Amphenol SOCAPEX	Doc. :	RTN 2301
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Technical note
Dark Tin Zinc (SnZn) protective plating on MIL Spec type connectors

Abstract:

This paper focuses on the properties and characterization of the Amphenol Socapex Tin-Zinc electro-co-deposit, specifically used as a sacrificial plating for aluminum connectors shells protection.

MIL-DTL-38999 specification [1] is the guideline to drive the finished goods functional properties and performances, particularly in terms of stringent environmental solicitations (corrosion resistance, wear, extreme temperature exposure …). Additionally, the authors describe several tin whiskers basics and how the relevant mitigating technologies have been implemented in the plating architecture and process.

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Date :	20/01/2023	20/01/2023

SUMMARY

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1. FOREWORD

This paper focuses on the properties and characterization of a Tin-Zinc electro-co-deposit, specifically used as a sacrificial plating for aluminum connectors shells protection.
MIL-DTL-38999 specification is the guideline to drive the finished goods functional properties and performances, particularly in terms of stringent environmental solicitations (corrosion resistance, wear, extreme temperature exposure …).
The hereafter discussions intend to demonstrate that the overall requirements of the specification can be matched by a Tin-Zinc protection, using a conventional thickness of layers stack-up, on the connector shells. Additionally, the authors review several basics about Tin whiskers, and the mitigation techniques that were adopted for this plating.

2. PRESENTATION OF THE TECHNOLOGY

2.1. Context

All industries are increasingly submitted to evolving environmental regulations, with the laudable intent of protecting and preserving both human health and environment.
Among others, REACH and RoHS are mostly paving the way for many other regional restrictions. Subsequently, in a globalized environment, several substances are likely to be banned worldwide, with significant impacts on the supply chain, for either availability or products performances, when it comes to professional electronic componentry.
For many years, the military interconnect community has progressively implemented new technologies in connector specifications, aiming at transitioning towards more environmental-friendly chemistries, predominantly in protective platings, in either the process of manufacturing or the components themselves.
As an example, chromated Cadmium, is widely used as a sacrificial plating, applied on most military connectors shells, made of aluminum alloys.
Without exactly substituting as a 1:1 drop-off, Zinc Nickel and Ni PTFE were introduced as viable and accepted alternates, complying to RoHS and sometimes REACH. Still, from a user experience perspective, trade-offs and derating are somehow necessary, for either overall aspect, comparative corrosion resistance, or backward galvanic compatibility *(figure 1)*.

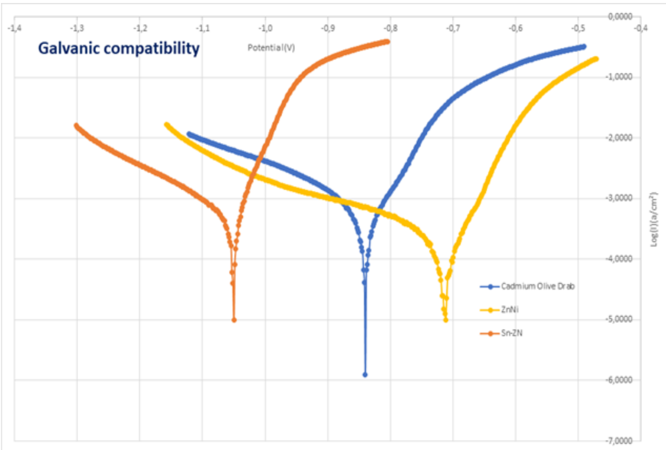

Figure 1: Galvanic potential of SnZn, Cadmium, and ZnNi, over Aluminium. ZnNi and SnZn are in the window of the sacrificial platings, galvanically backward compatible with Cadmium. corrosion barrier.
Amphenol Socapex France

2.2. General concepts

Recently, a legacy plating was promoted as an additional substitute to cadmium plating on aluminum, in several specifications, either in Europe or North America.
Indeed, Tin Zinc seems to show interesting performances, and can be considered as a promising candidate in the portfolio of sacrificial platings. Populating a library of platings may offer numerous possibilities to users, as there is still no direct equivalent to chromated Cadmium from our prospective of connectors manufacturer. Extensive research activities are thus still in progress in that purpose.

