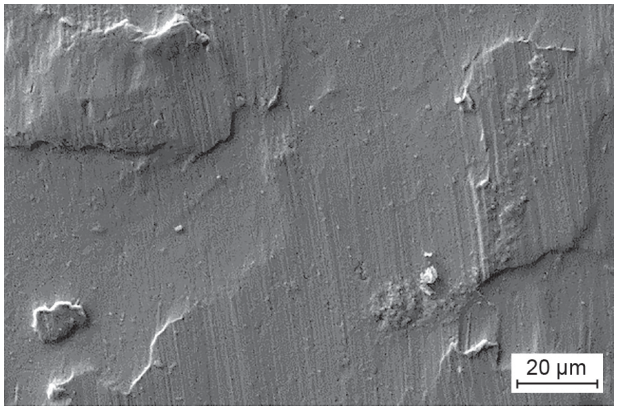


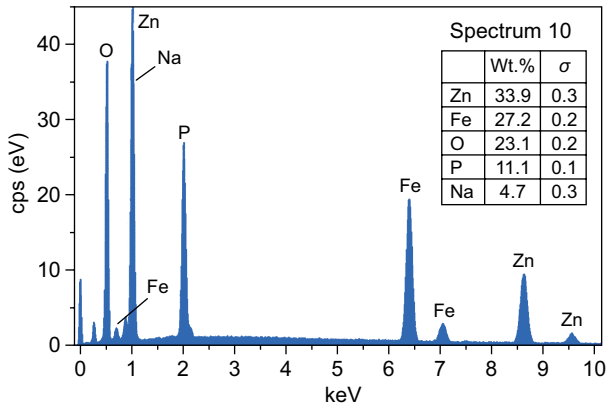
a) DC nontreated



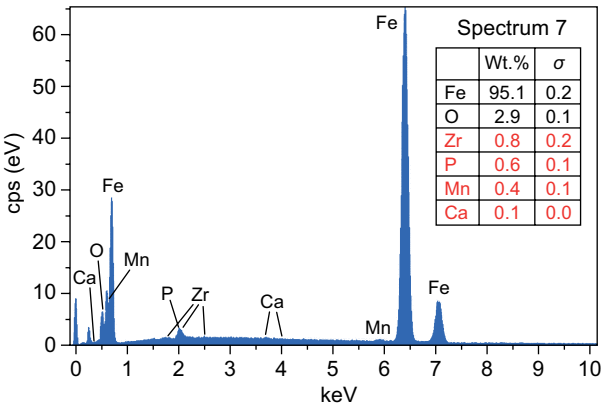
b) DC + iron phosphate





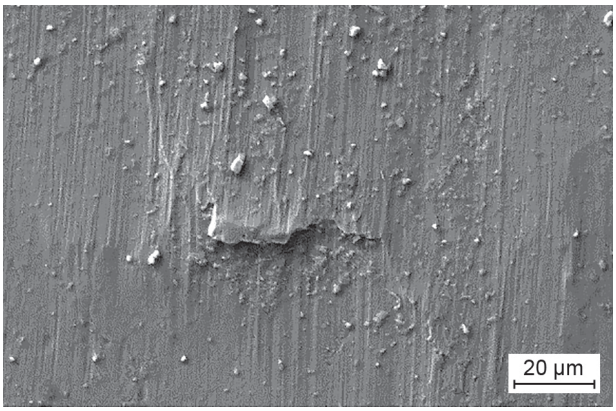


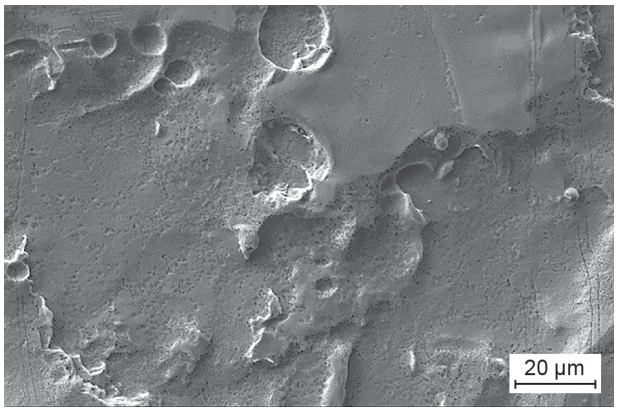
c) DC + zinc phosphate

