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Passivation of Zinc-Nickel Surfaces:
An optimal process control is essential to achieve a high corrosion protection and decorative appearance

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Abstract

The precise process control of passivates on zinc-nickel surfaces has a fundamental influence on the achieved corrosion protection. The exact control of passivation parameters like concentration, temperature, time and pH-value has a strong influence on the formation of the passivate layer which is important for a high corrosion protection on zinc-nickel surfaces.

The formation of passivation layers can be transparent, iridescent, black or blue. A very aggressive passivation as well as the zinc-nickel layer itself can lead to a strong decrease of corrosion protection (early red rust), if the nickel concentration in the zinc-nickel layer is too high.

As it is a known fact for zinc passivates, impurities in zinc-nickel passivates such as iron or a high zinc concentration have a negative influence on the layer formation process. They should be controlled in a narrow range (ionic exchange). A good rinsing technique as well as a good parts or passivation movement are needed to achieve a homogeneous surface appearance.

This paper describes the most important parameters of the process control and their impact on the capability of the passivation. Economic and ecological aspects are taken into consideration.

1. Introduction

The formation of a protection layer on a metallic material is called passivation. This conversion layer prevents or inhibits the corrosion of the base material. Nowadays passivates are based on complexed chrome(III) ions as well as cobalt-, nitrate- and complex ions (fluorides, organic acids etc.).

Chrome(VI) containing chromates which were used in the automotive industry in earlier days became illicit after introduction and implementation of the „End of Life Vehicles" rule 2000/53/EC" on

July 01, 2007. However, change to chrome(III)-containing passivates took place much earlier and the paper on hand will describe only chrome(VI)-free (chrome(III)-containing) passivates.

The creation of the conversion layer can be described in the following three reaction steps:

In the first step the acidic passivation solution (pH value usually between 1.8 - 2.2, but also solutions with a pH value up to 4.5) attacks the zinc-nickel layer under hydrogen formation (Eq. 1). Due to the reaction of hydrogen ions the pH rises on the metal surface (Fig. 1 and 2a).

$$Zn_xNi_{1-x} + 2\ H^+ \qquad Zn_x^{2+} + Ni_{1-x}^{2+} + H_2 \uparrow \quad x \leq 1 \qquad (1)$$
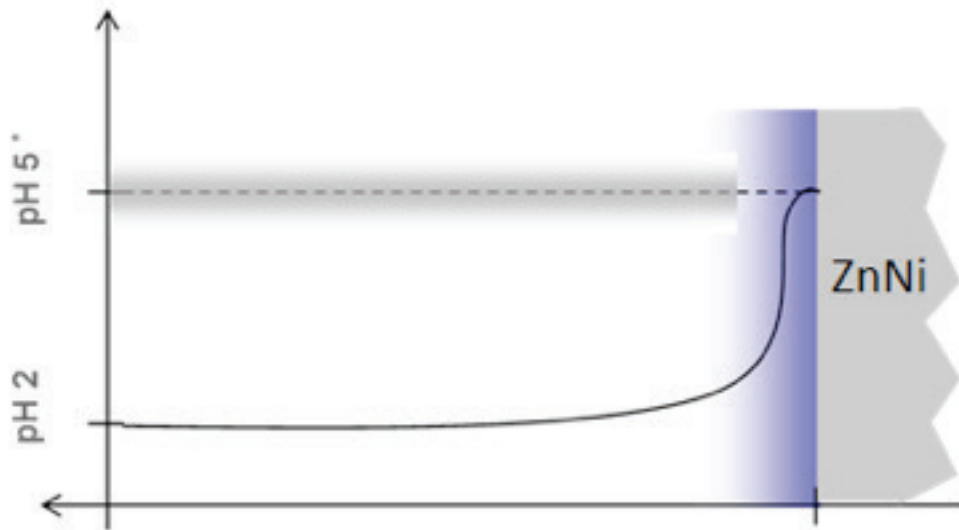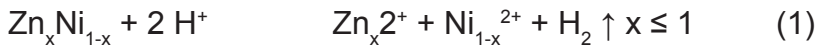

Fig. 1: pH-value rises on the top of the metal surface, formation of a chrome(III)oxide polymer structure [1]
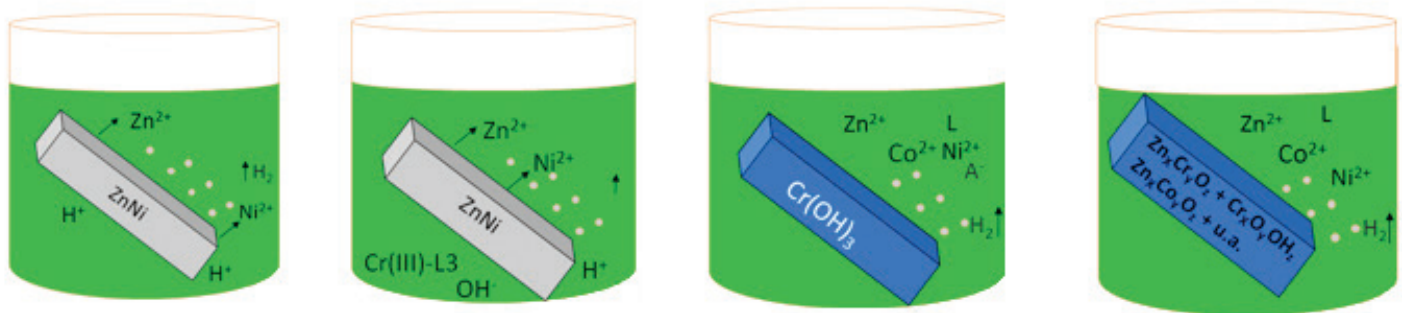