Consistently, several stakeholders are promoting this plating in the widely adopted MIL-DTL-38999 specification, as an alternate to cadmium, given their successful experience in other specifications (MIL-DTL-28840 [2] and MIL-PRF-28876 [3]).
Unusually, the project of this new class of plating, named "V", depicts the architecture very thoroughly, undoubtedly inspired by several existing designs that was successful on other aluminum connectors.
For instance, the detailed thickness of the different layers is specified, as the typology of these inner and outer layers. To a point that the genuine spirit of the standard, which is to open the market safely and widely for reliable technology meeting the industry requirements, is sacrificed.

Throughout this paper, numerous test data are clubbed, tending to prove that thinner layers of plating likely meet the requirements of the connector specification (corrosion resistance, electrical conductivity, extreme temperature exposure). In addition to being compatible with most of the current bare shells designs and offset, we believe that reducing the usage of chemicals is consistent with a more responsible usage of the resources, while opening the market to most of the connector industry.

2.3. Physical principles

The Tin-Zinc coating is obtained with a conventional electroplating process by direct current, with chemistries provided by several suppliers across the world.
The sacrificial Tin-Zinc coating layer is structured as a dispersion of Zinc into a Tin matrix *(figure 2)*.
From that perspective, it is not an alloy, but rather a co-deposit, as there is no clear evidence of crystalline structures.

A further step called passivation is applied after the electrodeposit, to bring the dark non reflective color, as well as other properties (corrosion resistance and electrical conductivity predominantly).

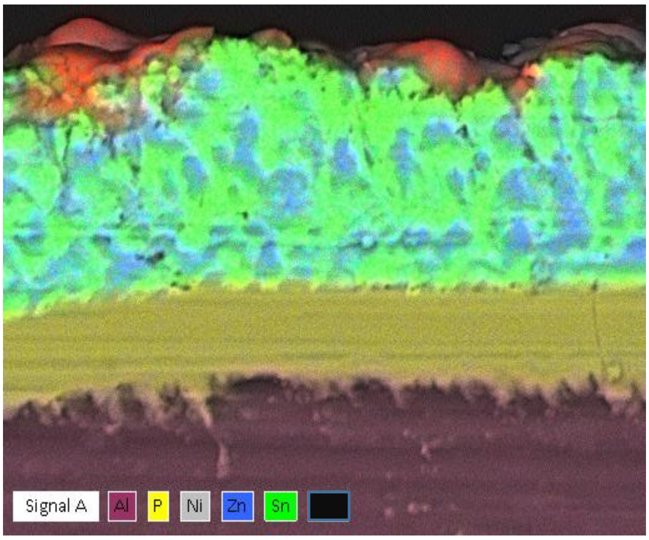

Figure 2: SEM picture of the Tin-Zinc/SnZn plating with Ni underlayer onto an aluminum shell in cross section (magnification X3000).
Amphenol Socapex France.

The Zinc w/w% in the layer shall be between 25 and 35%, to get these color and properties. A consistent Zinc dispersion into the layer is notably difficult to obtain, because of the current flow distribution into the tank. The thicker the Tin-Zinc layer, the more uniform and darker the color will be ultimately.
Amphenol Socapex have come up with an optimal structure allowing to meet the right color properties: 12-17µm of Tin-Zinc with 4-7 µm of consistent High-Phosphorus electroless nickel underlayer *(figure 3)*. This underlayer providing a classical and adequate barrier layer to corrosion.

