New Tin-Alloy Electrolytes for the Deposition of Decorative and Functional Layers

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Abstract

In the last ten years the electrodeposition of Sn-alloys like Cu/Sn, Cu/Sn/Zn and SnZn has gained increasing importance, not only for decorative applications but also for technical use as contact material or as corrosion protection.

One major use for plated Cu/Sn(Zn) alloys is as a replacement of allergenic Ni intermediate layers on parts which come into regular contact with the human skin, like costume jewellery, zippers, hooks and eyelets in clothings and other consumer goods. Such alloy depositions are white, respectively yellow if the Cu content is in the range of 80 %. A further plating on top of these layers with precious metals is possible. White Cu/Sn-deposits can also be used as final layers without further plating because of their good tarnish resistance.

Another application area for Cu/Sn(Zn) alloys is the high-frequency technology, where the diamagnetic bronzes are advantageous, whereas the paramagnetic Ni would lead to interferences.

Sn/Zn alloys are used as a very effective corrosion protection especially when a final chromate layer is applied. Such systems are by far superior to Zn or chromated Zn layers.

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Introduction

The electrodeposition of alloys in general has been done since years and is widely used for various applications. The most common processes are for example the plating of brass for decorative purposes or the plating of tin-lead deposits for electronic components.

However within the plating field the plating of a single metal is preferred by most users because such systems are easier to control and to handle. On the other hand there is a tendency to increase the demands for electrolytic deposited layers. For example, decorative layers also have to fulfill technical requirements such as high hardness, good corrosion and wear resistance. Even a functional coating has often to meet visual requirements like colour or pleasant appearance. The properties of the deposits of single metals can be changed only within certain limits. Process improvements are restricted to brightener systems and process conditions mainly.

It is a different story if one plates two or more metals simultaneously to form an alloy coating. Alloys can offer new properties that are not possible with plating one metal only. Secondly these properties can be varied due to the large number of alloying elements and subsequently different alloy compositions. Therefore the properties of the deposits can be tailormade to fulfill specific requirements. A good example is the plating of tin-alloys. These processes, introduced within the last ten years, are now being used for the plating of a large number of articles ranging from fashion jewelry to connector parts, this means for decorative and functional applications. Examples will be given for Cu/Sn-, Cu/Sn/Zn-, and Sn/Zn-alloy deposits.

1. Cu/Sn- and Cu/Sn/Zn-alloy deposits

Alloy composition

Depending on the alloy composition either white colored or yellow colored deposits can be plated. White deposits contain typically 55 % copper and 45 % tin, or respectively 55% copper, 30 % tin and 15 % zinc. Yellow coatings have a much higher content of copper. A typical composition of a yellow deposit is 80 % copper 17.5 % tin and 2.5 % Zinc. Typical alloy compositions are shown in **graph 1**. Each alloy composition is achieved by using an individual plating process. It is a target to achieve a large operating window of such an electrolytes in order to avoid significant deviations of the alloy composition during daily operation.

The deposition of Cu/Sn and Cu/Sn/Zn alloys are achieved with alkaline solutions containing cyanide and hydroxide as complexing agents. A brightener system to some degree helps to compensate fluctuations of the contents of the major components of the bath providing definite alloy composition of the deposits. The processes are available for both rack- and barrel plating. The usage of insoluble anodes (i.e.graphite anodes) is an essential tool to control the metal concentration of the processes. Recent developments also enable the operation of electrolytes with a fully organic based brightener system to avoid any co-deposition of heavy-metals, e.g.lead.

Properties of the deposits

Cu/Sn and Cu/Sn/Zn coatings are characterized by an excellent distribution of the layer thickness due to the alkaline character of the plating process. The deposits can be subsequently plated with other final layers. They show an acceptable solderability. Tin-alloys are diamagnetic. This feature is an important issue for the plating of connectors in the telecommunication field. The diamagnetic property of the layer avoids interference with RF signals. Another feature of the discussed alloys are their bactericide capabilities. These can be useful for applications where demanding hygienic standards are required. With regard to brightness and leveling of the coatings different degrees of leveling can be achieved. White deposits do typically have brightness – retaining character. The color of the deposit is whiter than nickel. Yellow layers are bright and leveling. For white deposits the applicable thickness is up to 3 micrometers, for yellow layers respectively 5 micrometers. Both deposits are being used as an intermediate layer, e.g. in combination with a precious metal. The white layer however with its high content of tin can be also used as a final layer for many applications due to its good tarnish and corrosion resistance. A typical example is the plating of zippers, snaps and buttons with a white tin-alloy as a final finish to replace nickel deposits which are potentially allergenic.