Fig. 2: Formation of a passivation layer, schematic description a) acidic attack on zinc-nickel surface according to Eq. 1 dissolution of zinc and nickel as well as hydrogen development, b) acid consumption on the top of the zinc-nickel surface leading to a pH value increase, c) precipitation of chrome hydroxide d) in parallel deposition of zinc and nickel ions as well as further cations and anions from the solution [2]
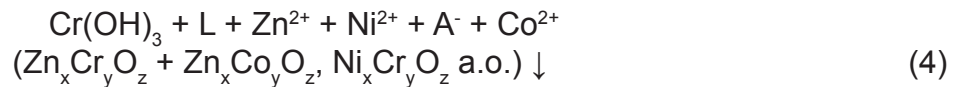
In chrome(III) based passivates the chromium ion is almost complexed (Eq. 2):

$$Cr(NO_3)_3 + 3\ L \qquad Cr(L)_3(NO_3)_3 \qquad (2)$$

A broad range of complexes are known. In the easiest case the complexes are formed with water molecules as well as fluoride ions or organic acids.

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The complexing agent has a significant influence on the creation of the passivation layer (k1, Eq. 3). Weak complexes (water) react very fast leading to a powdery and easy to wipe off layer. Strong complexes (fluoride) react slowly leading to a thinner and compact passivation layer.

Due to the pH increase on the top of the metal surface the chrome(III) complex will precipitate. Additionally, further active components which also have an influence on the layer properties will be deposited (Eq. 4, Fig. 2d).

$$Cr(III) - L_3 + 3\ OH- \quad \overset{k_1}{\underset{k_2}{\rightleftharpoons}} \quad Cr(OH)_3 + 3\ L \qquad (3)$$

$$Cr(OH)_3 + L + Zn^{2+} + Ni^{2+} + A^- + Co^{2+}$$
$$(Zn_xCr_yO_z + Zn_xCo_yO_z,\ Ni_xCr_yO_z\ a.o.) \downarrow \qquad (4)$$

During drying process chrome(III) oxide, hydroxide, zinc-chrome(III) oxide as well as nickel-chrome(III) oxide polymer structures are formed.

Depending on the type of passivate, the deposited amorphous passivation layers have layer thicknesses between 50 nm (transparence - blue, Fig. 3a) and 400 nm (iridescent - black, Fig. 3b) and a more or less crackly surface structure (Fig. 3c).
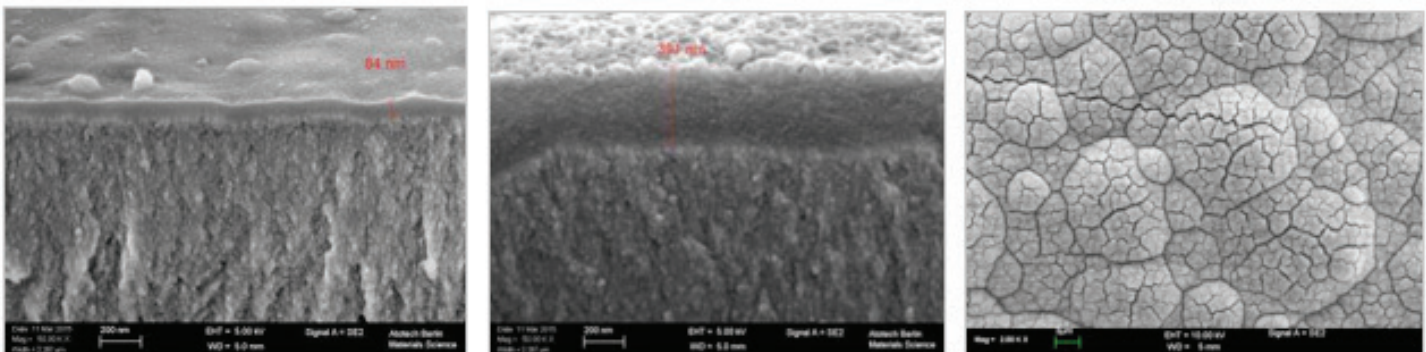

Fig. 3a Fig. 3b Fig. 3c
Fig. 3: Passivation layer thickness and structure, a = blue passivation, b = iridescent passivation (thick layer passivation), c = typical rough surface of a black passivation

Collodial suspension Si-particles (< 50 nm) can be added to the passivation solution as well. These particles are incorporated into the layer closing porse and cracks which leads to an increase of the barrier layer function.

2. Corrosion properties

Depending on layer thickness and integration of metal cations transparent, blue, iridescent (increasing layer thickness) or black passivation layers (black metal oxides, rough surface strong light diffusion) can be achieved. For corrosion protection not only the layer thickness is of importance but also the cracking of the surface. Blue passivation with a lower layer thickness (see Fig. 3a) of 50 – 100 nm but a compact and less crackly surface can lead to the same corrosion protection as an iridescent passivation (250 – 400 nm, Abb. 3b). The iridescent passivation is also called "thick layer passivation". According to DIN EN ISO 19598 [3] minimum corrosion requirements of passivates are requested. In practice they are achieved or even excelled (Fig. 4).
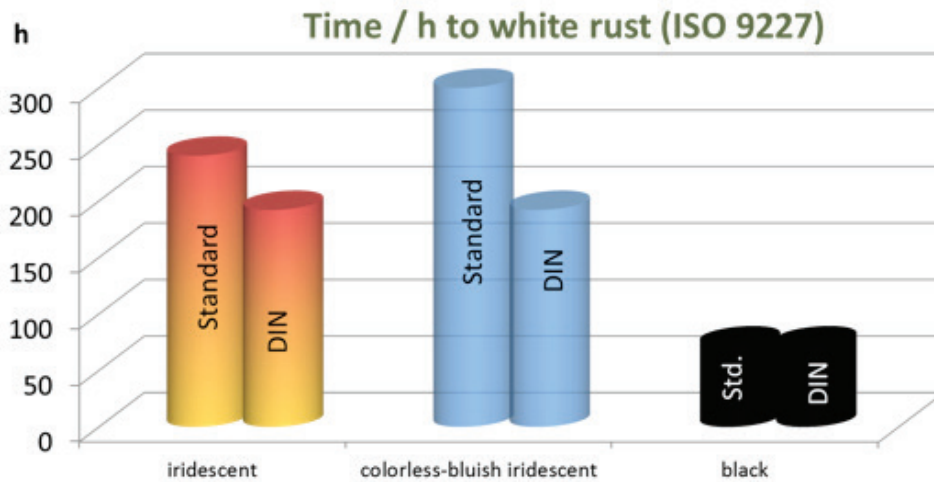
Fig. 4: Corrosion requirements (white rust formation) according to DIN EN ISO 19598:2017-04 on passivated zinc-nickel layers in rack application