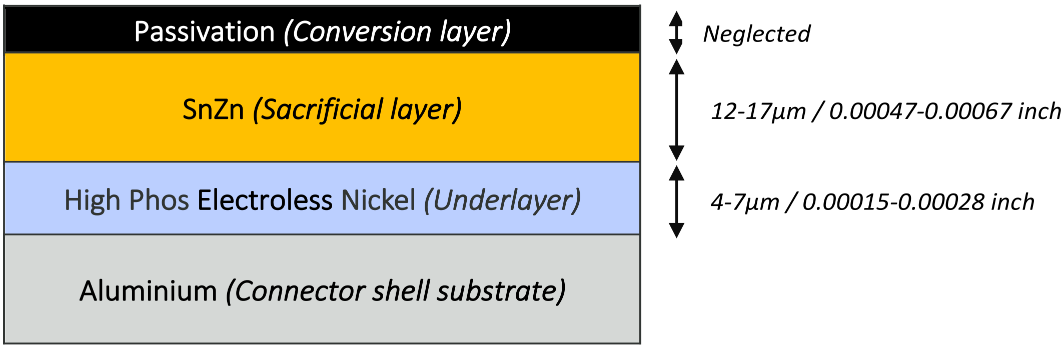

Figure 3: Illustration of a SnZn architecture over High Phosphorus Electroless Nickel and Aluminum.
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This stackup is the most optimized configuration matching all the standard technical requirements, providing the right balance in terms of cost, process yield, and accommodation to any standard bare aluminum shells, used for cadmium plated connectors.

2.4. Whiskers discussion

The scientific literature related to metal whiskers, specifically Tin whiskers, is well documented and prolific enough to provide a reliable understanding to the reader hereafter.

2.4.1. <u>General description</u>

A tin whisker is a growth of pure Tin that is commonly in the form of an elongated dendritic-like crystal. A whisker is expected to grow from more than a dozen of µm to several millimeters in some cases [4][5]. Whiskers typically appear from a Tin-based plating applied as a thin film (a few µm) on a substrate, usually copper-based for the purpose of conductor termination soldering, and corrosion protection [8]
Whiskers growth has been largely reported as a major issue for any electronic subassembly or system, which requires soldering attachment. In most cases, they are described as potential bridges between the termination of adjacent conductors, which in turn may result in a short

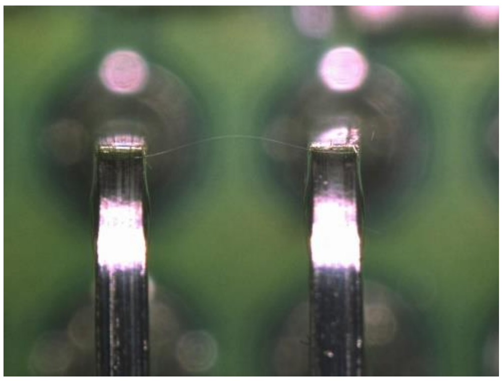


Figure 4: Illustration of a Tin whisker bridging two conductors.
https://nepp.nasa.gov/whisker/anecdote/2008shield/index.html

cut, leading to fatal electrical failures [4][5][6] *(figure 4)*. The latest being also possible from a free FOD (Foreign Object Debris) randomly travelling on an electrical circuit, between conductors.

Although there is to date no clear general consensus about the origins of whiskers growth, there is a collection of reasonable assumptions, accepted across many industries, about the mechanisms and fostering conditions of appearance: (i) a compressive stress in the Tin layer provided either by the plating process [4] *(figure 5)*, or a post-process mechanical stressing operation on the plated components [4], or by Inter Metallic Compounds (IMCs) formation between the Tin-based layer and the substrate [6]; (ii) self-diffusion of various atoms along the grain columnar boundaries of the Tin layer [6]; (iii) a surface oxides layer which is able to either contain the various stresses in the layer, so the whiskers growth [5], or exacerbate their growth, at very localized areas of surface layer breakages, releasing a significant amount of stress at punctual locations, authorizing vacancies for atoms migration [6].
Additionally, it has been reported that thermal stress could generate mechanical constraints between different layers, because of variables CTEs values, leading to differential material expansions [6].

