

Technical Paper

Overview of the Use of Silver in Connector Applications

Marjorie Myers

Interconnection & Process Technology
Tyco Electronics
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Introduction:

The separable signal connector industry uses predominantly electrodeposited gold (hard gold) and tin based finish systems for separable interface signal contact interfaces. These electrodeposition processes are widely available, well understood, fast, stable, and easily controlled.

Electrodeposited pure silver contact finishes are favored for higher current power transmission and often lower current separable power connector applications. Silver has the highest electrical and thermal conductivity of any metal leading to Contact Resistance (CR) values in the range of 0.1 - 1 m Ω at higher forces. The higher current power transmission connectors typically are designed to have very high normal force (10 – 100 N) that preferably incorporate wipe, have silver thicknesses greater than 2 and up to 20 μm and commonly do not have a nickel underplate. Lower current power connectors typically have a minimum of 200 cN of normal force with wipe, a nickel underplate (minimum 1.25 μm) with a minimum of 2 μm silver, and have low durability requirements.

Silver also functions well as a connector finish in many appropriate higher normal force/lower durability signal applications. Most other signal connectors operate at a significantly lower normal force with higher durability requirements. The fact that silver will tarnish in most connector environments and is not a durable finish may present a problem if used for these signal connector applications. Another factor complicating the application silver in many signal applications is that there is no accelerated testing correlation for silver finishes. The combination of potential corrosion mechanisms and application environments is complex and not fully understood [1, 2, 3, 4].

Two recent industry wide changes have driven connector interests to explore expansion of the use of silver as a signal separable contact interface finish. For gold finish applications, the significant increases in the cost of gold metal (Figure 1) provide the motivation to seek alternate finishes.

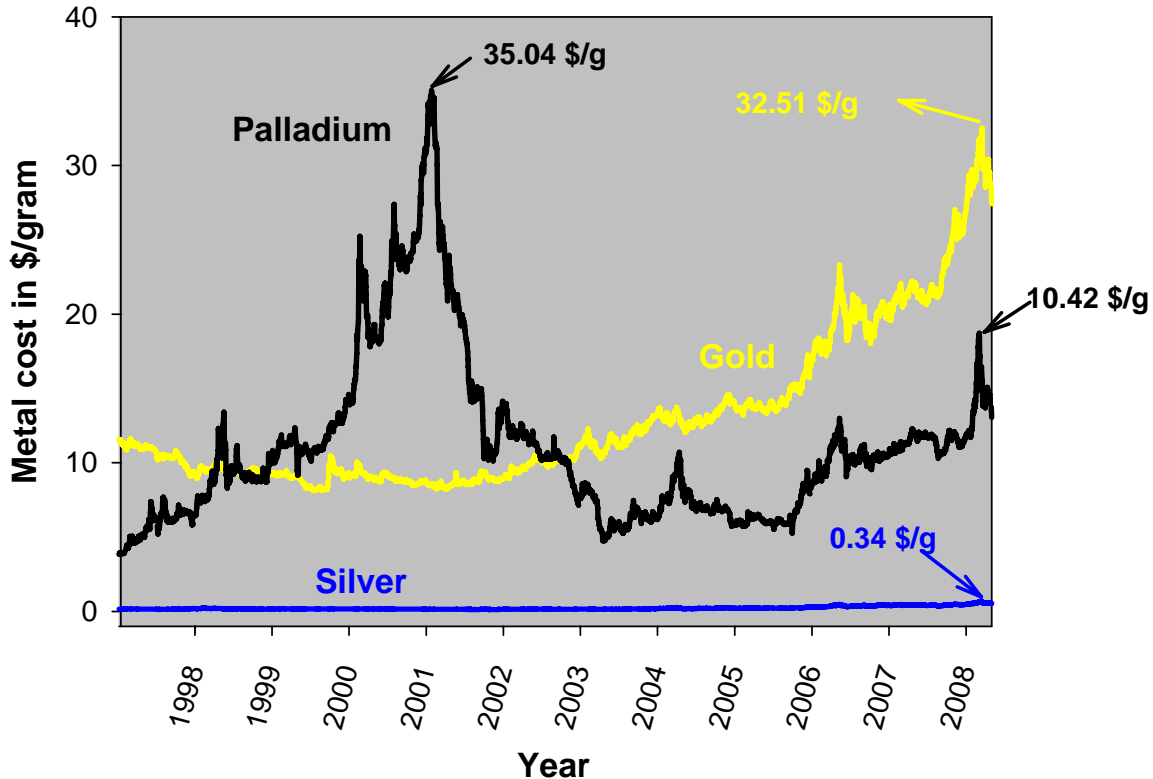


Figure 1: 10 year illustration of connector finish metal cost fluctuations (www.kitco.com).

For tin finish applications, it is the conversion to 'lead free' tin deposits. An effective way to minimize the risk of tin whisker related failures for most tin finished contact designs is to follow recommended design/application criteria and only use currently accepted whisker mitigating tin plating chemistries. In connector designs where these recommendations cannot be met, a cost effective alternative to tin may be required. Figure 2 shows examples of tin whiskers.

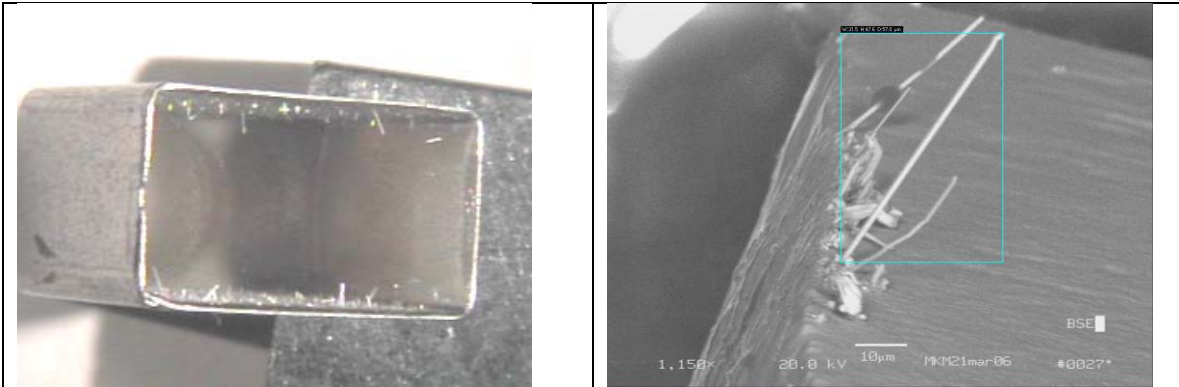


Figure 2: Examples of tin whisker formation.

