

The Protection of Silver Against Atmospheric Attack

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Tarnishing of silver and its alloys in certain environments is a persistent problem. This paper explains the various measures used to date to retard silver tarnishing in various applications, such as jewelry, the silversmith trade and electronics. Different anti-tarnish methods have been proposed by the scientific community, none of which perfectly satisfy the requirements of all applications. A method of incorporating fine organic and/or inorganic particles into silver-based electrolytic coatings is a very promising solution. However promising, we find it still needs further development.

The tarnish film appearing on silver surfaces limits the application of silver-containing alloys in many fields. Tarnishing is very harmful in electronic applications because of the added electrical resistance. In decorative applications, it ruins the workpiece appearance (color and brightness). In addition, the weldability of silver deteriorates.

Nowadays existing processes will retard the natural silver conversion but cannot completely eliminate it.¹⁻⁷ Any solution to the tarnish problem has to be a compromise between three fundamental aspects: (1) surface appearance, (2) contact resistance and (3) weldability.

There are several methods to protect silver against tarnishing. The most frequently used technique consists of depositing a protective film (organic, mineral or metal) on the silver object. Some protective methods are still under development while the others have already found widespread industrial application. They can be grouped into various categories.

Organic Deposits

Lacquers

The use of lacquers poses some problems for the surface appearance of the product. Indeed, a protective lacquer film degrades slowly over time and eventually alters the surface appearance, usually negatively. This film becomes yellow and can ultimately disappear after several months. Some films can be hardened with a thermal treatment and provide longer life. However, complete protection cannot be achieved with lacquers.

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Oils

Various oils or waxes can be dissolved in perchlorethylene, familiar as a common dry cleaning solvent. Objects to be covered are dipped into the solution and successively removed. After the perchlorethylene evaporates, the protective coating remains on the surface and protects the object from tarnishing. By a simple water or soap rinse, these oil films can be completely eliminated. This method is suitable for protecting details in storage. However, because of the low thickness of the film, any handling of the treated objects should be avoided.

Inorganic Deposits

At the moment, inorganic or metal coatings deposited by CVD/PVD, electrochemically or by immersion are most frequently used to prevent silver tarnishing. These methods can be classed into the following primary areas.

Chromate Conversion Coatings

Chromate conversion coating processes involve immersion of an object in a solution containing chromic acid, chromates and/or dichromates as primary ingredients. For example, the film obtained from a potassium dichromate bath insures ideal surface protection against tarnishing. Much work has been done in this area. Lacourcelle, *et al.*¹ described a bath containing:

- Potassium dichromate ($K_2Cr_2O_7$) 20 g/L (2.67 oz/gal)
- Potassium hydroxide (KOH) 20 g/L (2.67 oz/gal)
- Potassium carbonate (K_2CO_3) 40 g/L (5.34 oz/gal)

The solution concentration, temperature, pH and treatment time should be taken into account to avoid the appearance of an undesirable colored film that is detrimental to the final appearance.

Randin, *et al.*⁸ studied the electrochemical chromate conversion process as an anti-tarnish treatment on a variety

Nuts & Bolts: What This Paper Means to You

Work in nanotechnology is opening up new avenues in our industry, but meanwhile, silver still tarnishes. This age-old problem affects areas ranging from electronics to jewelry. Here, the authors have surveyed the work that has been done and is ongoing, to give us a *tour de force* of the means of preventing, if not eliminating the tarnishing of silver.

of substrates (In, Au, Ag and Cu) used in ornamental applications. The influence of the composition of the bath as well as that of other operating parameters was studied. The tarnish resistance of the chromate conversion coatings was investigated, in particular, after a weak abrasive treatment. The chromate conversion coating did not alter the surface appearance of any of the substrate materials studied and provided very effective protection against tarnishing. It could be cleaned in the isopropanol with no loss in tarnish resistance. However, it did not withstand the abrasive effect of polishing to the degree generally employed by jewelers. Chromating remains one of the most effective solutions for the protection of silver workpieces against tarnishing. However, the use of hexavalent chromium chemistry in the jewelry and silversmith trades is strongly prohibited because of its high toxicity.