For transparent layers (transparent – bluish) the corrosion requirement according to DIN EN ISO 19598 in barrel application is 120 h and in rack 192 h without white rust formation (DIN EN ISO 9227), for iridescent layers 120 h (barrel) and 192 h (rack). For a minimum zinc-nickel plating layer thickness ≥8 or ≥12 µm a base metal corrosion >720 h (ISO 9227) can be achieved. This is in accordance with DIN EN ISO 19598. In order to reach the corrosion requirements on black passivation for base coat and white rust formation a post dip or sealer should be used.

Black passivates usually have a rough and highly crackly surface which leads to a strong diffused reflection of light. This enhances a strongly preferable surface, which is free of iridescent light and can be even more improved when using an additional sealer (Fig. 5).
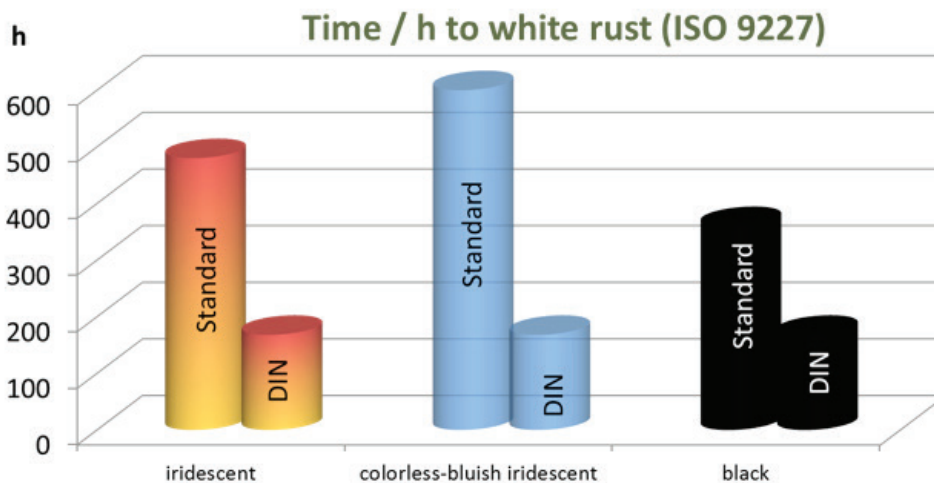

Fig. 5: Corrosion requirements according to DIN EN ISO 19598:2017-04 (formation of white rust) on passivated and sealed zinc-nickel layers in barrel application

The corrosion requirements for passivated and sealed black and iridescent zinc-nickel layers are 168 h (no white rust formation, as per ISO 9227) for barrel application and for rack application 240 h for sealed black passivates and 360 h for iridescent passivates (ISO 9227).

Ecological and economical aspects

Several ingredients of today's passivates are under observation from an ecological perspective. Some are banned worldwide such as boric acid and cobalt. But also fluoride is under observation in various countries due to the difficulty of waste water treatment. For some years substitute products with the same or even better corrosion properties have been available (see Fig. 6).
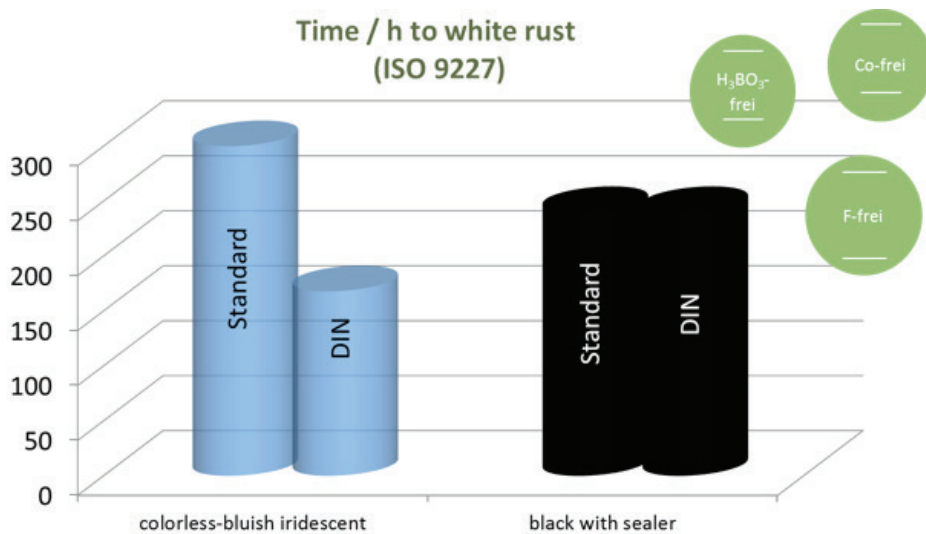

Fig. 6: Cobalt-, boric acid- and / or fluoride-free passivates for rack application, black passivation with sealer

New passivates use a much lower chrome(III) concentration, lower application temperature and higher pH values compared to first generation thick layer passivates. All this leads to money saving waste water treatment (Table 1).