A large part of what drives making contact finish choices is cost. What limits contact finish choice is performance requirements and manufacturing concerns. The finish appropriate for any connector application is determined not only by performance requirements, but also lifetime exposures under which it will have to function. Silver has a long history of performing well in the tarnished state in power applications and certain appropriate signal applications.

Characteristics of silver as a contact finish:

Positives:

Silver has a unique combination of material properties such as the highest thermal and electrical conductivity of any metal and a relatively low hardness. Theory and experience show how these aspects lead to very low CR values for mated clean silver surfaces [5, 6, 7, 8]. Current passing through a clean silver-to-silver contact interface sees a relatively large conducting area (less constriction) made up of adhesively bonded metal-to-metal asperity junctions. This unique combination of properties results in relatively low CR, superior thermal-rise performance, and excellent vibrational stability. The attributes make it attractive for use in power applications. Figure 3 shows CR readings taken from several common connector finish surfaces compared to silver.

Silver also has good solderability characteristics, even if the silver is somewhat tarnished. If the level of tarnish is excessive, a more active flux may be required. Immersion silver is widely used as a solderable finish on board applications but can have limited shelf life if the silver is exposed to the environment.

With any changes away from traditional finish choices comes the risk of unintentional finish combinations. Generally, it is recommended to mate 'like on like', that is to say, mating a silver plug to a silver receptacle. Fortunately, silver can be an appropriate choice for mating to either gold based or tin finishes. Performance levels and costs of such combinations will fall somewhere between the two different finishes. For example, if you are mating silver to tin, you will not appreciably improve durability and fretting failure could still be a risk; all at the higher cost of silver [9]. General rankings of the galvanic corrosion susceptibility of different contacting material combinations show that silver-to-gold and silver-to-tin are satisfactory combinations in many environments; with silver-to-tin presenting the most risk in harsher environments [10, 11, 12]. Therefore, a combination may have to be tested to determine its viability in more severe environment applications.

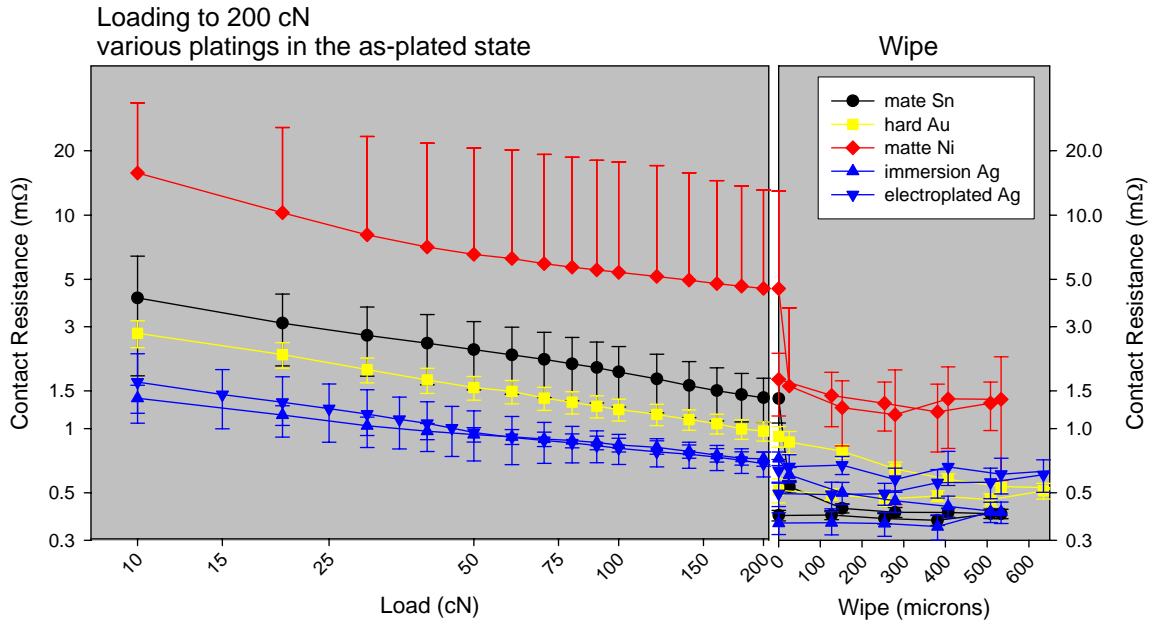


Figure 3: Contact Resistance (median with standard deviation) data for four standard contact finishes loaded to 200 cN, with wipe.

Potential Issues:

Unfortunately, silver has some less favorable contact performance attributes. Silver does not have the ‘noble’ character of gold and will form surface tarnish films when exposed to some reducible sulfur bearing atmospheres. Silver has a high Coefficient of Friction (COF) (high insertion forces) and poor wear characteristics (poor durability). Silver may be susceptible to electro-migration failures under specific conditions.

Silver tarnish films:

Silver tarnish films can be many colors, anywhere from yellow to tan to blue to black. Customers may object to this corroded appearance on contact interfaces because similar dark features on a tin surface (e.g. fret spots) or gold plated surface (e.g. corrosion product creeping from pore sites) generally lead to CR instability at the contact interface. A silver plated contact surface can appear discolored and still function very well if used correctly in the application.

