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# Zinc/tin alloy coating for improved corrosion protection,

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## Abstract

In order to enhance the corrosion resistance of a zinc coating, it is alloyed with small amounts of other metals, preferably more noble than zinc as Co, Fe, Ni, Sn. As a result, the alloy corrodes at a much slower rate than zinc alone, providing a better corrosion protection. A Sn/Zn alloy with a tin content of 70 % to 90 % has been investigated but it was limited to cyanide or acidic electrolytes, it is very expensive and can not be treated successfully with trivalent chromium passivations. It is important to mention, that Sn/Zn alloys with a tin content higher than 50% can be only treated with hexavalent chromium passivations. Hexavalent chromium compounds are considered to be carcinogenic and are forbidden by European norms. In this work, Zn/Sn alloys obtained from non cyanide alkaline electrolytes were studied. The electrolyte is based on tin in the oxidation state IV, that offers many advantages like a good throwing power, excellent metal-distribution with a uniform alloy composition and superior stability against any changes of the oxidation state of tin. The resulted Zn/Sn alloy with a tin content of 25 % to 35 % was passivated with trivalent chromium solutions free of Cr(VI) and offered a good corrosion resistance.

**Palavras-chave**: corrosion, eletrodeposition, Zn/Sn alloy. Cr(VI)free passivation**.**

## Introduction

Because of its excellent properties, steel is nowadays the most commonly used material for construction, automobiles, tools, many consumer articles, and industrial applications. On the other Hand, steel corrodes in contact with humidity and air under oxygen and/or hydrogen evolution, and it forms iron oxide/hydroxide which precipitates as a voluminous corrosion product at the surface = Red Rust. Iron oxide layers do not protect against further corrosion, unlike chromium oxide on top of chromium or aluminium oxide on top of aluminium.
This means, the corrosion at steel proceeds and eventually will impair the integrity of the parts. Therefore, steel must be protected against corrosion, and this can be done by the way of the following principal systems[1]:

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| | |
|---|---|
| - barrier layers | oil, conversion layers and/or lacquer, metallic layers |
| - redox buffers | less noble layers, conversions layers with different oxidation levels, organic corrosion protectors |
| - duplex layers | combination of redox buffer + barrier layer |

## Tin/Zinc alloys

### Cathodic Corrosion Protection by Zinc

Steel is often plated with zinc in order to protect it from corroding media of the environment. The corrosion protection of zinc is based on the fact, that it is less noble than the base metal. Therefore, in the first place it draws the corrosive attack to itself. This means zinc functions as a sacrificial layer. The base metal of the respective part remains unaffected as long it is covered with a continuous Zn layer. Consequently, the mechanical properties are maintained for a longer period of time, if compared with non-zinc-plated parts. Naturally, thick zinc layers provide a higher corrosion protection than thin layers – the corrosive degradation of thick layer simply takes longer. Very thick layers are costly because material costs and a very long plating time. In addition, thick layers may affect the dimensional accuracy and other specified properties, like deformability and heat resistance[2].

Fig. 1: Schematic representation of corrosion of zinc plated and passivated steel. The zinc coating functions as a sacrificial anode.

### Comparison of Pure Zinc with Zinc-Alloys

Actually zinc is more negative than it needs to be, and therefore, it corrodes relatively fast, forming voluminous corrosion products made of zinc oxide = white rust. It has been known for a long time, that the so-called cathodic corrosion protection, which is provided by the zinc, can be increased by alloying Zn with other metals such as iron, nickel, cobalt, tin chromium, or manganese[3,4].

Fig. 2: Electromotive series of the elements with respect to the standard hydrogen electrode

Depending on the element different mechanisms increase the corrosion resistance. Zinc alloys with iron, nickel, cobalt, or tin, the layer becomes more noble. That means, that the electrochemical potential is more positive than that of pure zinc, resulting in a slower dissolving sacrificial layer, that therefore provides a longer lasting corrosion protection.
Zinc alloys with nickel, cobalt, chromium, or manganese may provide an additional protection by the formation of highly insoluble hydroxides/oxides which would passivate the zinc alloy layer and additionally increase the corrosion protection.
For Zn/Ni, Zn/Co and Zn/Sn, the composition should stay in a range where the electrochemical potential is more negative than the potential of steel. Otherwise, the zinc alloy is not able to provide a cathodic protection anymore.
Since nickel is more noble than iron, the zinc/nickel alloy may become also more noble than iron, if the nickel content exceeds a certain limit. If this happens, then the zinc/nickel alloy is no more able to provide a cathodic corrosion protection anymore. The practical limit for good corrosion protection of more than 1000 hours until red corrosion in the neutral salt spray test