	Thick layer Passivation 1. Generation	Blueish Passivation	Colorless Passivation
Make up [kg/100 l]	17.1	11.2	12.8
Cr(III) [g/l]	9.6	1.5	4.2
Fluoride	No	No	Yes
Cobalt	Yes	No	No
Temperature °C	60 – 70 °C	20 – 35 °C	20 – 30 °C
pH	1.8 – 2.5	4.0 – 4.5	3.0 – 3.8

Table 1: Process parameters of different passivates

When processing hardened parts (e.g. screws with a quality class of 10.9) a baking step is essential to prevent hydrogen embrittlement. In most cases baking is done outside the plating line. Zinc-nickel plated parts must be dried, removed from the process and after baking loaded into the plating line again. In order to prevent this baking resistant passivates are available on the market nowadays. After passivation and baking the surface shows only minor or no discoloration and no reduction of corrosion protection (Fig. 7, 8). Baking can be done at the end of the process saving production costs.
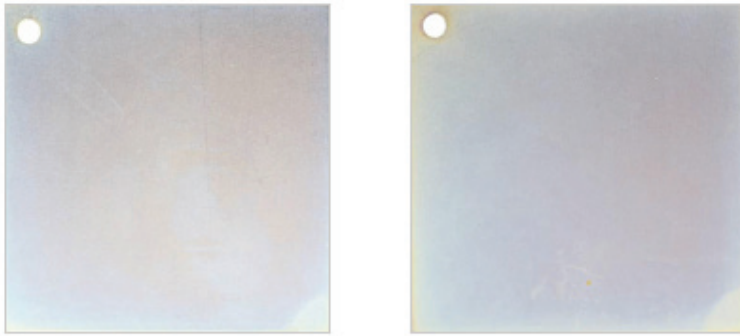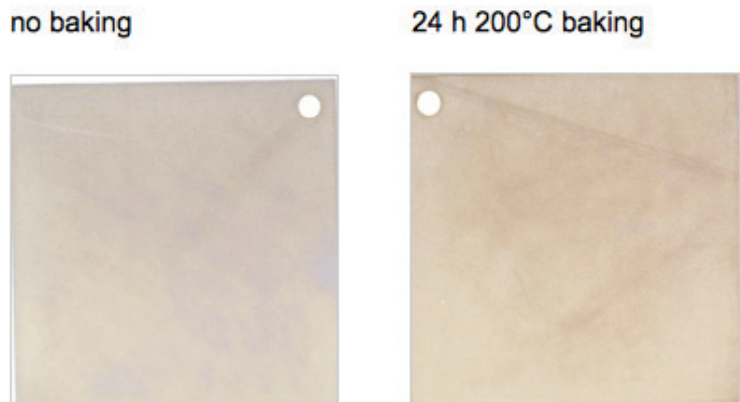
Fig. 7: No optical change after baking

no baking   24 h 200°C baking

Fig. 8: Optical change after baking

4. Increase of nickel during passivation and possible impact

During the acid attack of the passivation (Eq. 1) slightly more zinc is dissolved than nickel leading to an increase of the nickel concentration within the zinc-nickel layer (Table 2, Fig. 9).

Fig. 9: Increase of nickel concentration in the layer and decrease of layer thickness during passivation

Elektrolyte	Change of layer thickness during passivation	Change of nickel install rate
Layer before passivation	14 µm	14 %
Layer after passivation	12 – 13.5 µm	14.5 – 16 %
Change	Reduction: 0.5-2.0 µm	Increase: 0.5-2 %

Table 2: Increase of nickel concentration in the layer and decrease of layer thickness during passivation (nickel concentration is related to weight/%)

This can strongly influence the corrosion properties.

Open circuit potential measurements (OCP) in 5 wt/% sodium chloride solutions at 35°C are showing, that the potential can be shifted to more positive values depending on post treatment and nickel concentration inside the zinc-nickel layer, which may in rare situations lead to a potential more positive than steel (Fig. 10).
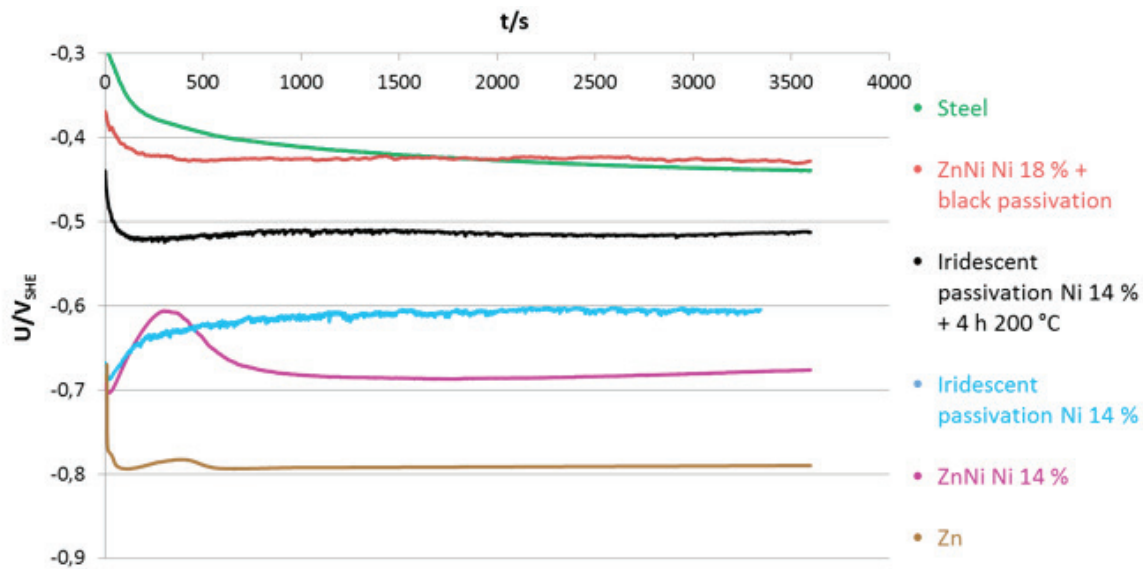