Compared to the base metals tin and zinc the deposits from Cu/Sn/(Zn) electrolytes do show a high hardness as shown in **graph 2**. With white Cu/Sn/(Zn) deposits a hardness of 550 Vickers is achieved which is close to the hardness of bright nickel deposits.

The comparably high hardness of the deposits enables to withstand abrasion quite well. **Graph 3** shows the results of abrasion tests of tin-alloys in comparison to bright nickel- and silver deposits. The test was done by using a Taber abraser.

Cast copper-tin (bronze) alloys are generally known to withstand corrosion quite well. Plated copper-tin-(zinc) deposits are no exception in this regard. By varying the ratio between tin and copper the corrosion resistance can be influenced as well. **Graph 4** shows the result of a corrosion test in a sulfur containing atmosphere (Kesternich-Test, according to DIN 50018-KFW 0.2S). The test results prove the superior corrosion resistance of tin-alloys against nickel deposits. By using different base-materials (copper, brass and iron) the test also outlines the preferred application for tin-alloys, namely the plating on copper and copper alloys. The more positive electrochemical potential of the tin-alloy compared to the one of iron and the large gap between both potentials can cause anodic attack of iron. In case iron shall be plated, the alloy composition should be changed to a tin-zinc-deposit.

Decorative applications of Cu/Sn- and Cu/Sn/Zn deposits

A requirement for the plating industry during the last few years has been to develop an alternative to electroplated nickel for some decorative applications such as fashion jewelry, accessories, watches and so on. These articles are typically plated with a nickel deposit to avoid diffusion of the base-material through the top layer, e.g. gold. In other cases nickel is also often used as the final coating.

When nickel is coming into intense contact with the human skin approximately 15 –20 % of women and approximately 5 % of men show an allergic reaction. The actual illness “nickel allergy” is preceded by a so-called sensitization phase. After the first contact of the allergen nickel with the immune system of the human body, e.g. during ear piercing, the metal salts combine with the protein components of the blood to form so-called haptens. The immune system identifies them as foreign and develops a counter strategy – a sensitization takes place. After repeated contact with the allergen, the actual allergic illness breaks out in the form of reddening of the skin or severe inflammation.

To avoid such an exposure of consumers to potentially allergenic nickel, a number of countries have taken measures to establish a consumer protection act against the use of nickel. An example is the European community, which introduced the EU directive 94/27/EG. This directive with the technical standards EN 1810, EN 1811, EN 12472, has been converted into national law within all countries of the European community by January 2000. This will result in a stoppage of imports and the manufacturing of such items by July 2000 and a subsequent prohibition of commercialization by July 2001. The directive 94/27EC outlines for example:

- Nickel may not be used in post assemblies which are inserted into pierced ears and other pierced parts of the human body during epithithelization of the wound caused by piercing, whether subsequently removed or not, unless such post assemblies are homogeneous and the concentration of nickel – expressed as mass of nickel to total mass – is less than 0.05 %.
- The use of nickel is subject to a maximum release of nickel of 0.5 $\mu g/cm^2$/week for products which come into direct and prolonged contact with the skin such as: earrings, necklaces, bracelets and chains, anklets, fingerings, wrist-watch cases, watch straps and tighteners, rivet buttons, tighteners, rivets, zippers and metal marks, when these are used in garments.
- If nickel is used in products such as those listed above and these products have a non-nickel coating, unless such coating is sufficient to ensure that the rate of nickel release from those parts of such products coming into direct and prolonged contact with the skin will not exceed 0.5 $\mu g/cm^2$/week for a period of at least 2 years of normal use of the product.

Whether there are legal requirements in other countries outside the EC or not, the nickel allergy issue is also affecting the United States and other countries. Therefore the plating industry can mainly use two alternatives for nickel for the mentioned applications:

One possible substitute for nickel is the usage of a thin deposit of palladium. However the development of the price of palladium which has by far surpassed the price of gold has drastically limited the usage of this metal.