A related potential visual issue with tarnished silver films has to do with the process control systems designed to visually image/locate the position of contacts during assembly. If this system requires (or is programmed for) ‘shiny’ or ‘white’ silver contacts and the silver contact surface has tarnished, the system may reject the part erroneously. Because the visual appearance of the tarnish films that can form on exposed silver surfaces can be so variable, it may be difficult to compensate for automatically.

In most stable connector application environments, the growth of silver tarnish has been reported to be linear and not self-limiting [1, 13, 14, 15, 16, 3, 17, 2, 4]. Tarnish films generated on silver finished surfaces exposed to most connector field applications are predominantly covalently bonded semi-conducting α silver sulfide (Ag_2S) and to a lesser extent, small amounts of insulating and harder to displace silver chloride ($AgCl$). Film morphologies are typically non-uniform and possibly greater around surface features where water can collect. These predominantly silver sulfide tarnish films are semi-conductive at ambient temperatures, inherently soft, and relatively easily displaced with contact interface wipe at sufficient normal loads (Figure 5). If substrate material corrosion products (e.g. copper) are incorporated into the silver sulfide film, CR issues will likely occur [18, 19]. This is one reason why a nickel underplate is recommended when possible, and thicker silver plating is used when a nickel underplate is not used.

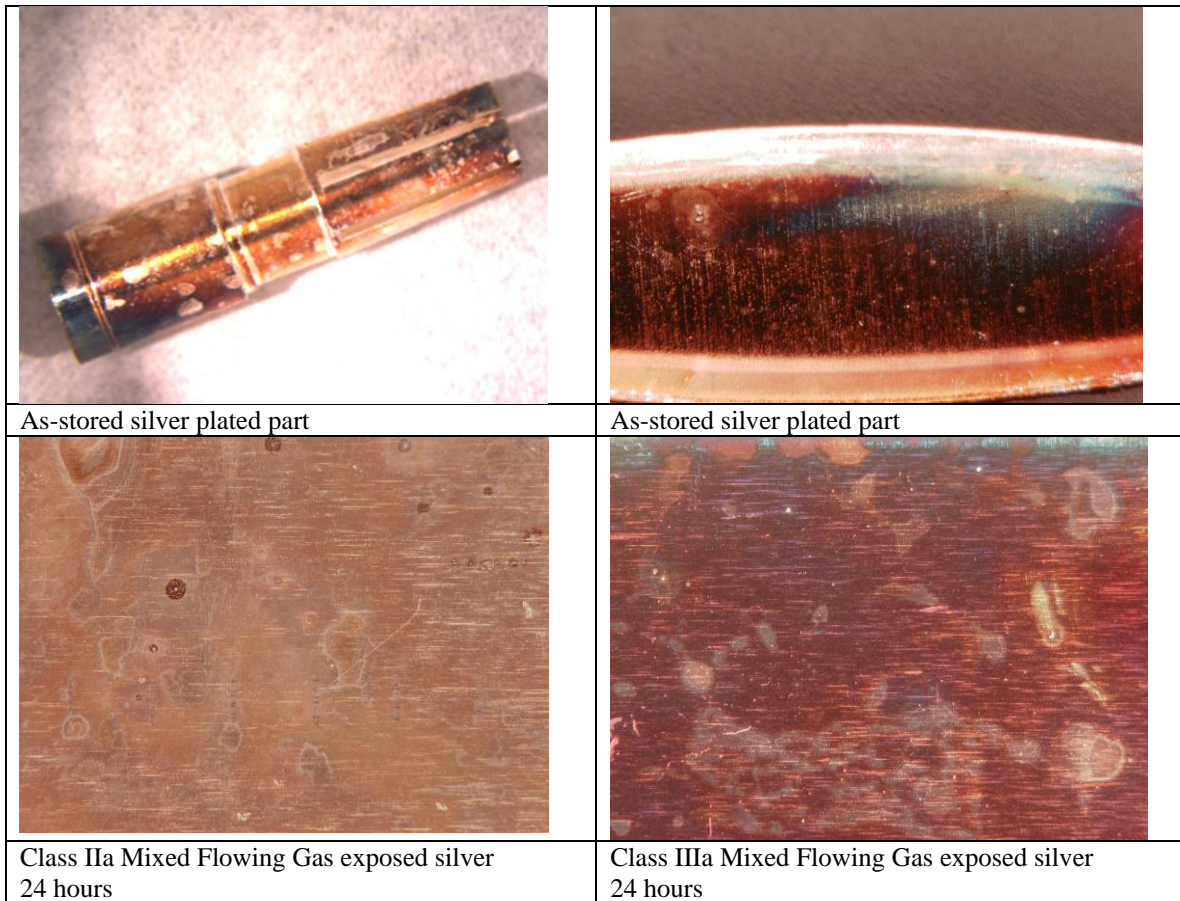


Figure 4: Examples of tarnished silver surfaces.

A history of using silver finished contacts has shown that low and stable CR is maintained in many applications using tarnished silver contact surfaces – even with films on the order of a thousand angstroms in thickness [17]. If the quality and level of silver tarnish is not excessive and wipe and sufficient normal loads are incorporated into the connector design, silver tarnish typically will not cause contact performance problems (Figure 5). The films can even lead to durability and insertion force improvements.

Silver sulfide:

Silver sulfide (Ag_2S) forms when silver atoms react with reduced sulfur (HS^-) dissolved in the water film found on silver surfaces in typical connector environments. The primary source of this reduced sulfur is dissolved gaseous hydrogen sulfide (H_2S), or to a lesser extent (less prevalent in the atmosphere) hydrolyzed carbonyl sulfide (COS) [20, 3, 4, 21]. Hydrogen sulfide comes from processes such as organic decay, combustion processes, volcanic activity, and manufacturing sources such as paper mills, sewage plants, and high sulfur packaging materials. Silver tarnish can become excessive if used or stored unprotected in environments with localized source of hydrogen sulfide [14, 15, 2].