(accord. to ISO 9227) is 15 % of nickel. If the nickel content in zinc/nickel exceeds 16 %, it is very likely that red corrosion appears within 24-48 hours. With tin-zinc alloys, this effect occurs only at a tin content of more than 93 % of tin[4,5].
Zinc/iron alloys do not have the problem of becoming more noble than iron, but if the iron content exceeds 0.75 % then the zinc/iron layer becoming very brittle and blistering is very likely to occur.
Zinc/iron alloys are very popular for plating of black parts with high corrosion protection. Zinc/cobalt alloys are not so common anymore because they do not offer any benefits compared to Zn/Fe and cobalt is toxic.
Zinc/chromium and zinc/manganese alloys increase the corrosion protection only slightly. Furthermore, zinc/manganese alloys cannot be used for decorative purposes, and the appearance of manganese oxide is reddish-brown, which makes it hard to distinguish zinc/alloy corrosion from base metal corrosion (red rust).
In all cases, an exact alloy composition plays an important role to achieve the desired properties. In general, electrolytical plating processes suffer from non-uniform current distributions. It is quite normal that the more noble metal of the alloy is preferably deposited in the low current density area, which leads to a non-uniform alloy composition among different areas of the plated parts. To quite a big extend this problem can be can be resolved by using suitable additives. Very important is also a good control of the process parameters.
Zinc/nickel and zinc/iron are big industrial scale plating processes. Tin/zinc alloys are often used for components to be protected against salt and humidity in marine environments. The typical alloy composition is 70-80 % Sn and 30-20 % Zn. These high tin alloys can be passivated only with hexavalent chromates, which are toxic and strongly regulated. For this reason tin/zinc alloys are only of limited use and only in industrial applications, but are not suitable for consumer articles.
The corrosion resistance of zinc and its alloys increases in the following series:

**zinc < zinc/chromium < zinc/cobalt < zinc/iron << zinc/nickel < tin/zinc**

Zinc/nickel and tin/zinc offer the very best corrosion protection on top of steel. Unfortunately both processes employ harmful substances. Nickel and its salts are known to cause allergies. Fine nickel particles are cancerogenous. Hexavalent chromates of tin/zinc passivates are very toxic. A desirable heavy duty corrosion protection on top of steel would abandon these harmful substances, while preserving the benefits provided by zinc alloys.
In order to achieve this objective target, the focus of the present work was the development of zinc/tin alloys (more zinc than tin, compared to tin/zinc which has more tin than zinc) that can be passivated without hexavalent chromium.

## Typical Electrolytes for Zinc and Zinc Alloy Plating

Pure zinc electrolytes are well known and there are processes ranging from acidic to weakly acidic up to alkaline with and without cyanide. These processes are sophisticated, well established, and widely applied. Alkaline electrolytes have a lower current efficiency but they have much better metal distribution which is very important for parts with high demands on dimensional accuracy. Acidic processes are used for high speed continuous plating lines, because the current efficiency is nearly 100 %. Weakly acidic electrolytes are preferably used for decorative plating applications and for plating of cast iron.
Acidic zinc/chromium electrolytes were developed for high-speed plating lines, but applications are seldom. For zinc/cobalt as well as for zinc/manganese alloy plating, acidic and alkaline processes are known.

Zinc/iron alloys are exclusively electroplated from alkaline non-cyanide electrolytes. These electrolytes are very similar to their pure zinc counterparts, and they share the same excellent properties e.g. to stability, metal distribution and plating speed.
Zinc/nickel can be electroplated from weakly acidic or alkaline electrolytes. The alkaline type is in the majority of the plating situations the preferred type because it provides for a much better metal distribution and a higher uniformity of the alloy composition. Acidic Zn/Ni electrolytes are used for continuous strip plating and for direct plating of cast iron and forged steel. In order to stabilize the Nickel in the alkaline electrolyte solution, the addition of high amounts of very strong complexing agents is necessary. These complexing agents and their degradation compounds make the waste water treatment very complicated and they decrease the stability and the service life of alkaline Zn/Ni electrolytes[4].

For tin/zinc plating, several different possibilities exist:

- Θ Weakly acidic electrolytes utilise tin(II) salts and contain complexing agents for controlling the alloy composition and organic additives for brightness and metal distribution. These electrolytes produce semi bright to bright layers. Tin(II) tends to oxidize to tin(IV), which disturbs the plating process. For this reason, reduction agents need to be added as stabilizers, and most of them are very toxic, e.g. hydroquinone[6].

