# Improved Tarnish Resistant Sterling Silver

Michael T. Roche
BHP Billiton, Townsville, Queensland, Australia

Frank E. Goodwin
International Lead Zinc Research Organization, Inc., Research Triangle Park, NC, USA
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## ABSTRACT

A cooperative research program to determine means of delaying tarnishing of sterling silver has been organized by the Silver Research Consortium, a group of silver producers and users seeking to improve uses of silver by carrying out research. Whereas in the past most approaches to improving tarnish resistance have been based on silver alloying additions, this project is taking a scientifically based approach to reducing the rate of tarnishing by use of thin coatings. The general technical approach being taken and an overview of the Silver Research Consortium are given.

## INTRODUCTION:

The principal sterling silver alloy, 92.5% Ag-5.7% Cu, has been used for silverware and jewelry since the 14$^{th}$ century. Alloying with copper strengthens silver and allows it to be used for these items, but it has always been susceptible to tarnishing. Tarnishing is a surface discoloration and mainly results from the formation of silver sulfide, $Ag_2S$, although other compounds have been recently identified which contribute to tarnishing.[1,2] Although tarnishing is not important for industrial applications because it does not change the electrical or contact resistance properties of silver alloys, it is important for applications where appearance is important. Reflecting this importance, many attempts have been made over the years to develop tarnish-resistant alloys that meet the 92.5% silver purity standard which is required if the alloy is to be called “sterling silver.” Some of these have reached limited commercialization, but all add cost and complicate the manufacturing process for sterling silver.

Recognizing the importance of this barrier to wider usage of silver in silverware, jewelry and coinage applications, the Silver Research Consortium selected, as one of its first projects, a cooperative effort to improve the tarnish resistance of sterling silver. The Silver Research Consortium was founded in 2002 and now includes the following members:

- Apex Silver Mines Corporation, Denver, Colorado, USA
- BHP Billiton, Townsville, Queensland, Australia

- Met-Mex Penoles, Torreon, Coah., Mexico
- The Silver Institute, Washington, DC, USA
- Asulab, Division of Swatch, Marin, Switzerland
- Eastman-Kodak Company, Rochester, New York, USA
- The Royal Canadian Mint, Ottawa, Ontario, Canada

Together with this tarnish project, the Silver Research Consortium is also conducting research programs on silver usage in wood preservatives and environment issues that are needed to ensure that silver is not unreasonably regulated in the future.

## PAST APPROACHES TO IMPROVING TARNISH RESISTANCE:

Fine silver, containing at least 99.5 wt.% silver is recognized as having very good tarnish resistance, however fine silver is too soft and weak for many applications. Therefore, sterling silver, containing at least 92.5% wt.% silver is used for many jewelry, tableware, ornamental and industrial applications. Traditionally sterling silver has been composed of 92.5 wt.% silver and 7.5 wt.% copper. Sterling silver can also be increased in hardness from an annealed condition of 80 VHN to 110 VHN compared with the annealed hardness of pure silver which is about 35 VHN. However sterling silver tarnishes easily and is also susceptible to “fire scale.”

Tarnish is generally caused by a reaction of sulfur, either from the surrounding air or perspiration that reacts with silver to form $Ag_2S$. Several species other than silver sulfide can also be found on tarnished surfaces. These include sulfate, chloride, oxide, organic carbon, and oxygenated organic carbon species and a carbonate or carbonyl. In some cases these species can be present at comparable or very much higher concentrations than silver sulfide. Particulate deposition can result in species such as sodium, potassium and silicon being present in the tarnished layer. The relative concentrations of each of these species will obviously vary, depending upon the environment to which the silver surface is exposed. Even if handled carefully, and exposed in closed cases, there is sufficient sulfur and other of the above species in most air to result in tarnishing of sterling silver after a few days, which appears as a black scale. To combat this problem, jewelry stores and others use cloth or similar strips treated to “getter” sulfur in display cases, lengthening the time before which noticeable tarnishing appears. Such a treatment, however, is not possible for sterling silver kept in environments that are not well sealed. Replacement of the sulfur absorption strips is also required after some time. It is therefore highly desirable to develop a sterling silver alloy, or treatment for sterling silver that is tarnish resistant, allowing it to be handled and stored without unusual precautions.

Many approaches have been taken to solving this problem in the past and most of these rely upon alloying of silver to make more tarnish resistant compositions. In traditional sterling silver, copper oxide forms “fire scale” which is typically a darkened portion resulting from melting or brazing. Fire scale is not limited to the surface of sterling silver, as in the case of conventional tarnish, but may penetrate the article to some depth and may not be removed by buffing and polishing.