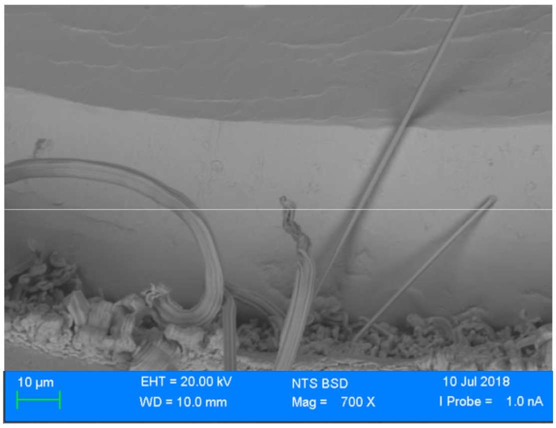


Figure 5: SEM picture of a starting site of Tin whiskers by compressive forces.
Amphenol Socapex France

2.4.2. Mitigation techniques

As for any random process, whiskers can appear at different timing of the equipment life, at early stage or after several years of usages. Also, the kinetics may vary depending on the origin of the growth [4][6], making of it a very unpredictable issue.
However, several mitigation strategies are well-known, and help to drastically reduce the risk of occurrence.

2.4.2.1. Tin alloying

As depicted above, pure Tin deposits provide a columnar grain structure, facilitating the migration of atoms up to the external face of the Tin layer, by utilizing available vacancies. Such a migration can be initiated by the mechanical stress induced by a wedge-shaped IMC (Cu_6Sn_5 for instance, in the case of Tin on Copper), applying compressive biaxial forces, released by Tin atoms travelling to the surface [8] *(figure 6)*. The stress can also be natively created inside the layer, during the deposit process by electroplating [4]. An intelligent way to avoid this migration is to provide alternative lateral paths to the atoms, alternatively to the direct path to

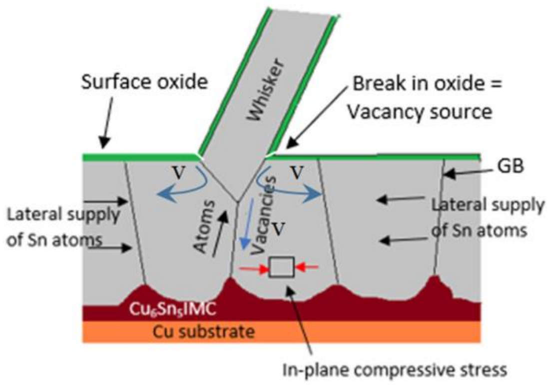


Figure 6: Schematic showing mechanism of whisker growth with vacancy flux directions marked as ''v,'' [6]
B.S. Majumdar and al. https://doi.org/10.1007/s11837-019-03933-7

the surface. This can be achieved by the creation of equiaxed grain boundaries, complementary to the columnar structure *(Figure 7)*.

Alloying Tin with Lead is a classical and successful manner to obtain a substantial increase of Tin whisker growth incubation time [7], or a reduction of their size [6]. The usage of lead is being progressively forbidden or regulated, across Europe through 2006 European Union Restriction of Hazardous Substances (RoHS), Japan, Korea, or even California.

As potential alternatives, several candidates for substitution were reported, such as Bismuth, Copper, or Zinc [7]. By an adequate electroplating method, the deposition of Zinc, with a concentration of 20% of Zinc in the Tin bath, resulted in favorable disruption of columnar grain structure of pure Tin into the desired equiaxed grain structure.

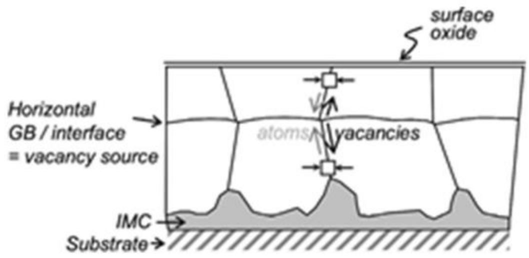


Figure 7: Schematic showing how horizontal boundaries act as vacancy sources (or atom sinks), absorbing the atom flux flowing up vertical boundaries. [6]
B.S. Majumdar and al.
https://doi.org/10.1007/s11837-019-03933-7

2.4.2.2. Electroless Nickel underlayer

Although contradictory experiences can be found about the efficiency of mitigation techniques applied to whiskers, there are consistent feedbacks when it comes to seal the substrate from the Tin or Tin-alloyed layer, with the assistance of an intermediate layer of electroless Nickel [4], generally accompanied by variable concentrations of Phosphorus.