- Θ Neutral to weakly alkaline electrolytes are also based on tin(II) and the problem of tin(IV) formation is even elevated, and therefore the addition of reduction agents is even more import. In other respects, these processes are quite similar to the weakly acidic types[7].

- Θ Cyanide alkaline electrolytes are based stannate (IV). Because of the cyanide, these electrolytes are not very common anymore, but they offer a good stability in depositing semi bright to bright layers[6].

- Θ Alkaline non cyanide electrolytes are also based on stannate (IV). These kind of elec-trolytes are not well established in the industrial production, because the appearance of the deposited layers ranges from mat to semi bright only. On the other hand these electrolytes are highly stable, because tin(IV) cannot be oxidized any further. The metal distribution is better than for acidic and neutral types. The application parameters must be held within their somewhat tight operation limits[8].

The electrolyte types which are based on tin(IV) operate at elevated temperatures, while the acidic and neutral tin(II) types are limited to operation temperatures below 30 °C, which quite often requires a cooling system. Deposits of all above mentioned electrolytes suffer a non-uniform alloy composition ranging from 60 to 80 % of tin and vice versa 40 to 20 % of zinc.

**Conversion Layers on Top of Zinc and Zinc Alloys**

The corrosive attack on the zinc or zinc alloy layer can be strongly hindered by a chromate layer (conversion layer) on top, and therefore also the base metal corrosion occurs later compared to a zinc layer without any conversion coating. In addition the appearance of the parts is preserved by a protective conversion layer for a very long period of time.
There are different types of chromates, depending on colour and corrosion protection. High corrosion protection can be achieved with hexavalent chromates, e.g. the hexavalent yellow chromate, and since some years, by the way of thick layer passivations based on trivalent chromium[9].

The passivation process itself occurs in two principal steps. In the first step, the metallic zinc is dissolved by oxidation. In this respect the hydronium ions of the acid and the hexavalent chromium serve as oxidizing agents.

$$Zn^0 + 2H^+ \xrightarrow{k_1} Zn^{2+} + H_2 \uparrow$$

Step 1: the metallic zinc is dissolved by the way of acidic attack and hydrogen formation:

In the course of the above reaction, hydronium ions are consumed and the pH will rise. The rising pH leads to the second step, the conversion layer formation by the way of zinc/chromium hydroxide/oxide precipitation.

$$Zn^{2+} + xCr^{(III)} + yH_2O \underset{k_3}{\overset{k_2}{\rightleftarrows}} ZnCr_xO_y + 2yH^+$$

Step 2: chromium(III) precipitates together with zinc(II), forming a film of non-stoichiometric zinc/chromium hydroxide/oxide, i.e. the conversion layer:

In the case of a zinc alloy, step 1 will only occur, if the difference between the electrochemical potential of the zinc alloy and the hydrogen potential is sufficiently high to force the given reaction. When the alloy layer is too noble, that means when its electrochemical reaction comes close to the hydrogen potential, the initial step of a conversion layer formation cannot occur with the hydronium ion as the oxidising agent alone, and in this case only hexavalent chromates can be used because of the very high oxidation potential of Cr(VI).
For this reason, tin/zinc alloys with 60-80 % tin can only be passivated with hexavalent chromates. These tin/zinc alloys are too nobel for trivalent chromates.
Nowadays hexavalent chromates are subject of several regulations like ELV and RoHS, and their use is diminishing in the industry. Consequently, tin/zinc alloys with high tin are almost vanished from the market of corrosion protection for steel[9].

## New Alkaline Non Cyanide Zinc/Tin-Process

Since tin/zinc alloys with a tin content of more than 60 % are not eligible for Cr(VI)free passivates with high corrosion protection, a new electrolyte was developed, that allows a repro-ducible adjustment of the Zn/Sn ratio of the plated alloy ranging from 90:10 to 10:90. In experimental series the optimal alloy composition which gives the best corrosion protection with trivalent passivations could be determined.

## Electrolyte Composition

Because acid tin/zinc electrolytes are much more problematic with respect of stability, metal distribution and uniformity of the plated alloy composition, an alkaline zincate/stannate(IV) base was chosen for the new Zn/Sn electrolyte.
Besides the uniform alloy composition, the plated Zn/Sn layers exhibit a very good metal distribution, i.e. the quotient of the layer thicknesses at a Hull cell panel(1 A,15min) HCD/LCD is ca. 2.
**At 2 A/dm2 a current efficiency of 50 % can be achieved. The appearance of the plated alloy layer is silver-like, semi bright.**

Fig. 3: Zinc/tin barrel parts with 8-10 µm layer thickness, tin content 25-30 %

The alloy composition was mainly controlled by the zinc and tin content in the electrolyte, and for a given setting, the alloy composition was indifferent against the current density over a wide range. The following chart shows the alloy compositions at different current densities.