Five different directions to alloying of silver to reduce the onset of tarnishing have been made:

US Patent 4,775,511, issued October 1988, describes the use of additions to silver-copper, silver-gold and silver-copper-gold alloys of at least one element of the following: Cr, Ta, Al, Ti, or Th, where the added amounts of these elements does not exceed 1.5 wt.% as a substitute for silver. These elements were found to form a thin oxide layer, which was stable and did not affect the properties of the silver based alloy. The elements were found to be self-healing, forming a layer of oxide and also reacting preferentially with sulfur to form sulfides, rather than formation of silver sulfide. In this way, tarnish resistance was improved. All of these elements were recognized as having heats of sulfide formation, which were higher than that of silver. The preferential additions to silver-copper alloys were Al and Cr at about 0.5 wt.% and for silver-gold and silver-copper-gold alloy Cr at 0.4 wt.%. An improvement of 10-12 times increase in sulfide tarnish inhibition for sterling silver was claimed. This increase could also be reached by adding 0.75% Ti, 1.25% Th or 1.5% Ta.

US Patent 5,817,195 describes a tarnish resistant alloy containing 6.57% Zn, 0.25% Cu, 0.25% Ni, 0.25% In, and 0.18% metal silicates. These silicates involve other alloying elements than those listed, because those listed are not silicate formers. However it is claimed that these silicates improve castability by making the molten metal more fluid. This alloy is claimed to have a more stable color than sterling silver. The nickel addition eliminates the brittleness of traditional sterling silver after casting. Zinc replaces copper to enhance tarnish resistance and improve overall corrosion resistance. Nickel must be added to the alloy in equal amounts with copper to cause all the constituents to remain in solution.

US Patent 5,039,479 describes the usefulness of the additions of silicon, boron and tin to an alloy similar to that described in US Patent 5,817,195. The preferred composition is 1.85% Zn, 0.05% In, 4% Sn, 1.44% Cu, 0.01% B, and 0.05% Si. Si is added as a deoxidizer and is claimed to reduce the porosity of recast alloys. B is added to reduce the surface tension of the molten alloy, Zn is added to reduce the melting point of the alloy, and whiteness to act as a copper substitute, to help in deoxidization and to improve alloy fluidity during casting. Sn is added to improve tarnishing resistance and for its hardening effect. In is added as a grain refining agent and improves the wettability of the alloy. The composition described is sufficiently pure in silver to qualify as sterling silver. A similar approach is taken by US Patent 5,882,441 which describes a tarnish resistant 4.5% Zn-2.9% Cu-0.1% S alloy.

Addition of more noble elements increases the cost of sterling silver, but is highly effective. US Patent 5,037,708 describes an alloy containing 5% Pb, 2% Cu and 0.5% In or Zn. In this alloy the Cu has been replaced by Pd to enhance tarnish resistance and corrosion resistance and also to improve color stability. The working and casting properties are also improved, and Cu and In also help reduce brittleness.

The hardness and tarnish resistance of fine silver, with at least 99.5% purity, is claimed to be improved by the claims of US Patent 6,139,652, issued October 31, 2000. Small additions of Al, Sb, Ca, Ga, Ge, In, Li, Mn, Mg, Si, Sn, Ti, or Zn are added. The cast alloy is then annealed in an oxygen-rich atmosphere to give internal oxidation, hardening the alloy. This allows it to be age hardened to at least 136% of its annealed hardness, improved tarnish resistance is also claimed, likely by formation of surface oxides rich in the alloying elements.

Various of these alloys have been commercialized. For example, Ney Paliney 6 is a platinum silver-based alloy used for throttle position sensors, guidance systems, potentiometers, trimmers, communications and bar code readers. Sterling "D" is a white colored sterling silver offered by United Precious Metal Refining. It claims to have excellent tarnish resistance.

The addition of Ge to sterling silver is also noted to reduce tarnishing and fire stain. This alloy is a cadmium-free alternative to the 2 and 4% cadmium bearing grades that have been used in the past. This composition is covered by UK Patent 2,255, 348B. A similar composition was claimed by Metaleurop in their German application 4,213,897 of November 5, 1992. This alloy contains between 0.5 and 3% Ge, the balance of Cu to give 7.5% alloy addition and 92.5% Ag to give sterling silver. This is described further in Ref. 1.