Fig. 10: OCP on zinc, iron and zinc-nickel layers after 1h in 5wt/% sodium chloride solution at 35°C. Equipment: PG-STAT302N Potentiostat (GPES-Software) flat cell EL-F-001 from Metrohm, working electrode 0.882 cm2, reference electrode SCE (0.2412 V vs. SHE 25 °C)

While a pure zinc layer (-0.79 VSHE) shows a much more negative potential than a pure iron layer (-0.44 VSHE) the zinc-nickel layer (Ni 14 %) is in between (-0.68 VSHE). The zinc-nickel layer is more novel than the zinc layer but still shows a cathodic corrosion protection against iron. An iridescent passivation leads to a small positive shift of the OCP to -0.60 VSHE. After baking (4 h 200 °C) there is once again a positive shift of approximately 90 mV to -0.51 VSHE.

As mentioned above the nickel concentration inside the zinc-nickel layer increases during passivation. Some black passivates show a strong acid attack which can lead to a nickel concentration >17 % in the layer after passivation. The acid attack takes place on the surface of the zinc-nickel layer and nickel is enriched only on the surface instead of through the whole layer. An aggressive passivation can lead to an OCP of almost -0.43 VSHE, which means more positive than steel (see Fig. 10 dark red line). Such a layer shows no cathodic corrosion protection and in case of defects will lead to an early red rust formation.

For this reason an accurate process control like immersion time, temperature and pH-value is of high importance.

5. Influence of passivation parameter
As it has been well known for zinc passivates for a long time, process parameters such as immersion time, temperature and pH-value have a significant influence on the corrosion performance and optical appearance of the passivation layer. All three parameters are influencing the thickness of the passivation layer. If the layer is too thin the barrier effect is not efficient enough. A very thick layer, however, becomes crackly and easy to wipe off. As chrome(VI) free passivates are colorless (except black

passivates, which may include metal oxides), there is a direct relationship between optical appearance and thickness of the passivation layer due to light diffraction and interference (Fig. 11).
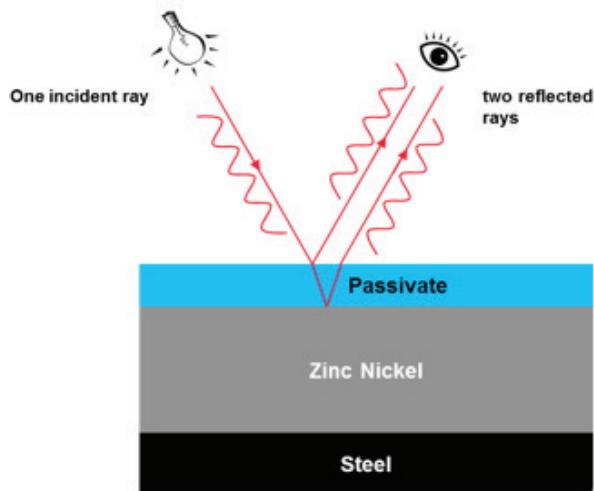

Fig. 11: Light diffraction and interference on a passivation layer

A bluish layer typically shows a coating thickness of 50 – 100 nm, an iridescent (yellowish, greenish, reddish) of 250 – 400 nm.

Higher temperature and longer immersion time leads to a thicker passivation layer. However, this does not necessarily result in a higher corrosion protection (Fig. 12).

35 s   75 s   180 s

Fig. 12: Influence of immersion time at constant temperature and pH-value

At 35 s immersion time the passivation layer appears colorless (approx. 50 nm), at 75 s yellowish iridescent (layer thickness 150 – 200 nm), and at 180 s violet redish (>200 nm).

Low pH values (in this case pH 1.6, optimum pH 2.5) lead to a strong attack of the zinc-nickel layer and a reduced passivation layer formation (back reaction). At pH 3.5 the acid attack is too slow and there is no efficient layer built up. The optimum in this case is pH 2.1 and 2.5 (Fig. 13).
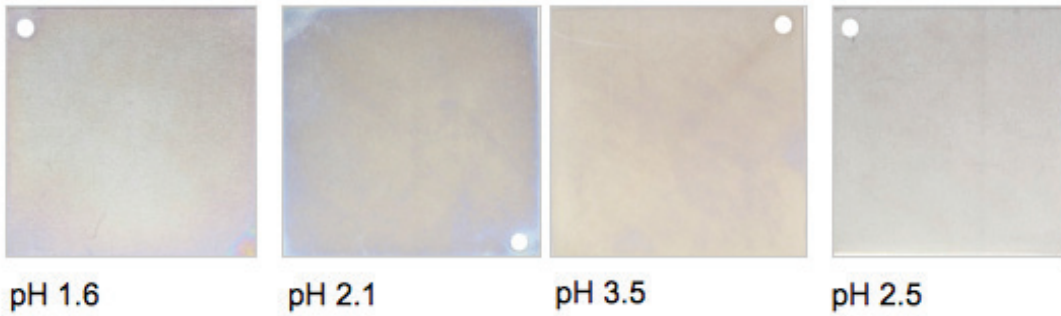
pH 1.6　　　　pH 2.1　　　　pH 3.5　　　　pH 2.5