Fig. 4: Tin content in the Zn/Sn alloy plated from differently adjusted electrolytes at different current densities ranging from 0.2-6.8 A/dm2. The alloy composition is very stable within each electrolyte category.

**Working parameters**

Working parameters for the 30 % tin category of the new zinc/tin electrolyte
(alloy composition of 25-35% Sn, 75-65 % Zn).

analytical values

| | | |
|---|---|---|
| zinc | 4 g/l | ( 3.8-4.2 g/l) |
| tin | 20 g/l | ( 18-22 g/l) |
| KOH free | 45 g/l | ( 42-70 g/l) |
| $K_2CO_3$ | 20 g/l | ( 0-60 g/l) |
| complexing | 200 ml/l | (200-220 ml/l) |
| additive | 1,0 ml/l | ( 0.5-2.0 ml/l) |

temperature: 53 °C (50-55 °C)
the chosen temperature should be kept in a small range of ± 1 °C

anodes: semi bright nickel plated expanded steel

current density: 2 A/dm2 (1-3 A/dm2)

plating speed: 0.25 µm/min at 2 A/dm2

movement: rack movement or barrel rotation

tank material: steel tank covered with PP or PVC

filtration: continuous: 2 times per h

heating: necessary: thermostatically controlled heating elements made of alkali resistant material
exhaustion: necessary

Fig. 5: zinc/tin plating line

**Process Sequence**

The recommended process sequence for steel parts:

1. alkaline hot degreasing, 60-80 °C
2. inhibited hydrochloric acid pickling, 5 min, RT
3. anodic electrolytical cleaning, 15 min
4. neutralisation
5. Zn/Sn plating

6. acid activation
7. passivation
8. hot air drying 60-80 °C

After each step triple cascade rinsing is required.

**Results**

The first survey has been done about different tin contents in the layer for determining the corrosion protection of the alloy without any passivation. The parts were put into a neutral salt spray test chamber in accordance ISO 9227, (see Fig. 6).

Fig. 6: Corrosion protection until red rust in the neutral salt spray test ISO 9227 of **non-passivated zinc tin alloys**.

As indicated by the regression line, the corrosion protection increases with increasing tin content of the alloy. As stated already, Zn/Sn alloys with more than 60 % of tin can only be hexavalently chromated, and without any passivation all alloys exhibit white corrosion within 24 h NSS, although, the white rust is less voluminous for the high tin alloys.

Fig. 6 shows the NSS corrosion test results of Zn/Sn alloy plated parts, which were passivated in a trivalent chromium thick layer passivation, under several different conditions. Again, the corrosion protection in NSS until red corrosion is higher with higher tin content, but good white corrosion results could despite all attempts to optimise the passivation parameters only be achieved for Zn/Sn alloys with low tin content. In the presented experimental series of several different parameter sets, the best corrosion protection results were 192 h against white corrosion and 1000 h until red corrosion for a Zn/Sn alloy containing 30% tin. These values are reproducible for an optimized parameter set (**as: activation, pH-value, Cr(III) concentration in the solution, immersion time, and temperature of the solution**) and marked in Figure 6 with green circles.

Fig. 7: Corrosion protection until white rust and red rust in the neutral salt spray test ISO 9227 of **passivated zinc/tin alloys**.

Hexavalent free Tin/Zinc above 40 % tin exhibit excellent corrosion protection against red corrosion but fails miserably for white corrosion which are always under 100 h in neutral salt spray test.
Figure 8 shows a comparison to the high tin tin/zinc alloy with 60-80% tin, to the new low tin zinc/tin alloy with 25-35 % of tin, these new layers, which can be passivated without hexavalent chromates have a better corrosion resistance against white rust, and still have a good corrosion resistance against red rust.

Fig. 8: Comparison corrosion protection until white and red rust in the neutral salt spray test ISO 9227 of **Cr(VI) free passivated zinc tin alloys**.

Figure 9 shows Cr(VI) free passivated zinc/tin (25-30% Sn) parts plated in a barrel process, the appearance is uniform grey.