To our knowledge, only limited work has been done on using metallic surface treatments or surface reactions to confer tarnish resistance to the traditional 92.5% Ag-7.5% Cu sterling silver alloy. Many possibilities appear to be of interest, including physical vapor deposition of alloying elements that are more reactive with sulfur than silver, conversion layer creation and other techniques. The Silver Research Consortium has funded its 2003 program to explore such techniques with compounds and elements of promise to see if more cost effective means of providing tarnish resistance can be conferred on sterling silver, compared with the bulk alloy techniques described above.

POSSIBLE TARNISH RESISTANT SURFACE TREATMENTS FOR STERLING SILVER:

Some surface treatments are possible to perform on sterling silver to increase tarnish resistance. These can be categorized as follows:

- Metallic coatings by electroplating, such as thin (150 Å) transparent coatings of Ni, Rh, Pt, Ir and Pd [3]. In addition electroplated silver alloy coatings containing Cd, Sb, Sr and Pd are possible. The application of these coatings is expected to be complicated and expensive, and no performance data are available to help judge their usefulness.

- Silver can be alloyed with sputter-applied coatings of Ta, Nb, Ti, and Al, however these are thought to provide only minimal protection [4].

- Oxide coatings of Al, Be, Zr, Mg, Ti, and Nb can be produced by sputtering or cathodic reduction of solutions containing the metal ions [3,4]. This is an expensive process and is complicated to deposit on curved articles. In addition the abrasion resistance of these coatings is poor. Some success has been realized with a sputter coating of $Nb_2O_5$ at a thickness of >700 nm. Silver watch cases have been protected from tarnish by the vapor deposition of a 100 Å coating of Mn followed by a 2 micron layer of $Al_2O_3$.

- Chromate conversion coatings are cheap, easy to perform, and provide relatively good corrosion resistance. These coatings can be applied by either chemical immersion or electrochemical treatment. One process has been patented that uses phosphate with 1-2% chromate followed by drying at 150°C [3]. Electrochemical chromate coatings are more expensive than the immersion systems but no performance data are available. All of the chromate processes use hexavalent chromium which is toxic and in many countries is either being banned or phased out.

- Non-chromate conversion coatings are generally based on tin compounds that are not as durable as chromate coatings [3, 5-7]. There are several coatings based on organic coatings, which provide hydrophobic films on silver that are resistant to tarnishing in accelerated tests. In some cases such as thiols, the stable complex of silver is formed but in no case are these coatings as durable as chromate conversion coatings.

- Organic coatings protect silver by forming a physical barrier, and are generally used for storage and display of silver items. Lacquers can be applied by brushing, dipping or spraying, and organic inhibitors can be added to improve protection. The main problem with these layers is that they are nearly always visible and if they are too thin they are not sufficiently protected.

- Polishes have been produced that claim to give tarnish protection and contain reducing compounds such as sodium dithionite and corrosion inhibitors such as morpholine [8]. There are no data on the extent of protection afforded.

The Silver Research Consortium program on tarnish resistant coatings is considering all of the above in its development of a more tarnish resistant coating for sterling silver. In considering the above approaches, together with newly conceived schemes, criteria to be used for selection in the investigation are:

- The protection afforded against tarnishing;
- The thickness of the coating;
- The durability of the coating, including its ability to withstand handling;
- The ease and availability of application and processing;
- The ease of repair of the coating, including ease of removal when desired;
- The environmental impact; and
- The cost.

Work on this program began during mid-2003 and has begun work by considering four different classes of coatings that offer promise:

- Precious metals including silver alloys;
- Passive oxides;
- Chromate-free conversion coatings; and
- Organic coatings with incorporated inhibitors.

Coatings selected for further investigation must be thin enough so that they do not impair the attractive surface appearance of sterling silver. At the same time, these very thin coatings must afford significant improvements to the tarnish resistance of sterling silver. Coatings on samples will be as thin as possible, as thin as 2 nm. A tarnish characterization test will be chosen from among several possible techniques. One accepted method is the Tuccillo-Nielsen tarnish test [9]. Conventional chlorine and/or ammonia testing has also been used to characterize tarnishing behavior. A more severe environment involves hydrogen sulfide gas. Results will be evaluated using a quantitative color scale. Deposition and process techniques for the tarnish resistant coating may include surface pretreatment, immersion or spraying, electrodeposition, electrophoretic deposition, anodic deposition, chemical vapor deposition, physical vapor deposition, sputtering, thermal treatment, laser treatment, electron beam treatment and ultra violet treatments. While these will be used to evaluate products in the laboratory, the Silver Research Consortium also recognizes that a very wide range of silver fabricators seek a tarnish resistance coating, ranging from small scale silversmiths to industrial applicators. Therefore as work proceeds, emphasis is being given to making the process as simple as possible, including the use of non-hazardous materials, so that it can be practiced by the full range of silver article manufacturers.