Provided it is widely accepted that IMCs between the substrate and the Tin create stresses [8], a barrier limiting their appearance was historically applied on a various array of substrates [5], dictated by numerous components specifications, and overall good practices in the electronic industry [1][2][3].

2.4.2.3. Oxides top layer

It has been shown earlier in the document that Tin atoms can migrate to the top of the layer, aggregating throughout a growing whisker, with the help of vacancies at the surface. Few studies suggested or demonstrated that a thick oxides top layer was an effective blocker of whisker filament growth [8]. The latest would need to pierce the layer releasing the layer stress [5]. However, as soon as a weakness or a breakage point appears through the oxides layer, the whole stress would release at that location, providing a significant opportunity for the whisker to grow [5] *(figure 8)*.

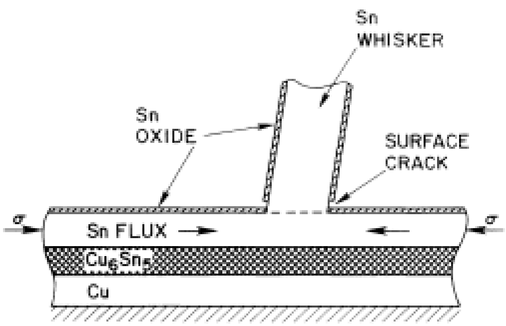


Figure 8: Illustration of the cross section of the Cu-Sn IMC and a whisker that grows from an oxide barrier breakage, growing by the migration of Tin atoms [8]
Tu K.N. Phys. Rev. 1994;49(3):2030–2034

2.4.2.4. Annealing

Annealing the Tin layer has been found to be an interesting technique by many aspects, while the numerous configurations and combinations of substrates, barrier layer, Tin-alloyed types etc … were not deeply explored nor exhaustively studied.
However, several benefits were reported, essentially as (i) a stress relief for Tin layer; (ii) an effective recrystallization or grain growth in the purpose of limiting the paths to the surface (iii) a leveling effect on the wedge-shaped IMCs, reducing the overall mechanical stress from the bottom of the layer [4][6][8].

2.4.3. Application to Tin -Zinc (SnZn) plating of Amphenol Socapex

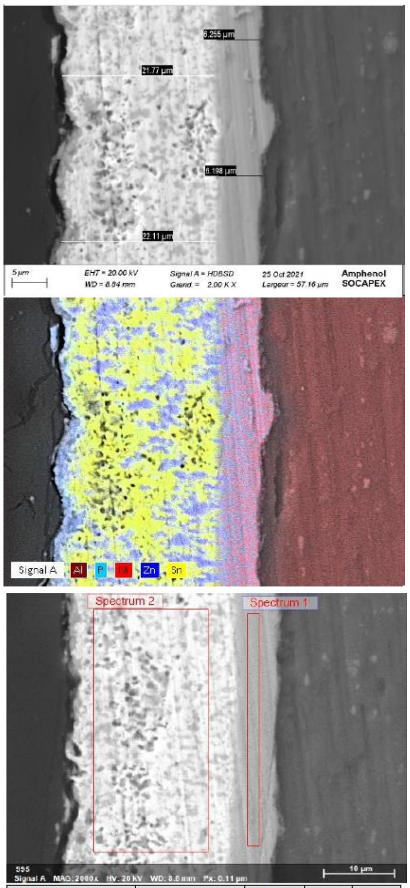
As depicted in § 2.3., in the purpose of bringing the appropriate level of reliability to their dark Tin-Zinc plating, Amphenol Socapex have applied all the mitigation techniques that were described hereabove, recommended across the electronic industries, and applicable to the product configuration *(figure 9)*.