Fig. 9: Passivated zinc/tin barrel parts with 8-10 µm layer thickness, tin content 25-30 %

## Conclusions

A non-cyanide alkaline zinc/tin alloy process based on zincate/stannate(IV) was developed, which plates very uniform zinc/tin alloys with a high plating speed and a very good metal distribution. The alloy composition can be reproducibly adjusted in a very wide range of Zn[90-50] : Sn[10-50]. It turned out that the most suitable composition, that can be passivated without hexavalent chromium and at the same time offers a heavy duty corrosion protection is Zn[75-65] : Sn[25-35].
With that corrosion protection in NSS was up to 192 h until the first appearance of white corrosion and 1000 h until red corrosion for ca. 10 µm of layer thickness. The relevant standards and specifications for zinc/nickel coatings with transparent thick layer passivations, are met easily. Therefore, this new environmentally friendly zinc/tin layer system has the potential to be a good replacement in a wide range of applications for the not ecologically safe zinc/nickel alloys.

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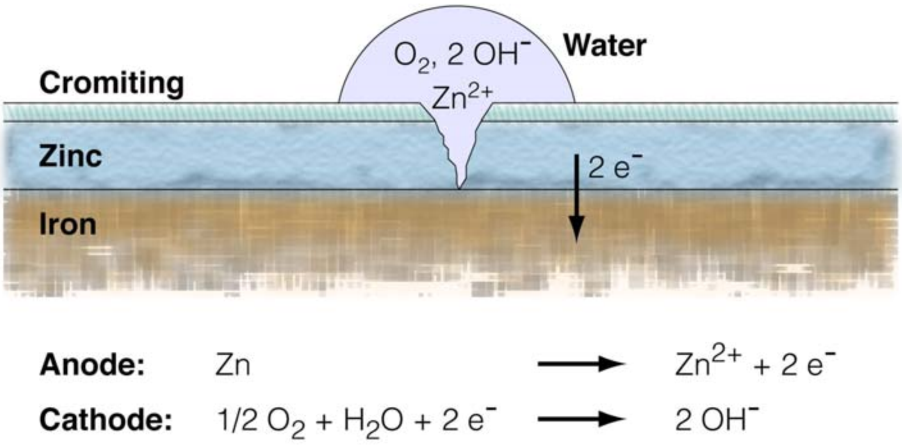


Fig. 1: Schematic representation of corrosion of zinc plated and passivated steel. The zinc coating functions as a sacrificial anode.

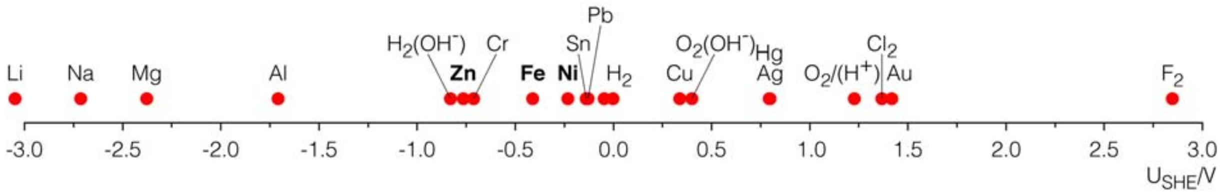


Fig. 2: Electromotive series of the elements with respect to the standard hydrogen electrode

$$Zn^0 + 2H^+ \xrightarrow{k_1} Zn^{2+} + H_2 \uparrow$$

Step 1: the metallic zinc is dissolved by the way of acidic attack and hydrogen formation:

$$Zn^{2+} + xCr^{(III)} + yH_2O \underset{k_3}{\overset{k_2}{\rightleftarrows}} ZnCr_xO_y + 2yH^+$$

Step 2: chromium(III) precipitates together with zinc(II), forming a film of non-stoichiometric zinc/chromium hydroxide/oxide, i.e. the conversion layer:

Fig. 3: Zinc/tin barrel parts with 8-10 µm layer thickness, tin content 25-30 %

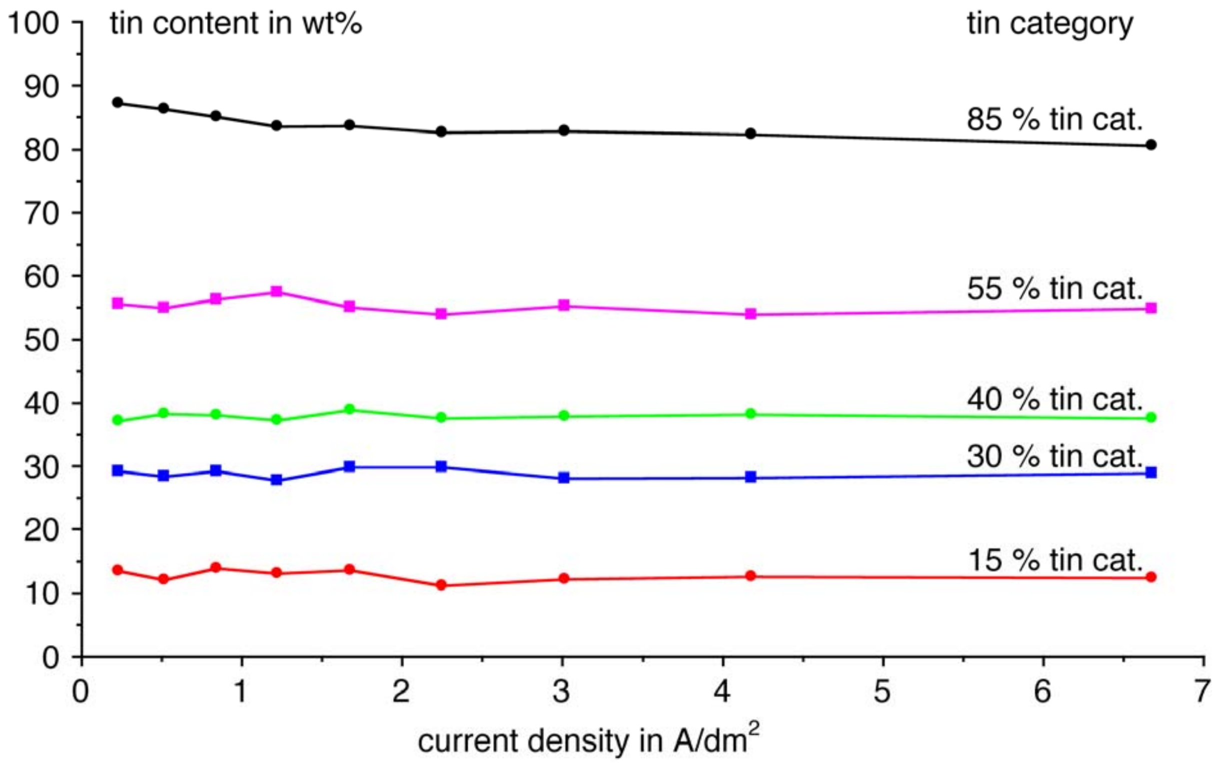


Fig. 4: Tin content in the Zn/Sn alloy plated from differently adjusted electrolytes at different current densities ranging from 0.2-6.8 A/dm2. The alloy composition is very stable within each electrolyte category.