The other alternative is to substitute nickel with a Cu/Sn or Cu/Sn/Zn alloy. **Graph 5** shows the plating process for nickel-free coatings for decorative applications.

Functional applications of Cu/Sn- and Cu/Sn/Zn deposits

As mentioned above, tin-alloys are diamagnetic and, therefore, are applicable as deposits for high frequency connector units. Tin-alloys show a lower intermodulation at higher transmission frequencies than nickel. The use of Cu/Sn/Zn-alloys on brass substrates is superior to nickel not only in terms of electrical interference, but also in corrosion resistance. Furthermore, Cu/Sn/Zn-layers offer a good wear resistance and low porosity. The thickness distribution of the deposit is excellent. This allows reducing total thickness. Typically 2 micrometers of alloy are plated. Advanced demands in terms of electrical properties can be met with an additional deposit of silver, typically 0,5 – 1 micrometer.

The excellent corrosion resistance of Cu/Sn layers on brass substrates is also used in the automotive industry. An example therefore are connectors used for the car-trailer interface (12volt). These parts have to perform under severe environmental attack such as chlorides used in winter. Cu/Sn layers are superior in this regard to e.g. nickel **(see graph 6)** and pure tin.

The mining industry uses Cu/Sn-deposits as a thick layer inside of guide bushes. The Tin-alloy layer offers emergency running properties if the lubrication fails.

2. Sn/Zn-alloy deposits

Alloy composition

The phase diagram describes tin/zinc as a plain eutectic alloy system. Therefore, nearly every alloy composition of the tin/zinc system can be electroplated by adjusting the parameters of the electrolyte. Examples are given in **table 1.** Typical electrolytes to deposit Sn/Zn-alloy are based on gluconate, diphosphate, fluoroborate, EDTA, hydroxide or cyanide. Alkaline or alkaline and cyanide containing electrolytes are superior in questions of alloy composition and stability in comparison to weakly acid electrolytes.

Properties of the deposits

Standard processes like e.g. Zn, Zn/Co or Zn/Ni, may not fulfill the increased demands in questions of corrosion protection for selected applications. Tin alloys like tin/zinc offer an interesting alternative. The best corrosion protection can be achieved with 70 % tin **(see graph 7).** The combination of a Sn/Zn-layer with a chromate conversion coating will lead to a resistance in salt spray atmosphere of up to 2500 hours (graph 7). Sn/Zn deposits were discussed as a possibility to replace cadmium due to the excellent corrosion properties in maritime and industrial climates. The contact corrosion between iron and aluminium can be reduced by using Sn/Zn-plating (with chromate coating) on iron. Additionally, the deposits offer a good weldability and solderability **(table 2)**. The hardness of Sn/Zn-layers is given with app. 50 Vickers (see **graph 2**).

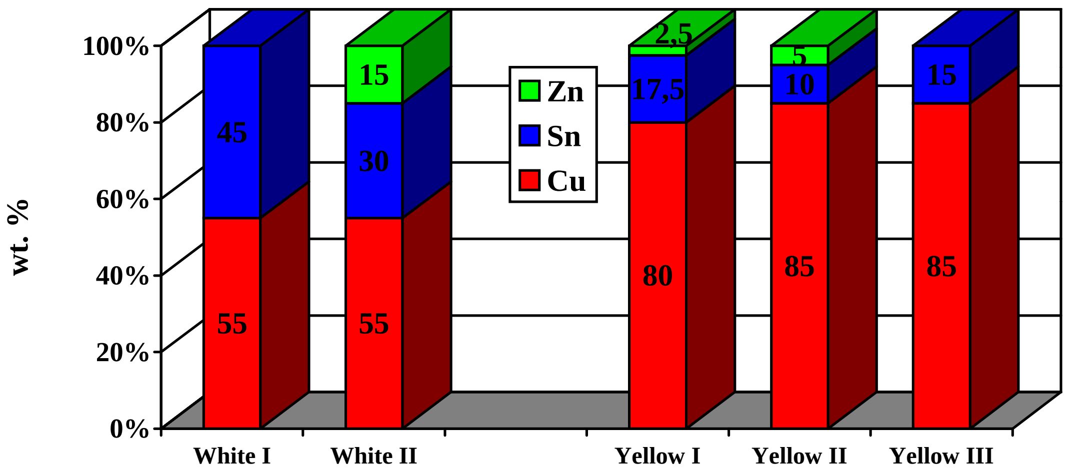
Applications of Sn/Zn-deposits

Sn/Zn-deposits can be used for hydraulic parts, joining elements, welding bolts, switches, aircraft or automotive parts, and electrical engineering. Sn/Zn-layers may be considered as a potential replacement of Sn/Pb-layers.