Figure 9: Pictures of MIL Spec type connectors, with shells protected by a dark Tin-Zinc/SnZn protective plating.
Amphenol Socapex France

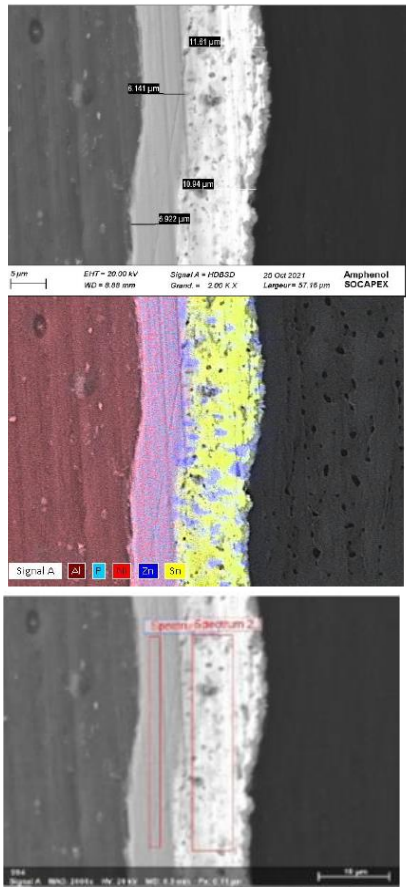
Although the Zinc is unevenly distributed over the surface, because of the physical galvanic rules, and the reduced current density in the internal surface of the connectors envelop, the Zinc w/w% is always comprised between 20% and 35% in the whole layer of Tin Zinc. Likewise, the equiaxed grain boundaries act with efficiency to relax, via the atoms migration, the potential mechanical stress from the Tin layer, wherever it comes from *(figure 10)*.
The 4-7 µm high phosphorus electroless Nickel underlayer provides a perfect, consistent, and fully sealing barrier to prevent IMCs generation, should it be inside or outside of the connector *(figure 10)*.

The passivation layer has notably exhibited the presence of oxides, on a substantial thickness. It is likely to provide an effective envelop to encapsulate the Tin-Zinc/SnZn layer and contain any potential whiskers growth.
Lastly, the connectors shells are submitted to a post-process baking operation for a limited time, which enables the relaxation of most of the stress contained in the layer, which in turn will avoid subsequent relaxation throughout random atoms migration.

All those measures shall offer a reliable management of whiskers mitigation.



Spectrum	phosphorus	nickel	zinc	tin
Ni underlayer	10.1	89.9		
SnZn layer			24.2	75.8



Spectrum	phosphorus	nickel	zinc	tin
Ni underlayer	9.8	90.2		
SnZn layer			26.1	73.9

Figure 10: SEM + EDX pictures and mapping, showing both external (left) and internal (right) surface profiles of Tin-Zinc/SnZn plated connectors, assessing the required thicknesses of the layers. The mapping shows an appropriate Zinc dispersion at the required w/w%.
Amphenol Socapex France

2.5. Technical demonstration and validation

After a bibliographic study, research, chemistries selection, and mock-ups, Amphenol Socapex have conducted extensive testing on various configurations in their MIL-STD-790 [9] qualified testing facility. This evaluation was mandatory, prior to execute a MIL-DTL-38999 typical qualification test list (W class, chromated Cadmium on Aluminum requirements), which is currently being finalized successfully.

2.5.1. Tests plan and sampling

All the evaluation tests were carried out in accordance with the test methods of the MIL-DTL-38999 Rev M, amendment 2, as well as the associated EIA-364 test procedures. Additionally, the industry standard JESD 201A [10] was utilized to perform mitigation testing of whiskers growth.