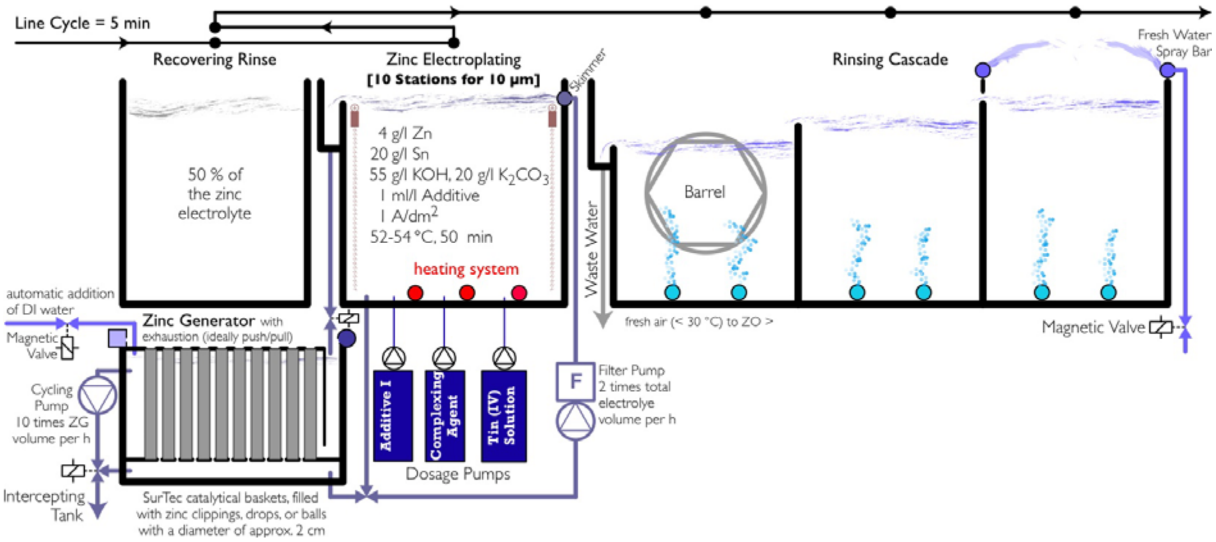


Fig. 5: zinc/tin plating line

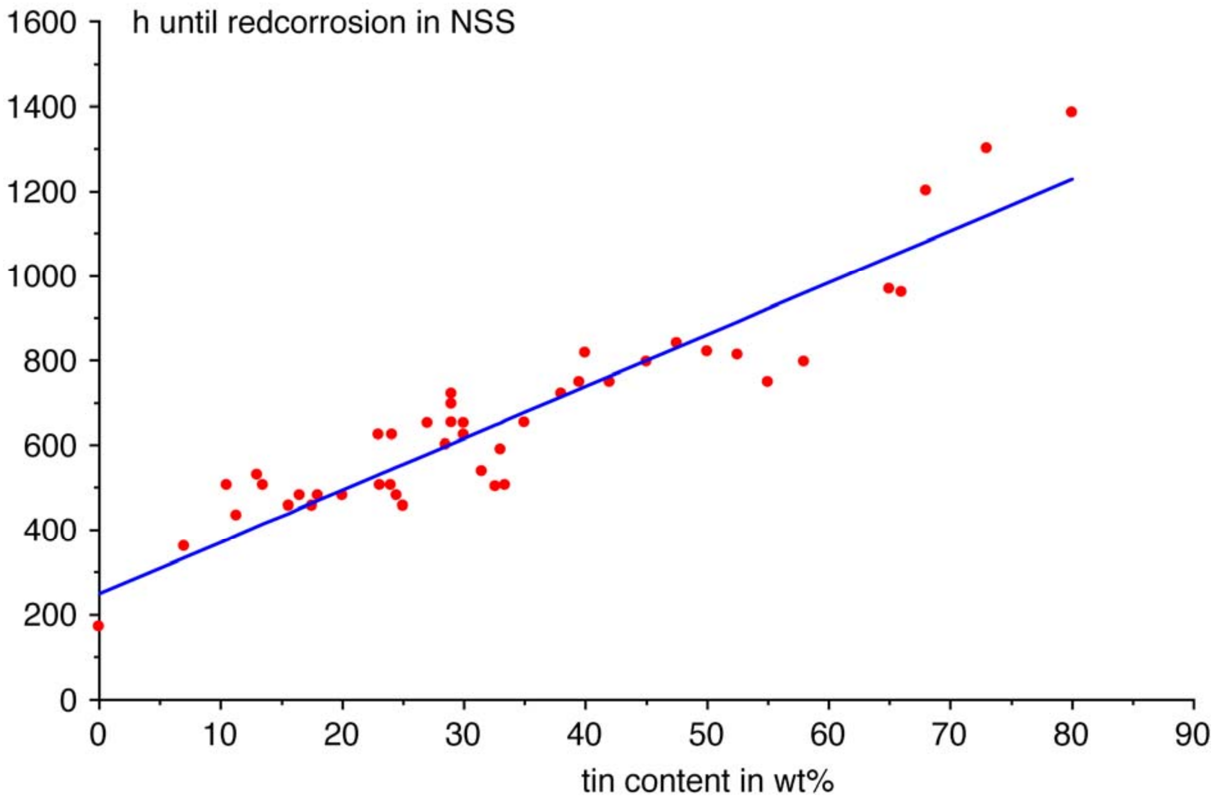


Fig. 6: Corrosion protection until red rust in the neutral salt spray test ISO 9227 of **non-passivated zinc/tin alloys**.