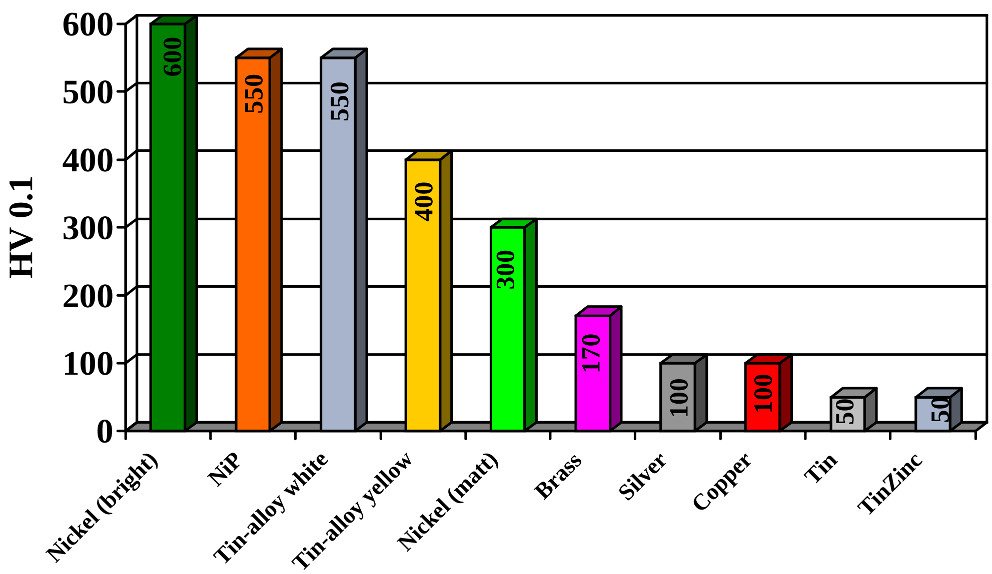
Summary

Plating of alloys offer the possibility to specifically tailor the deposit by selecting the alloy metals and the alloy composition. The plating of tin-alloys is a perfect example for this approach. By using tin-alloys, plating requirements such as the plating of corrosion-resistant-, diamagnetic-, or antiallergenic deposits can be fulfilled with a single process. Due to the development progress of the plating of tin-alloys, which has been made within the last few years, these processes are now being used for a variety of applications. These widely range from decorative parts such as zippers, fashion jewelry to functional deposits, for example the plating of automotive parts and RF-connectors.

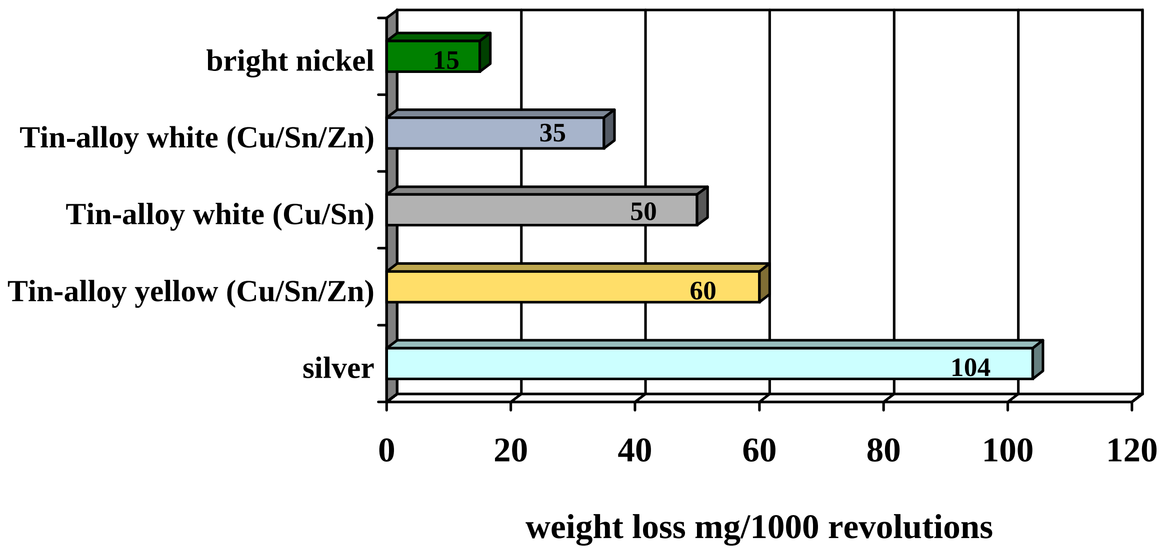
Graph 1: Typical alloy compositions of Cu/Sn- and Cu/Sn/Zn-deposits