Fig. 13: Influence of the pH-value at constant immersion time and temperature. Optimum pH-value for the given example: pH 2.5

6. Influence of Impurities

The dissolution of zinc- and nickel ions into the passivation cannot be prevented, because it is part of the reaction mechanism (see Eq. 1). The dissolution of iron ions can be prevented, if the parts are completely zinc nickel plated (no cavities or un-plated areas) and parts, which fall into the bath, are removed immediately.
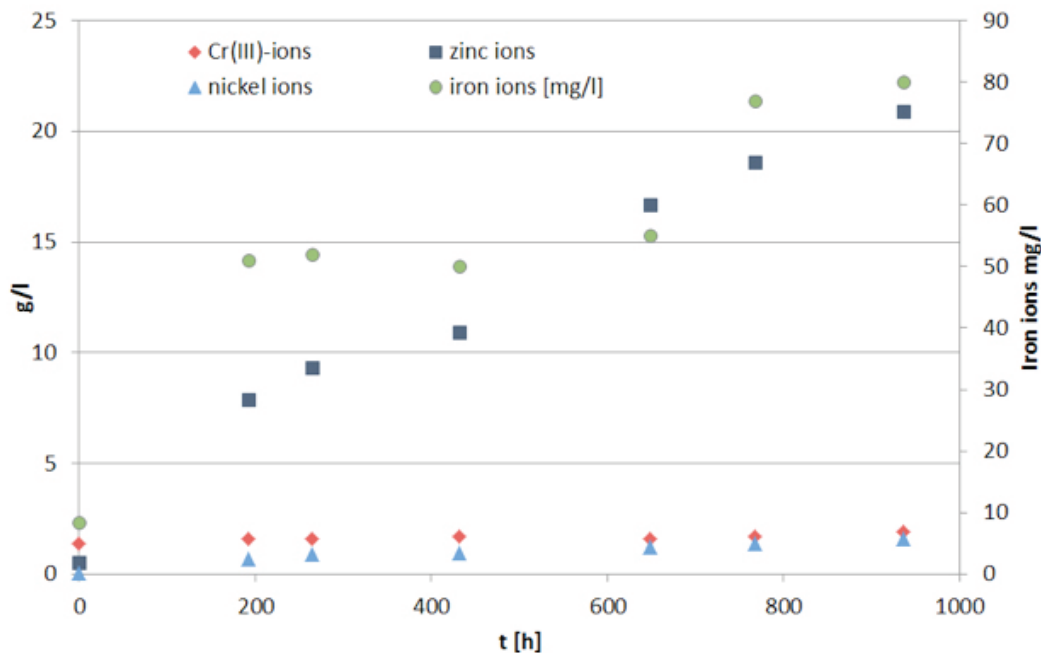

Fig. 14: Increase of impurities (Zn2+, Ni2+, Fe2+) into the passivation solution

Fig. 14 shows a typical increase of zinc, iron and nickel ions over time in a non-treated passivation solution with a constant production input. The nickel concentration is approx. 10 % of the total metal input. Depending on the passivation a zinc concentration >15 g/l leads to a strong change of optical appearance (hazy) and a strong reduction of corrosion protection (Fig. 15). Iron ions are even more critical. Even 50 ppm leads to a yellowish discoloration and a strong decrease of corrosion protection (see Fig. 16).

Thus passivates have to be diluted or even newly made-up, if a critical concentration of zinc or iron is attained. By using an ionic exchange resin, which preferably removes zinc- and iron ions from the passivation solution, the zinc and iron concentration can be kept below a critical limit resulting in an „infinite" lifetime (see Fig. 18). The application area can be kept in a much smaller range (Fig. 19).
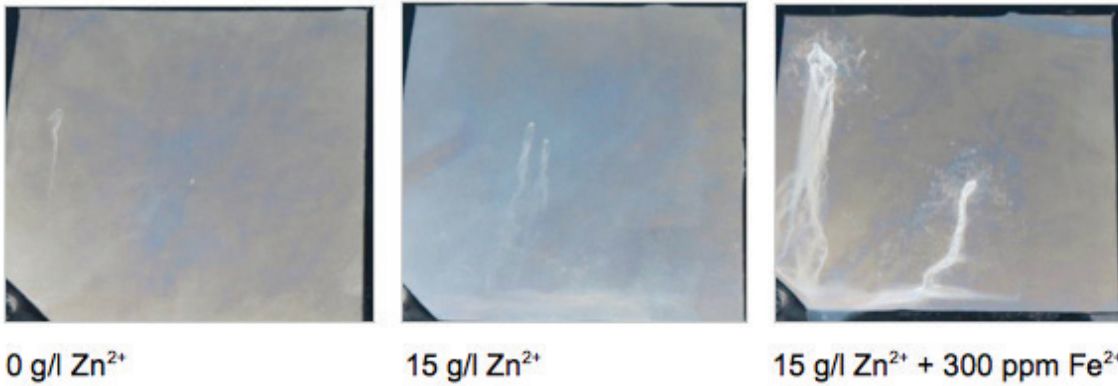
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0 g/l Zn²⁺ 15 g/l Zn²⁺ 15 g/l Zn²⁺ + 300 ppm Fe²⁺