Silver chloride:

To a lesser extent, silver chloride ($AgCl$) has been detected in some field exposed silver tarnish films. Silver is sensitive to the presence of chloride (Cl^-) and will react to form silver chloride [20, 14, 2, 4]. Chloride can come from species such as dissolved hydrochloric acid (HCl) gas or other chloride containing particulates (e.g. $NaCl$). Hence, silver chloride has been found in some field exposed silver tarnish films. The higher the level of harder insulative silver chloride in the tarnish film (relative to the level of softer semi-conductive silver sulfide), the more insulating and harder to displace the film becomes upon wipe leading to CR issues at thinner tarnish film levels [13, 20, 16, 14, 2, 3]. The reality is that in most field

applications environments, a predominantly silver sulfide film forms with sometimes minor amounts of silver chloride.

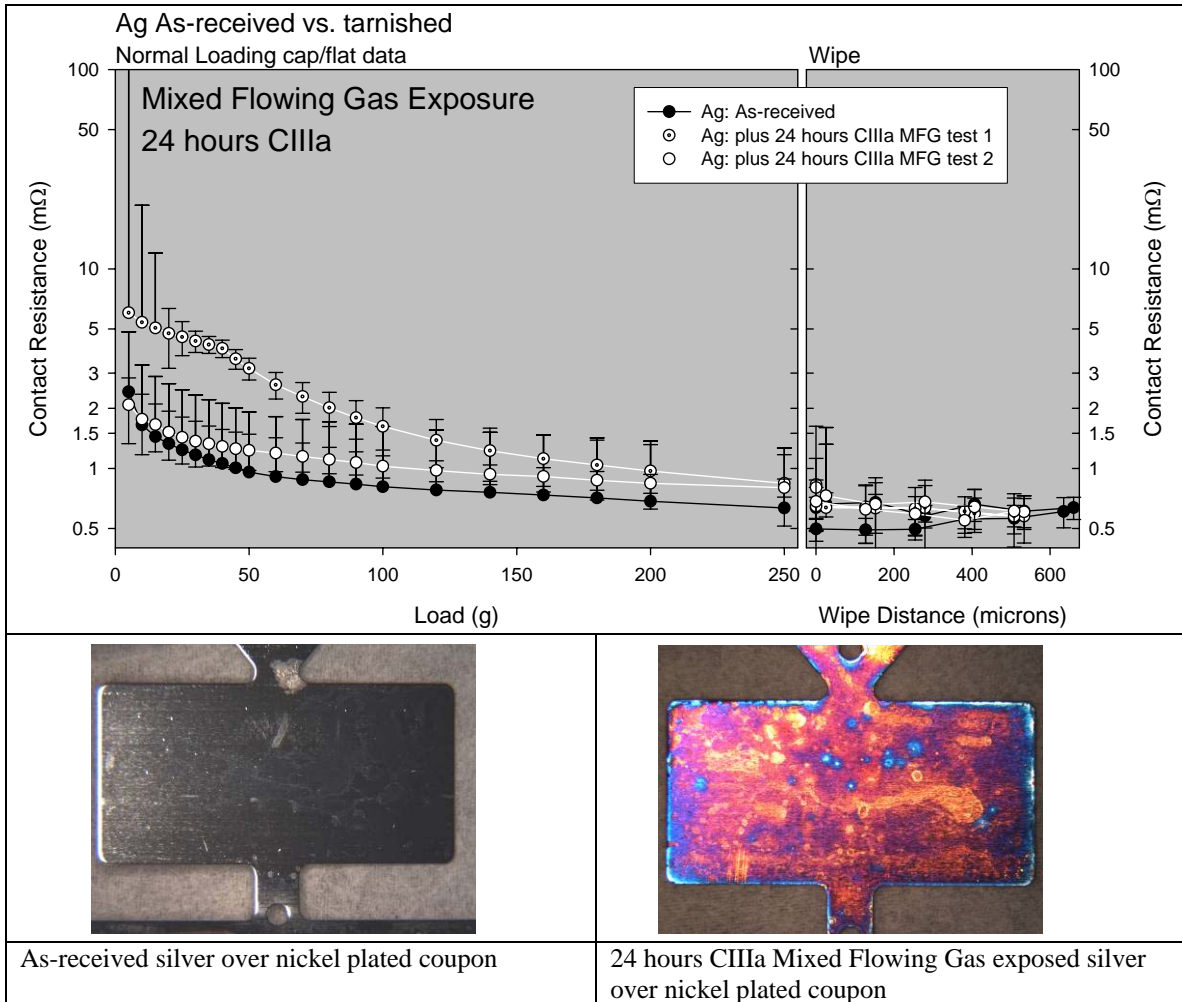


Figure 5: Contact resistance (median with standard deviation) data comparing as-plated and tarnished silver surfaces, with wipe.

Silver sulfate:

There is the possibility of forming silver sulfate (Ag_2SO_4) in the presence of sulfur dioxide (SO_2), but only appreciably in the presence of artificially high levels of sulfur dioxide that are two and three orders of magnitude higher than found in typical ambient environments [13, 14, 4]. Silver sulfate have not been found in tarnish films that have been exposed to typical connector environments.

Potential tarnish accelerating factors:

Chlorine gas:

Even though silver does not react directly with chlorine gas (Cl_2), its presence has a synergistic effect on silver tarnish formation when combined with hydrogen sulfide gas. This is especially evident on silver surfaces exposed to accelerating environments containing both hydrogen sulfide and chlorine gas. If the ratio of hydrogen sulfide to chlorine is great enough, the film growth rate begins to deviate from linear and approach parabolic. These artificial environment exposed samples develop tarnish films faster, and with a greater level of silver chloride than is found on most field tarnished samples [13, 20, 14, 16, 2, 3]. The reality is that chlorine gas, commonly used in mixed flowing gas testing, is virtually non-existent in the atmosphere. This synergy may account for silver chloride level and CR discrepancies between field and

accelerated environment exposed silver surfaces. This illustrates the risk of applying silver in particular environments that may have a local source of chlorine gas.