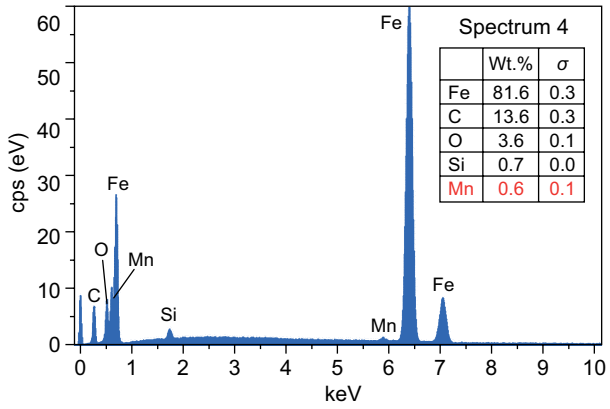


d) DC + zirconate passivation

Fig. 3. Appearance and EDX analysis of coatings, SEM *(Continue on next page)*

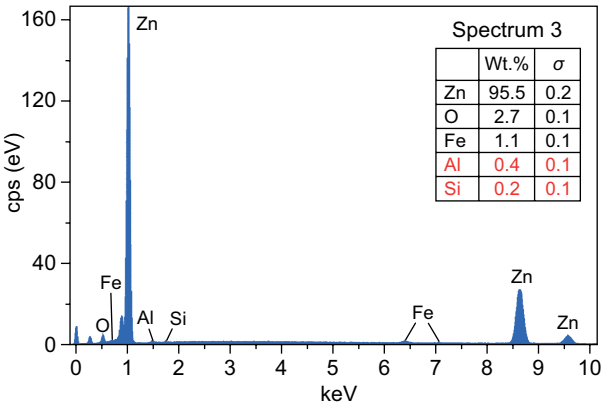






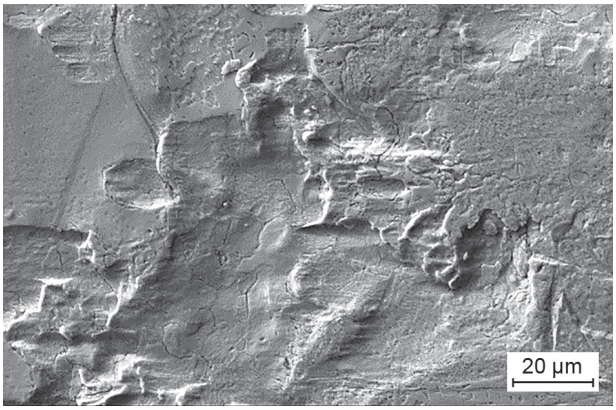
	Wt.%	σ
Fe	81.6	0.3
C	13.6	0.3
O	3.6	0.1
Si	0.7	0.0
Mn	0.6	0.1