Oxides

Many studies reported in the literature deal with the possibility of depositing a highly insulating film on silver objects (*e.g.*, oxides of the III-V elements). Price and Thomas⁹ proposed an effective way to avoid tarnishing. This process involved an anodization in an acidic solution (pH = 5.83) at approximately 5.0 A/dm² (46.5 A/ft²). The results of tarnishing tests were better than those obtained with chromate conversion coatings. A German patent¹⁰ describes oxide deposition by sputtering. Substrates were preheated between 100 and 200°C (212 and 392°F). Hard coatings of silica or alumina were deposited by sputtering at a pressure between 0.1 and 10 Pa (1.45×10⁻⁵ and 1.45×10⁻³ lb/in²). The layer thickness was between 0.1 and 10 μm (4.0 to 394 μ-in) [preferentially between 0.8 and 2 μm (31.5 and 78.7 μ-in)].

Tin (Sn)

Among other chemical processes it is important to note the tin chloride solution treatment.¹¹ Tin is used to protect silver objects because its color and hue are very similar to those of silver. Three methods of tin coating are usually cited.

Tin tempering. Objects to be protected are immersed in a bath containing 9 to 23% metal fluoroborate solution (the metal being less noble than silver, such as Cr, Pb, Ni, Co, Cd, In, Zn or Sn). After a visible film appears, usually in about 5 sec, the parts are removed from solution. This method is described in a U.S. patent.¹²

Degreasing – Tinning. Pieces to be coated are immersed in an alkaline hydroxide bath containing 0.5 to 10% of a bivalent organic or inorganic tin compound. The substrates become covered with a very adherent layer which protects against attack by hydrogen sulfide. This process is described in a German patent.¹²

Electrolytic tin deposition. Electrolytic tin coatings are used on a variety of silver alloys containing Cd, Zn, Al and Ag.¹³ This method is used mainly for non-decorative applications because the surface appearance after tinning differs from that of pure silver.

Electrolytic Silver Alloy Deposits & Others

A great number of silver-based coatings are cited in the literature. They are primarily intended for improved chemical resistance to hydrogen sulfide. However, most of these alloys are more sensitive to tarnishing than pure silver. Improved chemical resistance to H₂S is observed for some silver alloys such as Ag-Fe, Ag-Sn and silver alloyed with the platinum group metals.

Davitz, *et al.*¹⁴ proposed silver alloys consisting of In (17 to 22%), Pd (24 to 27%), Cu (5 to 30%) and Ru (0.25 to 1%). The ruthenium alloy can be heated to 1177°C (2150°F). It is used in jewelry and dental applications.

Sasaki and Nishiya¹⁵ developed silver alloys containing various elements including Ag, In (0.2 to 9 wt%), Al (0.02 to 2 wt%) Cu

(0.3 to 3 wt%) and/or Cd, Sn, Ga and/or Zn (0.01 to 6.5 wt%). These alloys can be used for decorative applications, but they need to be annealed between 220 and 900°C (428 and 1652°F) for 30 min. Finally, silver alloys containing about 6 wt% In, 1.5 wt% Al and 3 wt% Cu show improved results in tarnishing tests in aqueous solution containing 5% NaCl or 0.1% Na₂S. However, a silver alloy of similar composition (7 wt% In, 1.5 wt% Al and 4 wt% Cu) degrades rather quickly after immersion in 0.1% Na₂S aqueous solution for 10 hr. This example illustrates the complexity of silver tarnishing chemistry, and in particular the importance of the chemical composition of the silver-based alloy which can best retard tarnishing.