Three sizes were chosen for testing with a small (size 13), medium (size 15) and large (size 21), of series III sub-family. Three groups of tests were conducted, as per MIL-DTL-38999 standard, and two sequences of the JESD201A:

•MIL-DTL-38999 Gr 9:

Three samples per size: 9 samples in total. Below is the list of tests:

Visual and mechanical examination – MIL-DTL-38999 §4.5.1
Shell-to-shell conductivity – EIA-364-83 [11]
Temperature cycling – EIA-364-32 [12]
Dynamic salt spray – EIA-364-26 [13]
Coupling and uncoupling torque – EIA-364-114 [14]
Shell-to-shell conductivity – EIA-364-83
Post test examination – MIL-DTL-38999 §4.5.49

•MIL-DTL-38999 Gr 11:

One sample per size: 3 samples in total. Below is the list of tests:

Visual and mechanical examination – MIL-DTL-38999 §4.5.1
Ice resistance – MIL-DTL-38999 §4.5.40
Dust – MIL-STD-202-110 [15]
Post test examination – MIL-DTL-38999 §4.5.49

•MIL-DTL-38999 Gr 14:

Three samples per size: 9 samples in total. A cadmium plated backshell with copper shield braid has been associated on the plugs of the connectors. Below is the list of tests:

Visual and mechanical examination – MIL-DTL-38999 §4.5.1
Coupling and uncoupling torque – EIA-364-114
Backshell shield braid-to-shell conductivity – EIA-364-83
Resistance to indirect lightning strike – EIA-364-75 [16]
Backshell shield braid-to-shell conductivity – EIA-364-83
Coupling and uncoupling torque – EIA-364-114
Insulation resistance – EIA-364-21 [17]
Dielectric withstanding voltage – EIA-364-20 [18]
Post test examination – MIL-DTL-38999 §4.5.49

•JESD201A:
2 x 6 samples of different size ranges were submitted to each of the two following sequence, §5.3.5, with the prior required pre-conditioning:

Stress Type	Test conditions	Inspection intervals	Total duration
Temperature Cycling	-40 +0/-10 °C to 85 +10/-0 °C, air to air; 10 minutes soak; ~3 cycles/h (typ.)	500 cycles	1500 cycles
High Temperature / Humidity Storage	30 ±2 °C and 60 ±3% RH	1000 hours	4000 hours

Periodic inspections are conducted under conventional binocular and SEM + EDX microscopy, with typically no presence of whiskers allowed.

•Long time exposure in temperature

In addition to the hereabove derisking sequences, Amphenol Socapex have decided to expose several Tin Zinc plated shells to 200°C during 1'000hrs, with the purpose of fostering the appearance of Tin hillcocks which were reported to appear *in lieu* of Tin whiskers, with a high temperature stress [6]. Such a magnitude literally blocks the slow and progressive whiskers growth to the benefits of massive spontaneous hillcocks.

2.5.2. Results

- Group 9:

The tests were successfully achieved. The temperature cycling test did not damage the plating. The samples held up well to the dynamic salt spray test. The electrical continuity from shell to shell were better than usual cadmium before and after salt mist exposure. No seizing to report.
A whitening of the samples is visible after salt spray, as a classical Zinc oxidation. Except the aspect it does not affect the properties of the connector *(figure 11)*.

Figure 11: SnZn plated connectors size 13, 15, 21. Before (up) and after (down) Neutral Salt Spray test. ***Amphenol Socapex.***

Insignificant areas of corrosion on the knurling of the plug locking nut is noted on some samples. These corrosions do not affect the performances of the connectors *(figure 12)*.

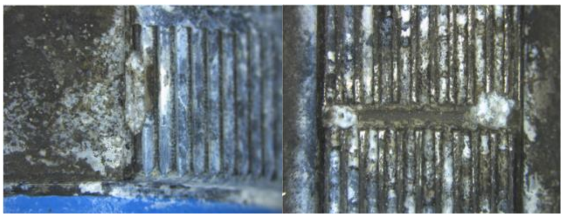


Figure 12: Corrosions areas onto knurling of the locking nut of connectors
Amphenol Socapex.