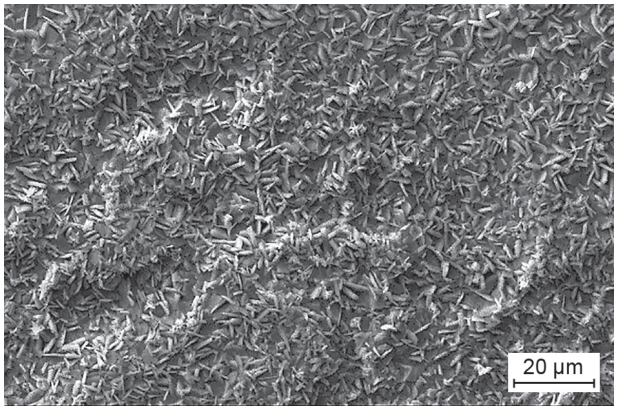
e) DC + organosilane

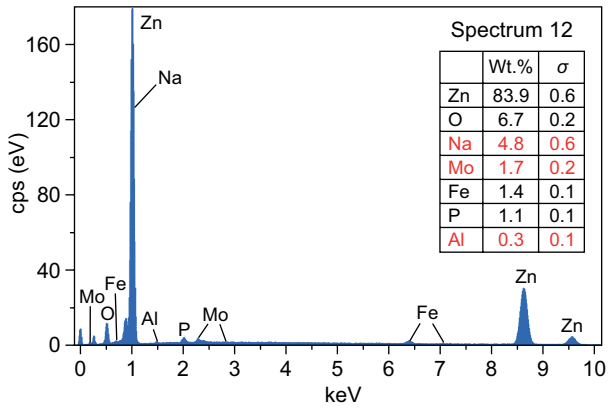


	Wt.%	σ
Zn	95.5	0.2
O	2.7	0.1
Fe	1.1	0.1
Al	0.4	0.1
Si	0.2	0.1

f) TL nontreated

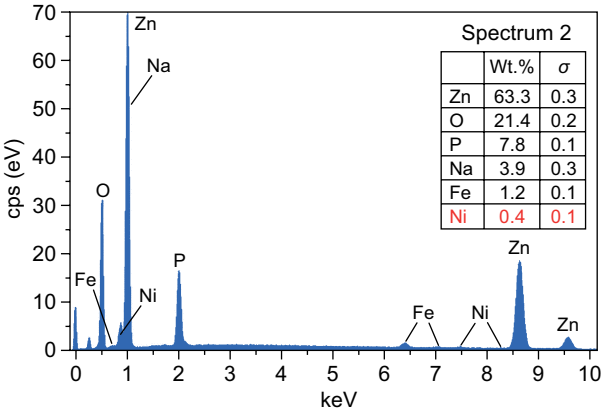






	Wt.%	σ
Zn	83.9	0.6
O	6.7	0.2
Na	4.8	0.6
Mo	1.7	0.2
Fe	1.4	0.1
P	1.1	0.1
Al	0.3	0.1