Water:

The presence of moisture is needed for silver to tarnish in response to corrosive environments. This moisture allows for the dissolution of corrosive elements leading to dissolution of metallic silver. Surface water films can either form as monolayers generated by humidity, or in a condensed form [2, 4]. The tarnishing of silver has been reported as both positively dependant on [22, 4], and independent of [14, 15], increasing relative humidity levels depending on the exposure environment.

Nitrogen Dioxide:

Though silver does not react with nitrogen dioxide (NO₂), it has also been shown that the rate of silver sulfide tarnish formation can be somewhat accelerated by the presence of nitrogen dioxide [20, 22, 2, 3, 4] – though the mechanisms are not well understood. It is not considered to be a dominant factor in silver corrosion.

Ozone/photocorrosion:

Another synergistic accelerant would be the presence of ozone (O₃) [3, 23]. The ozone does not react directly with the silver but if it is prevalent in an environment, the resulting accelerated formation of the tarnish film could become a problem for contact interface electrical performance. In fact, silver oxides (AgO and Ag₂O) are formed which are very insulating and difficult to displace if trying to make electrical contact [13, 4]. Ozone is not found at significant levels in most connector application environments.

Another related potential accelerant of tarnish film formation is photons capable of driving photocorrosion. This phenomenon is not well understood in connector environments, but data suggests it would be a possible cause of failure in some cases [4]. It would not be a factor in an enclosed connector system that would block light from the contact surfaces. It could possibly be a factor in light exposed applications. Initial data from another study has shown that both ozone and Ultra Violet (UV) exposure are required for the silver oxides to form [24].

Silver tarnish creep across gold surfaces:

Silver tarnish films have a tendency to creep/migrate across any adjacent gold surfaces [25, 26, 27, 15, 28, 21]. This can lead to high CR values because it is much harder to displace the tarnish films formed across the harder gold sub-surface. This is also why silver is generally not used as an over plate for gold finishes. This risk can be avoided in most designs.

Galling - adhesive bonding and wear:

Unfortunately, part of what makes silver contact finishes work so well electrically (relatively soft => large contact area) also contributes to its inherently poor mechanical/durability performance. Clean silver has a relatively high Coefficient of Friction (COF) and is not a durable finish (Figure 6).

Upon mating of two clean silver surfaces, the surface material supporting the load is plastically deformed. The material supporting the load between the surfaces is plastically deformed and work hardened (deformation zones) to form a contact interface of multiple metallurgically bonded (*e.g.*, cold welded) metal-to-metal junctions with a relatively large total contact area. If clean, the adhesive bonds can be as strong as an inter-crystalline grain boundary. Because the material around the original asperity junction interface has been work hardened, any relative motion (*i.e.*, sliding) at that interface will cause sub surface material shearing as the asperity junctions are broken. Where ever the weakest juncture in the composite structure is located is where the damage occurs. The severity of wear increases with increased normal forces.

Poor wear durability is evidenced by clean silver's inherently high COF (Figure 7). Clean silver surfaces that have been pressed together require some force to pull apart resulting in material being ripped out of either surface. Because silver contacts are typically used at relatively high normal loads for electrical reliability reasons (relative to hard gold), the durability of silver finishes is further limited. These factors contribute to the high insertion forces found with clean silver contacts. Silver is usually inappropriate for high durability applications.

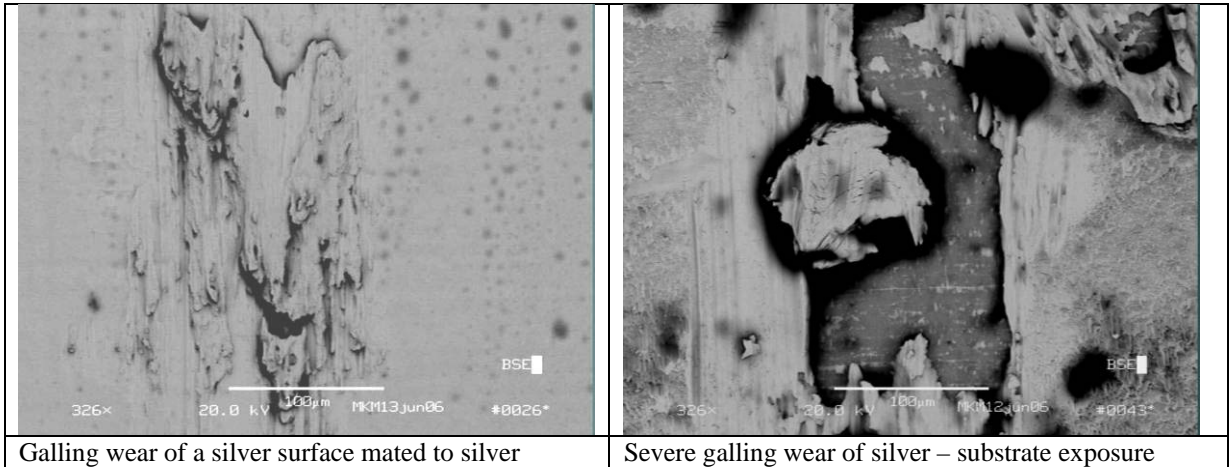


Figure 6: Images illustrating the poor wear characteristics of silver plated surfaces.

The combination of higher normal forces and silvers’ high COF promotes vibrational stability of a contact interface by preventing mechanically or thermally driven relative micro-motion (e.g. fretting) from being transferred to the contact interface. Silver itself is not susceptible to fretting oxidation in typical connector environments. If conditions are severe enough for fretting motion to occur, silver is susceptible to severe adhesive fretting motion wear (galling). Fretting motion could quickly lead to exposure of nickel and/or copper substrate materials which are susceptible to fretting oxidation failures and unacceptable CR increases.