Fig. 15: Influence of metal impurities on corrosion protection, 192 h ISO 9227

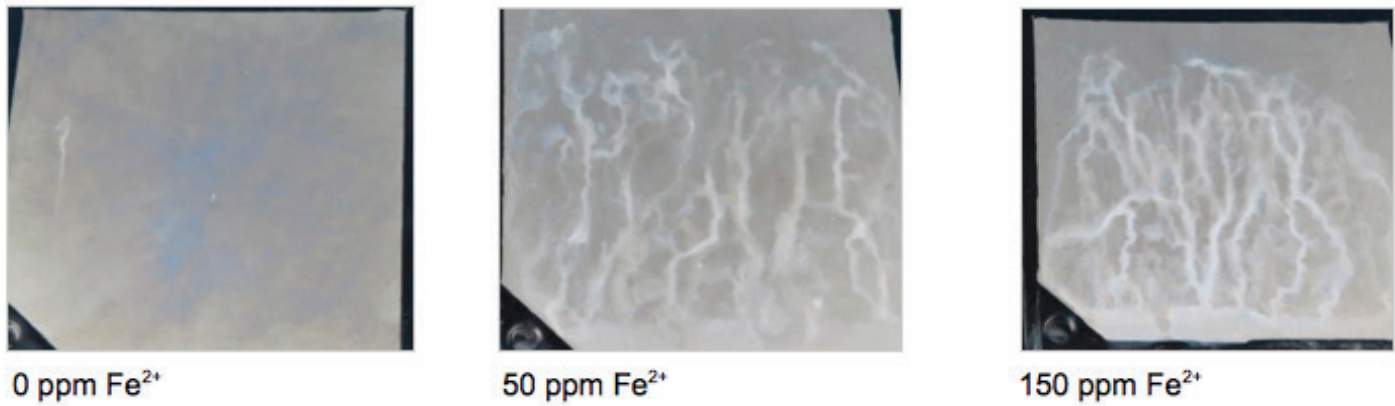
0 ppm Fe²⁺ 50 ppm Fe²⁺ 150 ppm Fe²⁺

Fig. 16: Influence of metal impurities on corrosion protection, 192 h ISO 9227

As it could be demonstrated in several test series nickel ions have no negative influence on corrosion protection, Fig. 17.