All laboratory work in this project is being carried out in the physical metallurgy division of Mintek, Randburg, South Africa, according to the schedule shown in Table 1. Mintek has extensive experience in processing and characterization of precious metals and is seen as an ideal location for carrying out this work. In addition to the tarnish resistance characterization noted above, characteristics of candidate tarnish resistance layers such as composition, thickness, adhesion and durability will be examined. The color of each coded sample will be measured in a spectrometric color measurement machine prior to testing and compared with an uncoated sample to ascertain the effect of the coating on the color. If more sophisticated techniques are needed to determine the composition and thickness of the tarnish layer, then optical ellipsometry, Auger or X-ray photoelectron spectroscopy may be required. However, in this first stage, it is expected that the work will be fairly empirical in nature.

FUTURE WORK:

After selection of approximately six candidates for tarnish resistant coatings on sterling silver, two additional projects are planned:

- “Product and Process Optimization:” For each of the six tarnish-inhibiting candidates identified in the first project, the different possible coating application processes will be investigated, and the best one chosen for further optimization. These processes may include electroplating, vapor deposition by various means, deposition of a liquid chemical precursor and others. All work will be carried out on the typical 92.5% silver-7.5% copper sterling silver alloy in as-cast form. The minimum coating thickness that allows tarnishing behavior to be substantially improved will be sought and the effect of deposition process on this coating thickness value will be determined. The possibilities of avoiding subsequent heat treatment will also be explored, potentially reducing processing costs.

  Samples will be characterized using the same methods employed for the first project, measuring the change in tarnish resistance that occurs. Conventional characterization of surface hardness, surface contact resistance and bulk electrical conductivity will be made. From these tests, no more than three combinations of coatings and their application processes will be determined.

- “Joining Process Development:” Many sterling silver alloys require joining as part of their fabrication into useful articles, whether decorative, domestic or industrial. Joining methods include the tin-based solders (now largely lead-free) and brazing. The influence of the selected coating types and techniques of the second project on joining processing will be determined. The joining processes typically used for sterling silver in various applications will be determined and baseline data gathered for the uncoated alloy. The applicability of baseline techniques to the coated alloys will be determined and process modifications made if needed to give successful joints. Peel and shear strength of joints will be carried out to characterize their quality. Recommendations for joining processes for the coatings and their processes selected in the second project will be made.

SUMMARY:

Tarnishing of sterling silver is a well-known problem that has been a shortcoming of this valuable alloy for several hundred years. The ability to produce new, transparent coatings on sterling sliver that make them resistant to tarnishing is now being explored, together with a wide range of coating deposition techniques. Development of a tarnish resistant coating could result in a significant expansion of demand for silver if the attributes of a tarnish resistant sterling silver material allow capture of markets from other materials, both precious and non-precious. The Silver Research Consortium program currently underway is conducting a basic exploration of tarnish resistant coatings based on the fundamentals of protective scale formation and consideration of processes that could be used to provide these protective layers. Layers are sufficiently thin, 2-8 nm, so they will not detract from the attractive appearance of sterling silver. If simple enough to apply by the wide range of silver fabricators in the marketplace today, they should allow applications such as silver coinage to be developed on a much broader scale than in the past, increasing the consumption of silver as a consequence.

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**Table 1. Schedule of Work for Silver Research Consortium Project**

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| **Phase 1. Literature Review and Coatings Selection** | |
| Literature Review | August-October 2003 |
| Selection of Coatings | October 2003 |
| Report on Phase 1 | November 2003 |
| **Phase 2. Sample Fabrication and Qualification** | |
| Preparation of Substrates | September-October 2003 |
| Preparation of Coated Samples | November 2003-April 2004 |
| Evaluation of Coatings | December 2003-April 2004 |
| Report on Phase 2 | April 2004 |
| **Phase 3. Tarnish Testing and Evaluation** | |
| Tarnish Tests:<br>• Tuccillo-Nielsen<br>• ISO 10271 | January-March 2004 |
| Evaluation | February-April 2004 |
| Final Report | June 2004 |

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