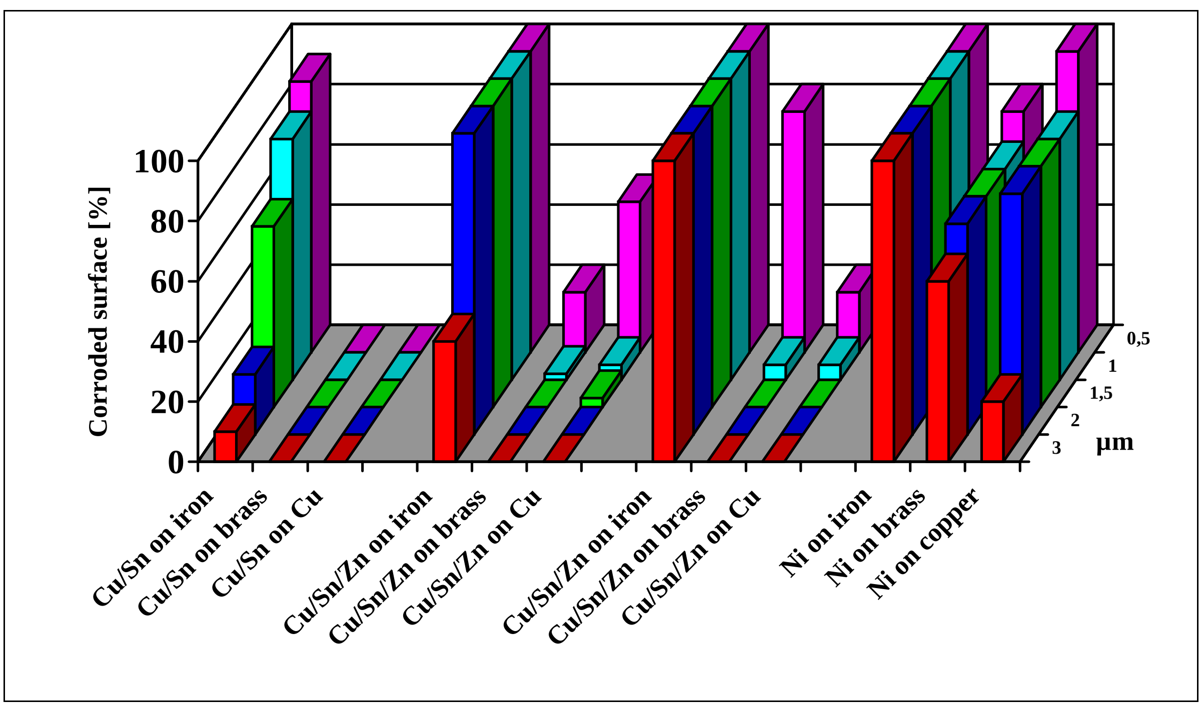
Graph 2: Hardness of deposits of tin-alloys in comparison to other metals