g) TL + iron phosphate



	Wt.%	σ
Zn	63.3	0.3
O	21.4	0.2
P	7.8	0.1
Na	3.9	0.3
Fe	1.2	0.1
Ni	0.4	0.1

h) TL + zinc phosphate

Fig. 3. Appearance and EDX analysis of coatings, SEM *(Continue on next page)*

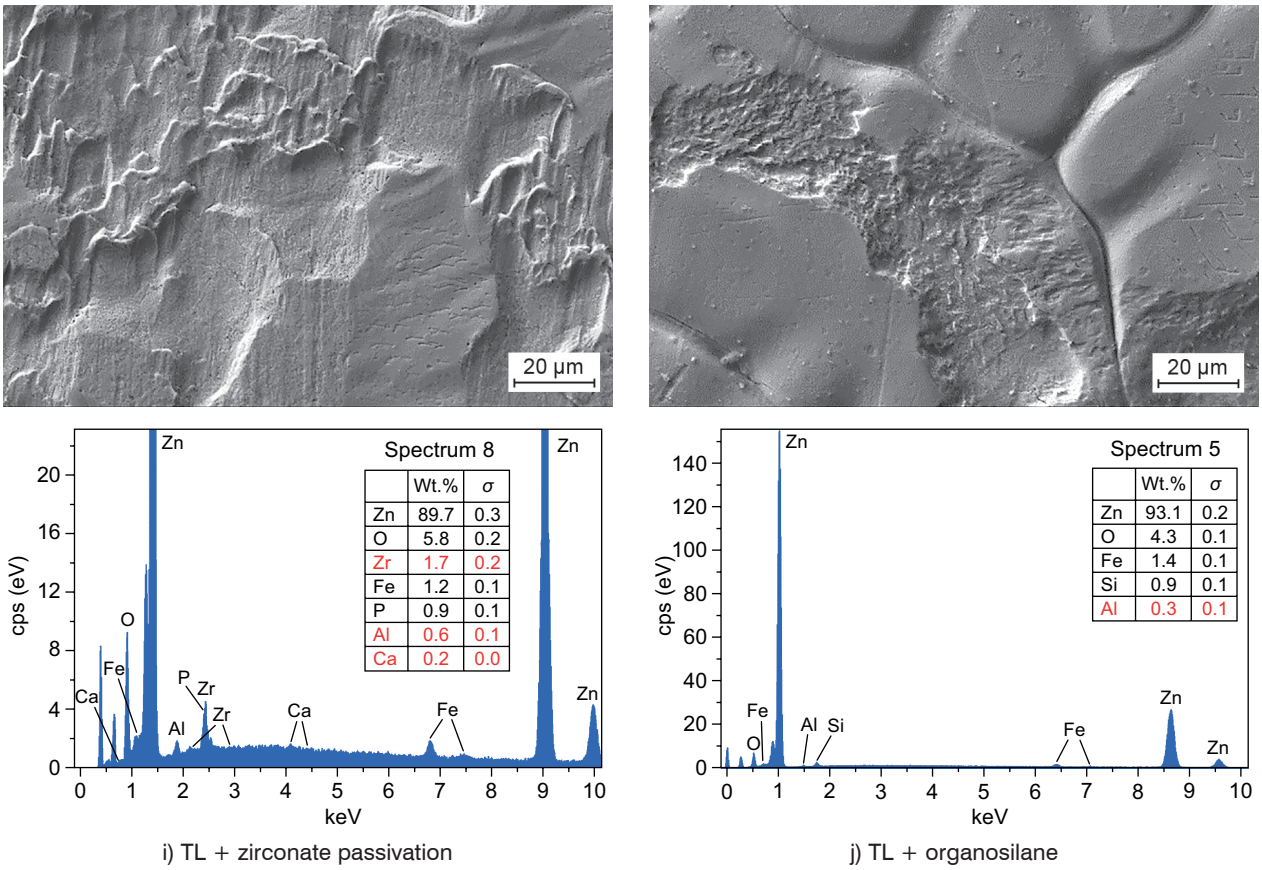


Fig. 3. Appearance and EDX analysis of coatings, SEM

Formation of a layer of iron phosphate is proved by the presence of the elements Fe, O and P in EDX analyzes.

Based on relevant references [2,13] is known, that zinc phosphate consists of two phosphate layers with different compositions and structures. The first is a layer of zinc-iron phosphate ($Zn_2Fe(PO_4)_2 \cdot 4H_2O$, phosphophyllite), on which a thicker layer of zinc phosphate ($Zn_3(PO_4)_2 \cdot 4H_2O$, so-called hopeite) is later formed. The presence of the zinc phosphate layer is confirmed by the elements Zn, O, Fe, P in EDX analyzes.

Chromate-free zirconate passivation reacts with the surface of the substrate, binds to it and forms a protective layer. It does not contain chromium ions or other environmentally harmful substances. It passivates microscopic areas of pores or other inhomogeneities in the phosphate coating, thus increasing its corrosion resistance. It also passivates active surfaces of unphosphated steel, aluminum-magnesium alloys, zinc coatings and zinc castings after degreasing or otherwise activated metal surfaces. The presence of this layer on the surface is evidenced by the zirconium present in the EDX spectrum.

The organosilane gel coating contains organomodified SiO_2 nanoparticles. On the substrates, the presence of this layer is demonstrated by silicon in the EDX spectra.

Linear polarization

The polarization curves for deep-drawing DC steel and for galvanized material TL are shown in Figure 4 and the results are shown in Table 4 and 5.