- Group 11:

The tests were successfully done *(figure 13)*. The connectors have demonstrated an usual resistance to ice and dust tests. The mechanical properties are not affected, the coupling and uncoupling torques are compliant.

Figure 13: Series III SnZn plated connectors size 13, 15 and 21 (from left to right) after Gr 11 tests before cleaning (after dust test)
Amphenol Socapex.

- Group 14:

The tests were carried out successfully. All samples were compliant. The electrical conductivity of the plating was compliant.
The connectors withstood the lightning test *(figure 14)*.

The coating remains conductive, the torque values are compliant, and the insulating parts have successfully passed the IR and DWV tests *(figure 15).*

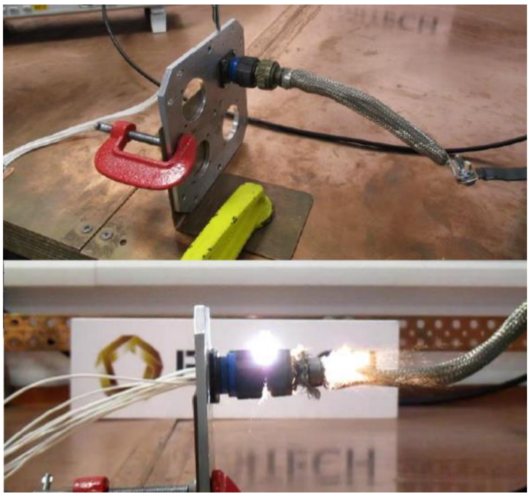


Figure 14. Indirect lightning test setup (up) and testing (down)
Amphenol Socapex.

Figure 15: SnZn plated connectors size 13, 15 and 21 (from up to down) after Gr 14 tests
Amphenol Socapex.

- JESD201A

These tests are still being conducted in the same test facility, with no whiskers reported to date.

- Long time exposure in temperature

After 1'000 hours of exposure at a temperature of 200°C, no hillcocks, nor whiskers were reported of the samples.

3. GENERAL CONCLUSION AND PERSPECTIVE

As demonstrated above, the Tin Zinc protection on MIL Spec connectors, future V class of MIL-DTL-38999, is a good candidate as a Cadmium alternative, and provides substantial benefits as electrical continuity and corrosion resistance. Other assessments are being successfully conducted by Amphenol Socapex, such as, and not limited to, vibrations in temperature, EMI shielding efficiency, sand and dust.

These results were obtained with a classical stackup of plating layers, similar to the historical Cadmium architecture, with notably an electroless High Phosphorus nickel underlayer of 4 to 7 µm/ 0.00015-0.00028 inch, for a total thickness of 20 µm/ 0.00079 inch average. The standard bare aluminum shells of connectors can thus accommodate this architecture, providing a comfortable and secure transition to new platings.

The actions for mitigation of potential Tin whiskers growth were taken appropriately and applied on the parts and in the process of plating. Although no specifications have been identified, addressing the typology of parts and applications of such MIL Spec type connectors envelope, Amphenol Socapex have chosen to conduct JEDEC recommended ageing tests, with no reported whiskers appearance to date. The end of evaluation is expected for Q3 2023.

Hence, based on these conclusions, the authors would recommend opening the V class description to a free thickness of the Nickel underlayer.

For further details on our research, results, and technology, please contact the authors.

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[12] EIA-364-32G – Thermal shocks (Temperature cycling) Test Procedure for Electrical Connectors and Sockets
[13] EIA-364-26C – Salt Spray Test Procedure for Electrical Connectors, Contacts and Sockets
[14] EIA-364-114 – Coupling And Uncoupling Force Test Procedure For Electrical Connectors, Socket, And Applicable Accessories
[15] MIL-STD-202G w/CHANGE 2
[16] EIA-364-75B – Lightning Strike Test Procedure for Electrical Connectors
[17] EIA-364-21F – Insulation Resistance Test Procedure for Electrical Connectors, Sockets and Coaxial Contacts
[18] EIA-364-20E – Withstanding Voltage Test Procedure for Electrical Connectors, Sockets and Coaxial Contacts