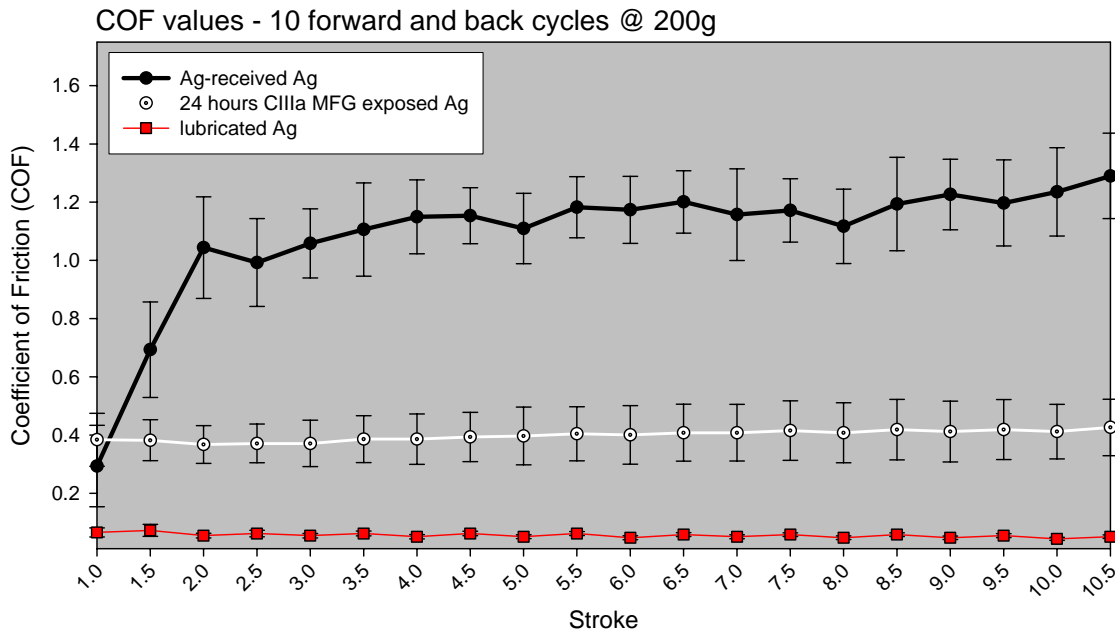


Figure 7: Coefficient of Friction (median with standard deviation) data for 10 forward and back wear passes comparing as-plated, lubricated, and tarnished silver surfaces.

The presence of even minor amounts of silver tarnish at the surface can weaken the adhesive metal-to-metal contact interface bonds by providing a shearable layer at the asperity junctions. The existence of even minimal storage generated silver tarnish on mating silver surfaces has a tendency to initially reduce

COF (Figure 7 strokes 1.0 and 1.5). It can reduce the level of galling/wear and insertion force and may improve durability performance with little or no impact on CR performance.

Electromigration:

Electro-migration shorting failures can occur when metallic bridges form between closely spaced metallic current paths under certain conditions. Many metals have been shown to be susceptible to electro-migration under particular conditions, (e.g. copper, tin, lead, etc.), but silver is considered to be the most active. Several conditions need to exist simultaneously for electro-migration failures to happen: an electrolyte path for the metal ions to flow (e.g., water plus ionic contamination), a voltage sufficient to drive the process, and enough time at potential/path conditions to complete the formation of the metallic bridge (dendrite or 'stain').

In the past, silver electro-migration failures had primarily been a potential issue for electrolytic silver plated small centerline Direct Current (DC) board applications where there was a chance to form a relatively short water based ionic electrolytic path in the presence of a sufficient driving voltage [31, 32]. In the printed circuit board industry today, where the problem is most likely to occur, the use of thin immersion silver and improvements in design, processing, testing, and applications requirements have led to the wide spread use of silver in board applications without such failures [33, 28].

Electromigration failures generally do not occur in separable connector interface applications because the combination of geometries and application conditions are rarely susceptible. For the very limited design/applications that might have all the qualities required to potentially lead to electromigration, there are several ways to mitigate the risk - the first one being to avoid the use of electroplated silver. Others would be to maximize line spacing, minimize differential voltages (driving force), use hydrophobic materials, limit features that could trap water (e.g., scratches, cracks, board crevices, etc.), apply hydrophobic and/or conformal coatings, overplate the silver with a less active metal, limit or eliminate the chance of ionic contamination (e.g., avoid no-clean flux residue, exclude paper fibers, etc.), and otherwise minimize water film formation. In a situation where silver is mated to a gold plated board pad configuration and the combination of design and conditions could make electro-migration a possibility, testing may be warranted [32].

Recommendations for use of silver in typical connectors:

Normal force and wipe:

Since silver has poor durability and the tarnish films are unpredictable, a design needs to be able to wipe/displace the films away from the contact interface upon mating. Therefore, it is recommended that silver finished contact interface designs have a relatively high normal force and incorporate wipe whenever possible. Typical silver plated contact designs use 200 cN of normal force.

Durability considerations:

To compensate for silvers' poor durability characteristics, silver is recommended for use in low durability applications (e.g. <= 10 cycles). The actual appropriate number of durability cycles a particular connector could tolerate would be design and application dependant. The use of a wear reducing surface treatment (e.g. lubricant) could increase the number of durability cycles that a silver finish could tolerate and still function properly for a particular application (Figure 7).

Centerline considerations:

Most connector designs would not have a problem with this failure mode. Historically, electromigration failures between relatively thick electroplated silver finished board traces were an issue in certain smaller centerline board applications using hygroscopic board materials operating at relatively high voltages. Improved board manufacturing has led to the wide spread use of immersion silver in board applications without such failures. As the connector industry is migrating to smaller and smaller form factors, electromigration may need to be tested for in very specific situations.