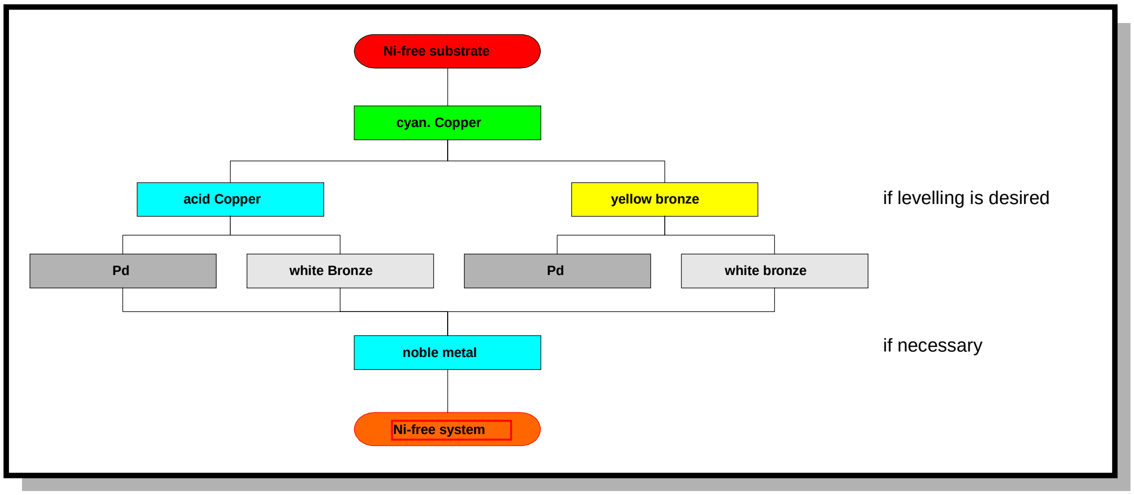
Graph 3: Abrasion resistance of tin-alloys in comparison to other plated deposits (Taber abrasion/Erichsen test)



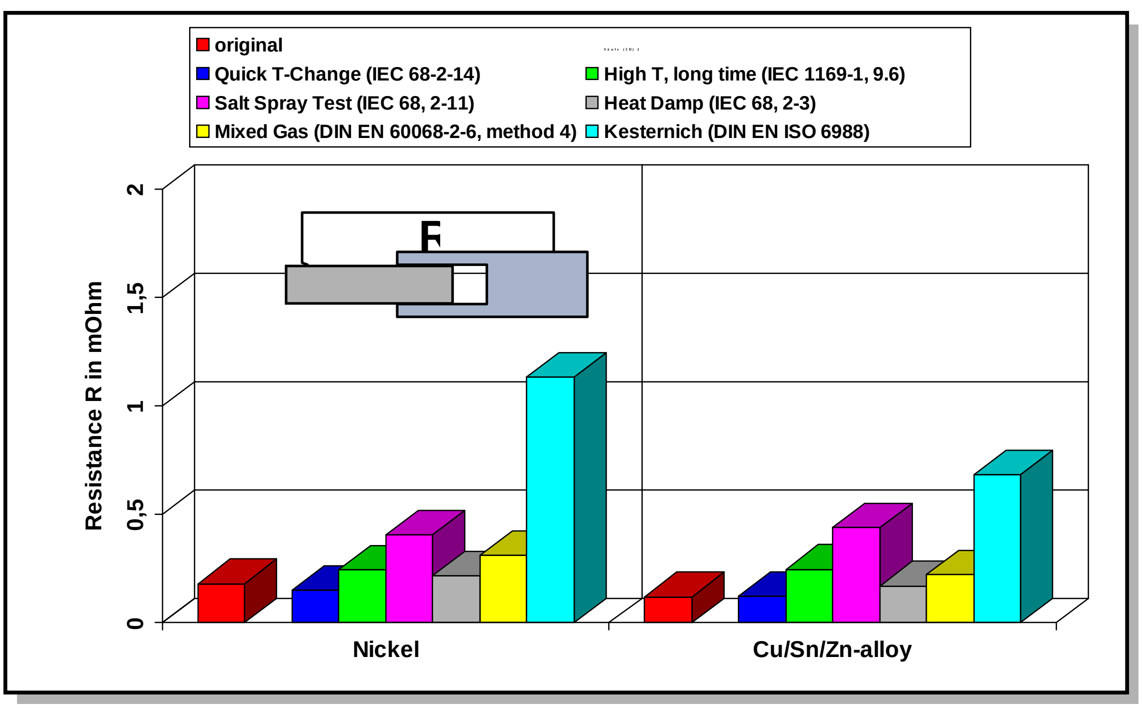
Graph 4: Results of a corrosion test of tin-alloys and nickel which are plated on different base materials in sulfur containing atmosphere (Kesternich Test/DIN 50018-KFW 0.2S). Variation of base-material and thickness (0.5 – 3 µm).