The individual surface pretreatments are compared with the untreated surface and the main parameter for comparison is the polarization resistance Rp. The polarization resistance of iron phosphated DC steel is lower than for untreated DC steel, the conversion layer itself did not improve the corrosion resistance of the base material. Another type of conversion layer having a lower Rp is organosilane. Thus, both of these pretreatments also have a more negative Ecorr value than the base material. A slight increase in Rp was observed with Zr passivation and a significant increase in Rp was shown for zinc phosphate. The Ecorr of both treatments is more positive compared to the untreated base material.

For the TL material (Tab. 5), each type of surface pretreatment has a positive effect on the Rp value. Iron, zinc phosphate and organosilane have a similar Rp value, a significant increase in Rp was recorded with Zr passivation, more than threefold. For all surface treatments, the E_{corr} value was more positive than the base material TL. Thus, we can state that all selected surface treatments of the TL material have a positive effect on its corrosion resistance, even if no further surface modification follows.

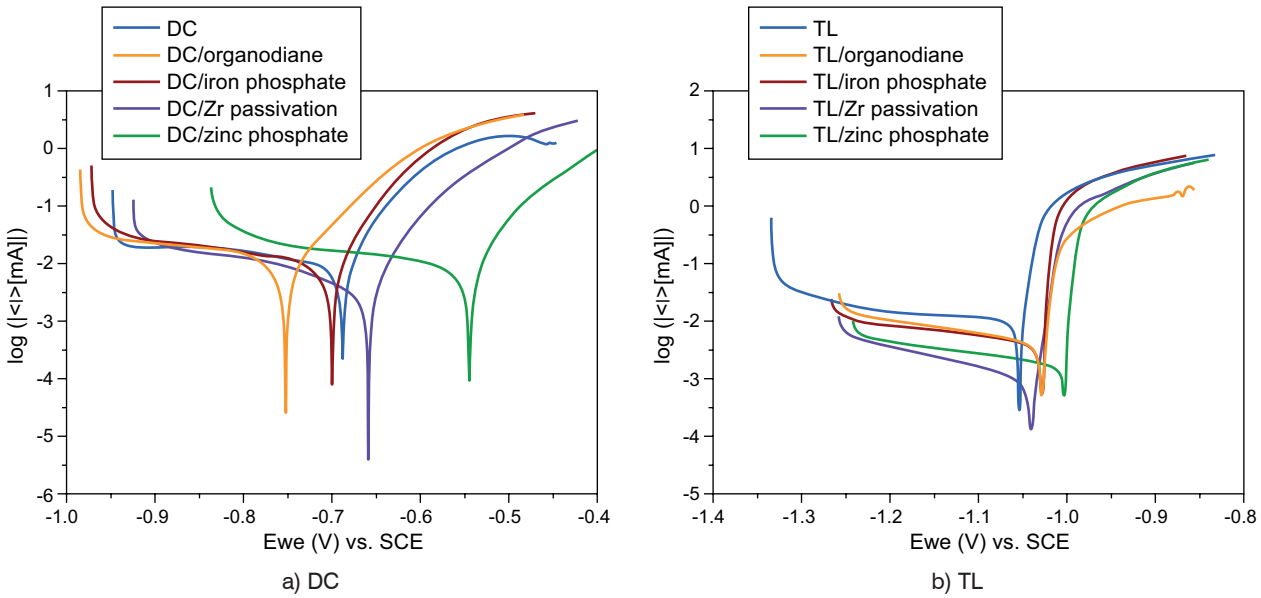


Fig. 4. Tafel curves for: a) DC and b) TL material

Tab. 4. Results of linear polarization for DC material

Preparation	E_{corr} [mV/SCE]	b_a [mV]	Rp [Ω]
No preparation	-685.6 ± 3.8	60 ± 5	2081 ± 443
iron phosphate	-702.2 ± 3.3	50 ± 5	1882 ± 139
Zinc phosphate	-534.3 ± 10.7	58 ± 4	3410 ± 233
Zr passivation	-664.9 ± 4.8	64 ± 2	2528 ± 105
Organosilane	-746.1 ± 0.8	73 ± 5	1388 ± 18