Nickel underplate:

It is recommended to use a nickel underplate (minimum of 1.25 microns) whenever possible. The nature of the tarnish film will change significantly if copper alloy elements from the substrate reach the surface of the

silver. This can occur through mechanisms such as diffusion or corrosion creep at breaks in the silver electrodeposit (similar to what happens with gold). This will most likely lead to an increase in CR if these more tenacious films get into the contact interface [18, 31]. At higher temperatures, oxygen will diffuse through silver to the copper alloy interface at a relatively fast rate and could lead to blistering if no nickel underplate is used. A nickel underplate also will prevent a relatively weak layer of silver-copper intermetallics from forming at temperatures greater than 150°C which could lead to adhesion problems [30].

Silver Thickness:

What silver thickness is appropriate is dependant on application factors such as environmental severity, time at temperature considerations, durability requirements, nickel underplate, and surface treatment. Silver plating thicknesses are typically in the range of 2 µm or greater in most separable contact interface applications that use a nickel underplate. If no nickel underplate is used, a greater thickness of silver may be required to prevent substrate corrosion products from getting to the surface [18]. These higher thicknesses also provide more silver material between the atmosphere and the substrate material(s), possibly leading to more wear cycles before any substrate material is exposed.

Higher reduced sulfur and/or chlorine and/or ozone containing environments:

Silver finished contacts are generally not used in applications where they would be openly exposed to outdoor or industrial environments due to concerns with excessive reduced sulfur exposure and tarnish levels. Exposure to environments with high levels of hydrogen sulfide (e.g. paper plant), chloride (e.g. salt spray), chlorine gas, and/or ozone should also be avoided for silver plated contacts. If silver is to be used in such environments, environmental sealing may be required to avoid excessive tarnishing.

Managing Silver Corrosion:

Surface treatments can be an effective way to attenuate tarnish formation, reduce insertion forces, improving durability, and minimize the risk of electro-migration where functionally appropriate. They come with their own set of possible issues. Liquid based lubricants and other surface treatments (e.g., Self Assembled Monolayers (SAM)), are commonly used. There are many commercial versions available.

Coating silver surfaces with a thin solid top layer to prevent tarnish has been done. Any solid layers on the relatively soft silver will no longer provide protection in the contact region if they are wiped away upon mating. Therefore, this approach is probably only potentially effective in keeping silver surfaces that are not disturbed 'tarnish' free and will have limited effect in a contact area. Attempts have been made to use a gold flash to protect the surface of the silver from tarnishing. There are three reasons that this approach is risky. The facts that silver and gold will readily inter-diffuse, silver sulfide will creep/migrate across gold surfaces, and gold is very susceptible to arc erosion leads to this approach having marginal value [34]. Such considerations have to be taken into account when considering these types of coatings.

For a surface coating to be effective, it has to perform without losing functionality or causing an unacceptable increase in CR. They generally do not interfere with any subsequent soldering operations, but they can be rendered ineffective or harmful if removed during assembly and use, or exposed to temperatures above or below their proper operating range. If excess surface treatment material can migrate to other regions of the connector or system and is a problem, the use of such a surface treatment may not be acceptable. Whether or not a surface treatment can be used effectively for a silver finished connector is dependant on the performance requirements, application exposures, design limitations, visual requirements, and customer perception.

There are non surface treatment methods to shield silver surface atoms from environmental corrosive elements (e.g. hydrogen sulfide). Anything that limits the ingress of sulfur to the contact area has an effect. These methods are also known as physical blocks. Two metallic surfaces pressed together helps limit the flow of corrosive elements into and around a formed contact interface, leading to less corrosion in the immediate area. In fact, formed functioning contact interfaces will remain electrically stable if not disturbed mechanically. The shielding effect of a connector housing (closed or actively sealed) can be quite dramatic, as well as the effect of any equipment enclosure or environmental controls (e.g., air conditioned, filtered) [17]. Additionally, sometimes greases or gels are used in conjunction with a

connector housing (e.g. the housing is 'filled' with a grease style lubricant) to further mitigate flow of corrosive elements to the contact interface.

Most packaging cardboard and interleaving paper contain and release high enough levels of sulfur to cause accelerated tarnishing on packed silver plated parts. Therefore, 'low sulfur' products are usually used to package silver plated parts. Products such as Silver Saver paper are commonly packed with silver plated parts and serve to absorb environmental sulfur limiting the amount that can reach and react with the plated silver.

Common connector testing methods associated with silver finished product:

Due to the poor durability and high insertion force characteristics of silver finished connectors, durability and insertion force testing are widely used. What specific level and type of testing is depends on all the characteristics of the connector as well as the intended application. Therefore, the parameters of such testing are product and application specific.

Chloride exposure (e.g. salt spray) can lead to tenacious and resistive tarnish films containing excessive levels of silver chloride. Therefore, occasionally salt spray (fog) [35, 36] testing is done on silver finished connectors if there is a risk. Silver is not generally used as a contact finish in these types of environments without some form of environmental shielding/sealing. This type of testing is also used to determine the susceptibility of a given dissimilar metal connection to galvanic corrosion conditions.

Electromigration testing [32] is rarely done for separable contact interface designs. There are some cases where it may be warranted depending on the application.

Mixed Flowing Gas (MFG) testing is done by exposing contact surfaces to elevated levels of multiple corrosive gases under specific temperature and humidity conditions. Typically for specific time intervals as part of testing sequences prescribed by product qualification testing requirements. These MFG tests were developed after a long process of comparing field trial data taken from connectors with a variety of finishes to corresponding laboratory tested sample data in an effort to correlate lifetime exposure performance to accelerated testing results. In the end, no industry accepted accelerated MFG laboratory vs. field life correlations could be developed for silver due to the complexity of the silver corrosion process, the synergy between differing levels of multiple gases, and the fact that silver is so sensitive to typically erratic field fluctuations in hydrogen sulfide gas levels [1, 13, 20, 16, 2, 3, 4, 21]. Alternate single gas testing environments (e.g. hydrogen sulfide, flowers of sulfur) were also determined to be misleadingly benign and not representative of silver field exposures [1, 13, 2, 3].