Graph 5: Examples of possible nickel-free layer combinations



Graph 6: Comparison of nickel and Cu/Sn/Zn-alloy plated connectors. The resistances of 30 connectors were measured before (original) and after different corrosion tests.



Graph 7: Salt Spray test according to DIN 50021 of Sn/Zn-layers (70/30; 5 micrometers) in comparison to zinc deposits (8 micrometers).

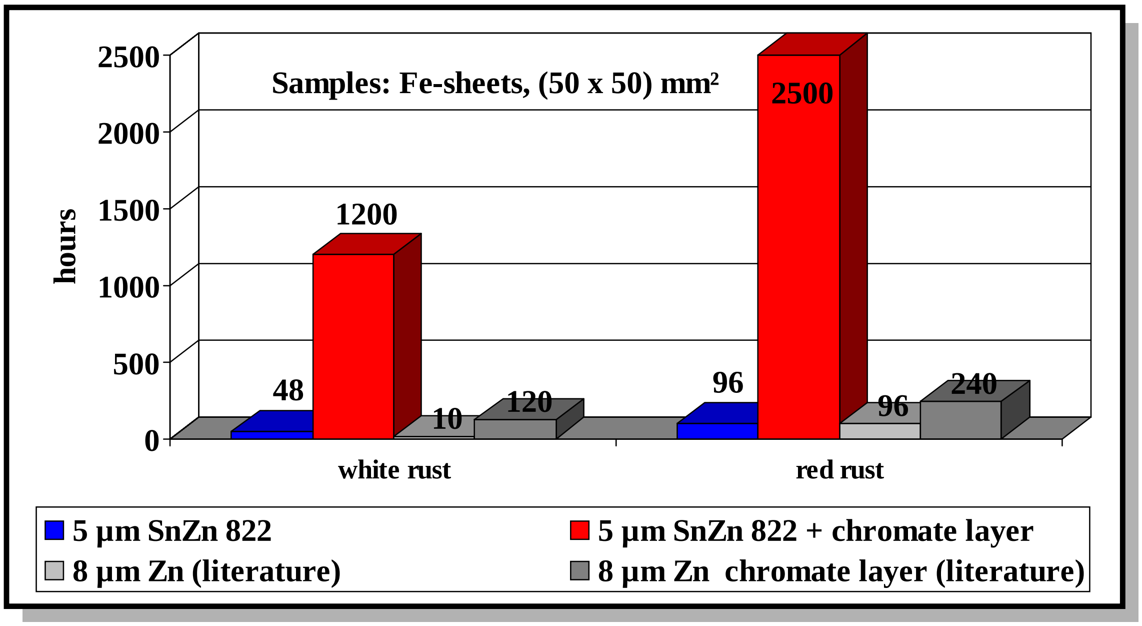


Table 1: Composition of tin/zinc processes

Alloy ratio Sn/Zn:	50/50	70/30	80/20	90/10
Tin	22 g/l	22 g/l	22 g/l	22 g/l
Zinc	2.4 g/l	2.4 g/l	2.4 g/l	1.5 g/l
KCN	30 g/l	30 g/l	30 g/l	30 g/l
KOH	30 g/l	15 g/l	8 g/l	8 g/l
Brightener	10 ml/l	10 ml/l	10 ml/l	10 ml/l
Current density at 60 ° C	1 – 2 A/dm^2	1 – 2 A/dm^2	1 – 2 A/dm^2	1 – 2 A/dm^2
Remarks		very good corrosion protection	Good corrosion protection	eutectic, low melting point

Table 2: Solderability of Sn/Zn-layers in comparison to tin and tin/lead. Aging: 155 ° C, 16 hours; solder: Sn/Pb (60/40), 230 ° C ; Flux: R-type; ZCT = Zero Crossing Time (Trans IMF, 1998, 76(3), B34-B37)

Deposit:	ZCT after plating	ZCT after aging
Tin	2,1 sec	4,6 sec
Tin/Zinc (70/30)	1,1 sec	2,5 sec
Tin/Zinc (90/10)	1,4 sec	1,8 sec
Tin/Lead (60/40)	1,4 sec	1,9 sec
Tin/Lead (90/10)	2,0 sec	2,1 sec