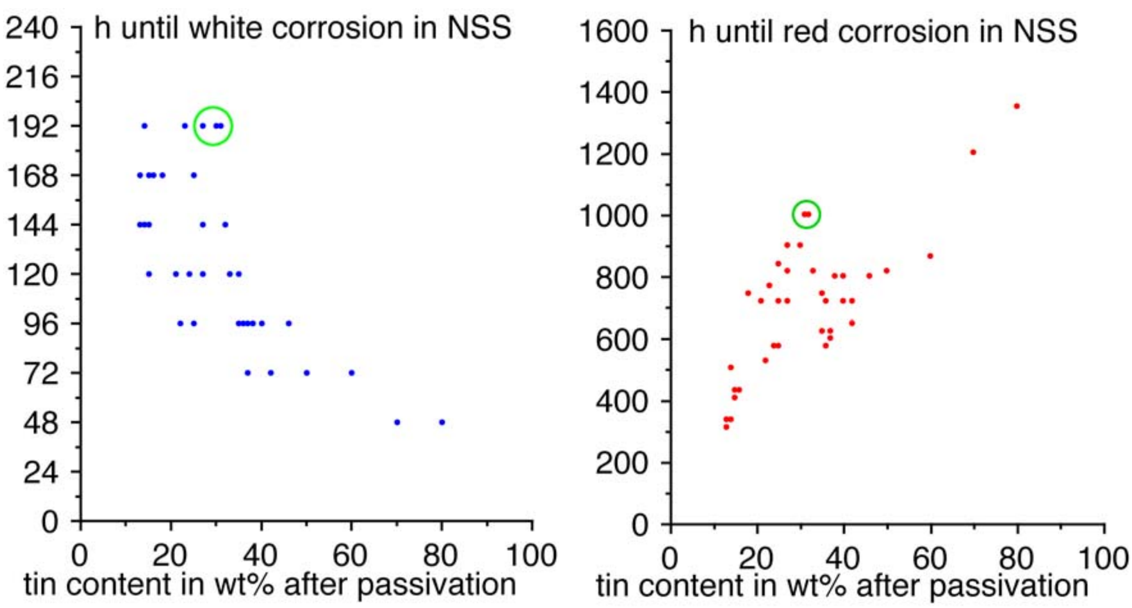


Fig. 7: Corrosion protection until white rust and red rust in the neutral salt spray test ISO 9227 of **passivated zinc/tin alloys**

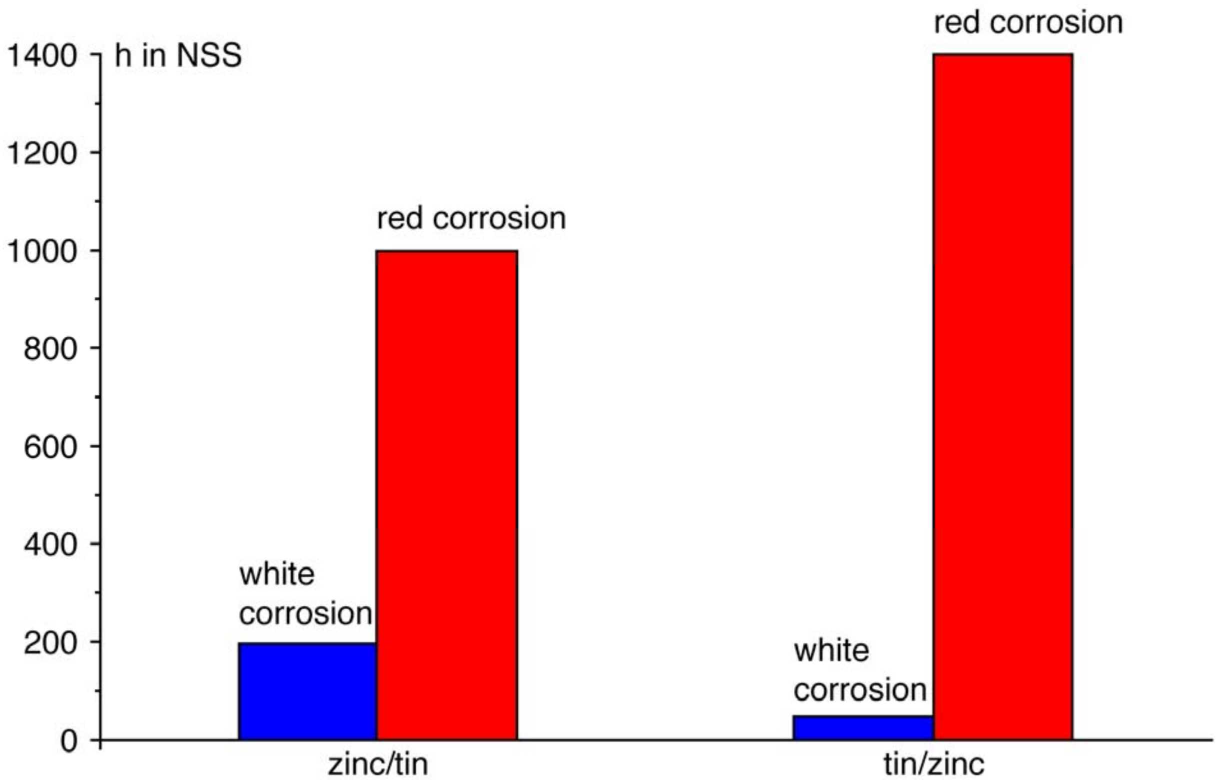


Fig. 8: Comparison corrosion protection until white rust and red rust in the neutral salt spray test ISO 9227 of **passivated zinc/tin alloys with zinc/tin (30% Sn) and tin/zinc (80% Sn)**

Fig. 9: Passivated zinc/tin barrel parts with 8-10 µm layer thickness, tin content 25-30 %