MFG testing was ultimately developed primarily for copper and gold surface finishes on nickel plated copper alloy substrates [37, 38]. There are several versions in use, but the most common are four gas Class IIa (Indoor) and Class IIIa (Outdoor). Generally, they are not used for silver finished connector qualification. Because these standard sulfur bearing gas environments are repeatable, available and will generate some level of silver sulfide and/or silver chloride containing tarnish films on silver surfaces, occasionally they are used for testing. Their use is customized to a particular application, customer requirement, or analysis. This type of testing doesn't have 'real life' silver field exposure correlations and won't necessarily form films with the same morphology, chemistry, or qualities a particular field exposure would.

Silver alloy considerations:

Typically, either matte or semi-bright pure silver electrodeposits are used in separable connector interface applications. Any as-plated hardness imparted by semi-bright 'pure' silver deposit additives (e.g. organic sulfides, selenites) will decrease significantly within months and do not degrade the CR performance significantly [30].

Alloyed, or hard, silver finishes are not generally used in separable contact interface applications. There are not many production level silver alloy baths available. These alloyed silver deposits are usually hardened by a metallic additive (e.g. antimony, bismuth, gold). The idea is to improve the brightness and

durability of the deposits. The hardness imparted by these alloying agents may also reduce with age. Unfortunately, these alloying elements also tend to significantly increase the resistivity and/or CR of the deposit (Figure 8). If the alloying element itself is susceptible to corrosion, it will probably render any such alloyed silver tarnish film more insulating, tenacious and more difficult to displace [20, 15, 19] (Figure 8). These factors are the reason silver alloys are not widely used in separable contact interface applications.

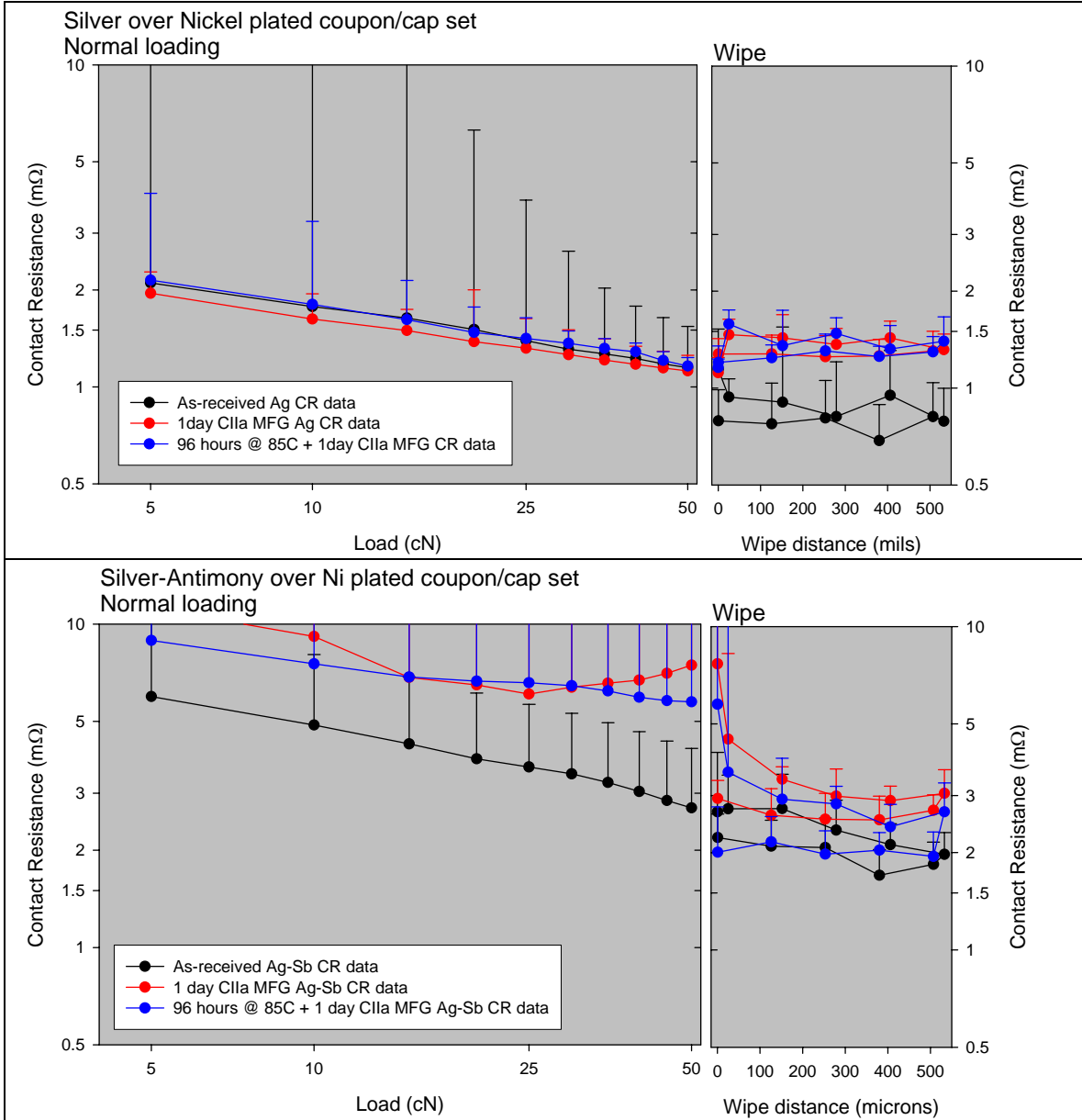


Figure 8: Contact resistance (median with standard deviation) data comparing pure silver to alloyed silver performance as-plated vs. aged.

Conclusions:

Having outlined the qualities and implications of using silver as a contact finish, there are many signal connector applications where it may be a very good finish choice alternative – but only if the design characteristics and application requirements are appropriate. Appropriateness should be determined by design and application analysis as well as product testing and by addressing customer needs and perceptions where needed.

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