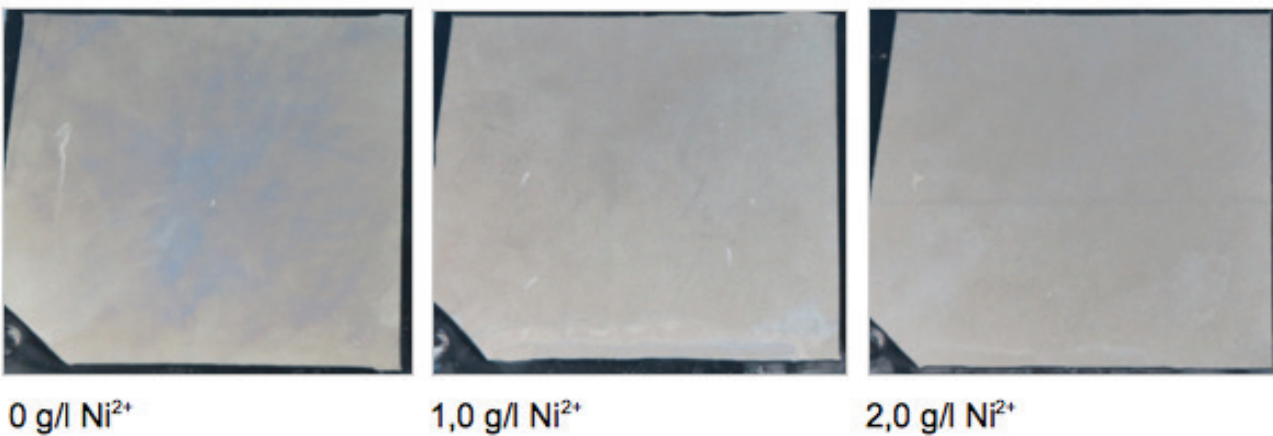0 g/l Ni²⁺ 1,0 g/l Ni²⁺ 2,0 g/l Ni²⁺

Fig. 17: Influence of metal impurities on corrosion protection, 192 h ISO 9227

Fig.18 shows an installation of ionic exchange equipment with two separate ionic exchange columns. While one column is used to regenerate the ionic exchange resin, the other column is used to remove zinc and iron ions from the passivation. When saturating the ionic exchange resin the columns are pumped off and changed. When adhering to such a procedure, a continuous zinc iron removal is possible.
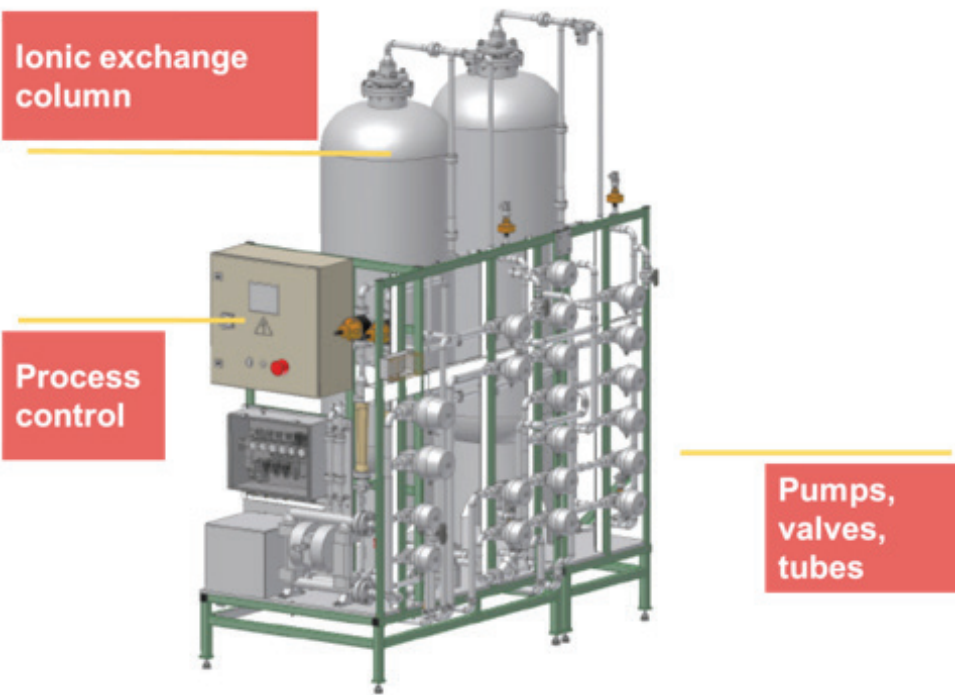
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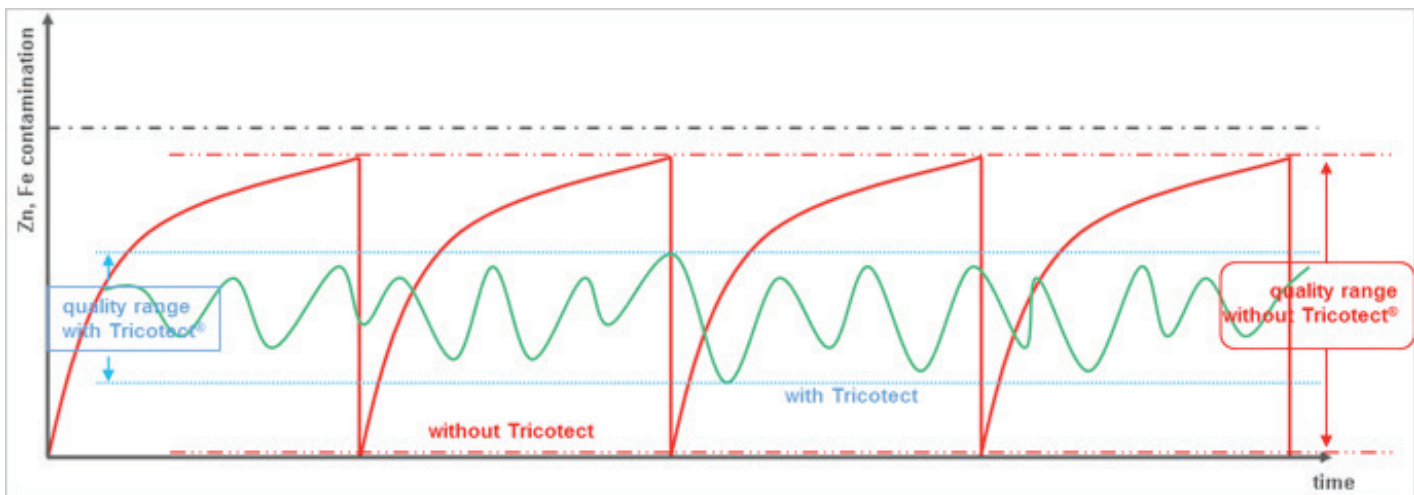Fig. 18: Drawing of an ionic exchange equipment

Fig. 19: Production area with (green line) and without (red line) ionic exchange

7. Influence of Installations

An efficient rinsing, but also line parameters like parts and passivation movement have an influence on the passivation layer formation. As it was shown in fig. 1 there is a pH value increase on the top of the zinc-nickel surface within the diffusion layer leading to a precipitation of chrome(III) ions (Eq. 3). The thickness of the diffusion layer (and therefore the gradient of the change of the pH value) depends on the parts and passivation movement. Especially an inhomogeneous movement on rack application leads to an indifferent formation of the passivation layer. Fig. 20 clearly demonstrates that parts in the center of the rack are not black caused by an inhomogeneous air movement.

Fig. 20: Inhomogeneous formation of the passivation layer due to an indifferent solution movement

8. Conclusion

Commercial chrome(III)-based passivates on the market are a key stone for excellent corrosion protection of zinc-nickel layers. These passivates on zinc-nickel layers exceed the requirements of DIN EN ISO 19598 with a significantly lower chrome concentration, lower temperature and higher pH value compared to thick layer passivates of the first generation. From an ecological perspective there are passivates available, which do not need cobalt, boric acid or fluoride. Several passivates are heat resistant (baking) which simplifies the process flow leading to a reduction in costs.

An accurate process control is crucial especially for aggressive black passivates to avoid a strong increase of the nickel concentration in the zinc-nickel layer. This can lead to a free corrosion potential more positive than steel. Such a layer shows no cathodic corrosion protection and in case of defects will lead to an early red rust formation.

Zinc- and iron impurities have a negative influence on the optical appearance and corrosion resistance of the passivation layer and have to be controlled frequently. Ionic exchange equipment can remove these ions from the passivation leading to an „infinite" lifetime. Nickel ions do not show a negative influence. Homogeneous parts or passivation movement is important particularly for black passivates in order to achieve a consistent black appearance.

9. Literature

[1] R. Sarmaitis et al., Transt. Inst. Metal Finishing, 86(7), 53(1999)
[2] E. Karapinar et al., Interne Schulungsunterlagen Atotech 2015
[3] DIN EN ISO 19598, Metallische Überzüge- Galvanische Zink- und Zinklegierungsüberzüge auf Eisenwerkstoffen mit zusätzlicher Cr(VI)-freien Behandlung (ISO 19598:2016)