Tab. 5. Results of linear polarization for TL material

Preparation	E_{corr} [mV/SCE]	b_a [mV]	Rp [Ω]
No preparation	-1058 ± 5	25.8 ± 6.7	1022 ± 90
Iron phosphate	-1031 ± 1	11.5 ± 0.8	1583 ± 220
Zinc phosphate	-1003 ± 2	11.5 ± 3.2	1882 ± 116
Zr passivation	-1038 ± 4	14.8 ± 0.8	3380 ± 30
Organosilane	-1032 ± 4	17.1 ± 6.8	1530 ± 168

Load-bearing capacity of adhesive joints

Previously mentioned tests give us an idea of the corrosion behavior of conversion coatings themselves. However, in practice, they are almost always used in combination with other surface treatments, most often organic coatings. They ensure excelent mechanical anchoring of the coatings to the substrate, thus preventing undercorrosion and strengthening the corrosion resistance of the applied coating system.

Here, however, we used the conversion coatings as surface preparation under adhesives, as many adhesives are based on the same material base as organic coatings – epoxy, polyurethane and others.

During the PV1200 climate test, the temperature varies between -40 °C and + 80 °C and the relative humidity between 30 and 80 %. The thermal stresses associated with these cyclic conditions create preconditions for disrupting the adhesion between the adhesive and substrate, and, subsequently, can cause undercorrosion. This would result in a rapid decline in the load-bearing capacity of the joints after the climate test.

The results of the load-bearing capacity of the mixed joints (DC+TL) prepared with individual surface treatments, in the as-bonded state and after the climatic test, are shown in Figure 5.

In Figure 5, the force corresponding to the yield point of the weaker substrate of the bonded pair (DC) is indicated by a green line. The red line represents the force corresponding to the minimum shear strength of the individual adhesive at a given overlap area. If the joint is loaded above the red line, cohesive failure of the joint can occur.

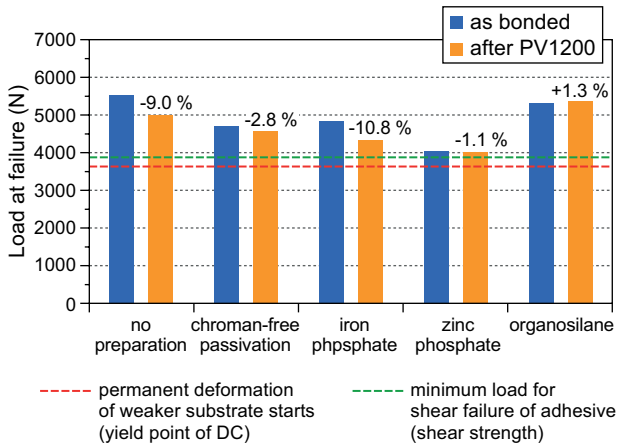
An effective joint should have a load-bearing capacity at the level of the onset of plastic deformation of a weaker substrate (DC). It does not make sense to improve the adhesion of the adhesive above the yield strength of the substrate, because plastic deformation of the substrate is an undesirable phenomenon. Ideally, the adhesion of the adhesive to the substrate could be at least at the level of the cohesive shear strength of the adhesive. Figure 5 shows that the first condition was met – all types of conversion layers ensured the bond strength of the joint at least at the level of the yield strength of the DC substrate (i.e. 3940 N at a sheet thickness of 0.8 mm and a sample width of 25 mm).

The adhesion of the Epoxy/PVC adhesive to the substrate was higher than the minimum cohesive strength of the adhesive and thus the maximum use of the properties of the adhesive was achieved.

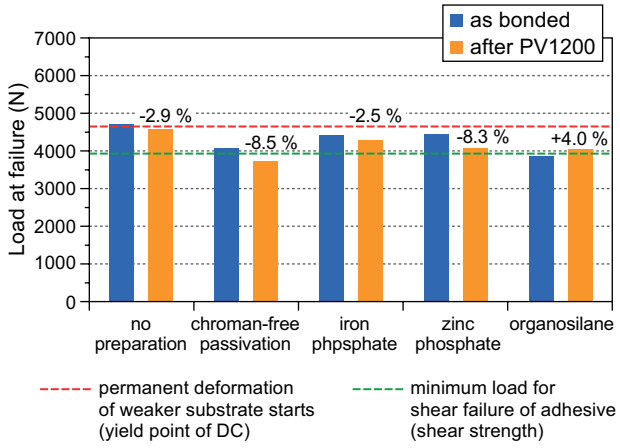
The properties of the rubber adhesive were also used effectively – the load-bearing capacity of the joints was between the values of plastic deformation of the weaker substrate and the cohesive strength of the adhesive.

The load-bearing capacity of the joints with the epoxy adhesive exceeded the yield strength of the substrate. However, the cohesive strength of the adhesive is much higher, i.e. a suitable surface preparation of the substrates could even lead to a higher load-bearing capacity, but only if higher strength substrates were used for adhesive bonding.

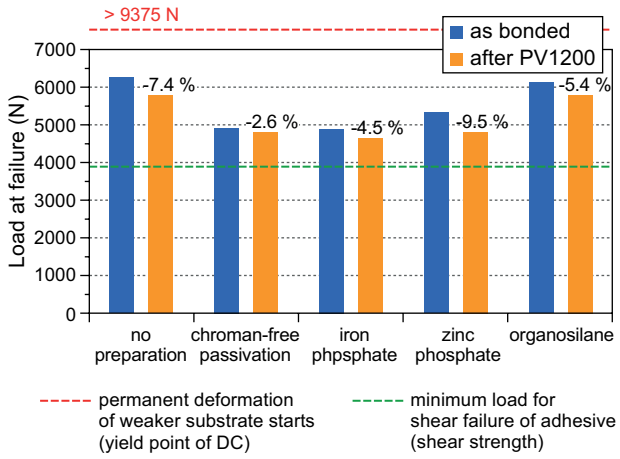
Due to the low mechanical properties of the DC substrate, it is not effective to further improve the adhesion of the adhesive to this substrate. All types of conversion coatings have been used appropriately and have been able to form effective joints. The decrease in load-bearing capacity of joints due to the climatic test is shown for individual pretreatments as a percentage in the graphs (Fig. 5). A slight decrease in the load-bearing capacity of the joints may indicate undercorrosion of the adhesive during the climatic test. Among all pretreatments, organosilane pretreatment stands out, in which, even after a climatic test, the load-bearing capacity of the joints was improved for the two adhesives used.



a) Epoxy/PVC-Polymerblend with glass beads



b) Rubber structural adhesive



c) Epoxy resin

Fig. 5. Change in load-bearing capacity of mixed joints after climatic test PV1200

CONCLUSIONS

Experimental measurements show that chemical pretreatments of substrates with conversion layers alone may not improve the corrosion characteristics of the substrates, especially when applied to non-galvanized steel. For hot-dip galvanized steel, all surface treatments have a positive effect on the corrosion resistance, because the conversion layers formed only made the corrosion resistance of the protective zinc layer more pronounced. However, it is necessary to perceive the surface treatment as a whole – pretreatments in connection with organic coatings or adhesives. Chemical pretreatments improve the adhesion of applied organic coatings or adhesives by various mechanisms – e.g. by forming a morphology suitable for mechanically anchoring the coatings or adhesives (phosphate coatings), or bonding the organic coating or adhesive chemically, by forming strong chemical bonds with the coating or adhesive and thereby creating a strong barrier protection effect (organosilanes).

However, the organosilanes must contain a functional group compatible with the coating. It has been experimentally confirmed that organosilanes have this "click" effect even in the case of adhesive joints. Even if they are not applied to the conversion layer but to the substrate itself. The advantage of organosilanes is also a very simple, rinsing or rinsing-free application, which can be carried out at room temperature and could be easily integrated into the production process. The formation of a strong chemical bond between the substrate and the adhesive by means of an organosilane is the best protection against undercorrosion of adhesive joints.

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