Electrolytic composite coatings have been studied with an eye toward tarnish resistance. For this purpose, De Bonte, *et al.*¹⁶ studied the incorporation of fine germanium oxide (GeO₂) particles in electrolytic deposition processes. Silver alloy coatings containing up to 6 wt% germanium were electrodeposited from a cyanide solution without brighteners. Codeposition of germanium with silver improves tarnish resistance in the thioacetamide test (ISO 4538) when compared to pure silver. The coating surface became yellowish instead of darkening, and the corrosion products could be easily removed by simple water rinsing.

Similar results were obtained for silver-germanium and silver-copper-germanium alloys studied by Rateau.¹⁷ In two cases, it appears that the formation of Ag₂S layers was inhibited by a protective effect caused by GeO_x species.

Incorporation of fine PTFE particles by electrolysis was studied to improve the tarnish resistance of silver and its alloys by Gay² and Puipe.¹⁸ In some cases, silver coatings with PTFE contents up to 25 vol% were found to be good candidates to block the formation of Ag₂S.

The use of rhodium, palladium and platinum coatings for silver tarnish protection is strongly suggested for luxury jewelry items.¹² The use of zinc and the cadmium, on the other hand, does not show promising results.¹² As for mercury, its use is prohibited because of its high toxicity.

Organic Inhibitors

Lohmeyer, *et al.*¹⁹ proposed inhibitors based on long-chain aliphatic thiocyanates as giving suitable protection. Inhibitors dissolved in an organic solvent are deposited on the surface of the object. The deposited layers had no significant effect on the electrical contact resistance whereas their tarnish resistance and tribological behavior were improved.

The use of the cyanuric acid as a silver tarnish inhibitor has been suggested.²⁰ This inhibitor together with other detergents containing peroxides or whiteners can be used in dish-washing formulations.

Recent work by Moeller, *et al.*²¹ quoted the use of acids or some hydroxamic salts as tarnish inhibitors. For example, 2 vol% Me(CH₂)₄CONHOH and CONHOH used in detergent formulations, provides complete protection of silverware against tarnishing.

According to Franey, *et al.*²² the use of polymeric materials, so-called reagent polymers, presents interesting results. The polymers consist of a mixture of resins (polyethylene, polypropylene, ABS and PVC) and stable additives in solid state in form of bags, tubes, patches or sheets. The authors claim high protection efficiency in aggressive atmospheres such as hydrogen sulfide (H₂S), carbonyl sulfide (COS) and hydrogen chloride gas (HCl).

Conclusion

The best protection against silver tarnishing is with the use of chromate conversion coatings.¹ However, this method cannot be employed in the silversmith trade because of chromium toxicity

considerations. Using a silver-based alloy with improved chemical stability is a good alternative. An efficient though expensive solution can be obtained by rhodium or platinum plating.

Electrodeposition of silver coatings incorporating organic or inorganic particles has only been mentioned in a few studies to date. In light of this, it would be interesting to study the tarnish resistance of certain novel composite coatings, including Pd or PTFE particles incorporated into a silver matrix. It should also be noted that, because of the low cost of this material, its use for silver protection will present a significant commercial benefit.

Acknowledgement

The authors acknowledge the collaboration of CETEHOR** for financial support and technical help in this research.

References

1. L. Lacourcelle, *Traité de galvanoplastie*, Galvano-Conseils édition, 1996; p. 408.
2. P.A. Gay, *Elaboration de revêtements composites électrolytiques à base d'argent : relation entre microstructure & résistance à l'usure & à la sulfuration*, Thesis, University of Besançon, Besançon, 2002.
3. K. Hallett, D. Thickett, D.S. McPhail & R.J. Chater, *Applied Surface Science*, **203-204**, 789 (2003).
4. H. Kim & J.H. Payer, *J. Corrosion Sci. & Eng.*, **1**, Paper 14, (<http://www2.umist.ac.uk/corrosion/JCSE/Volume1/paper14/v1p14.html>), (1999).
5. T.E. Graedel, J.P. Franey, G.J. Gualtieri, G.W. Kammlott & D.L. Malm, *Corrosion Science*, **25**, 1163 (1985).
6. L. Volpe & P.J. Peterson, *Corrosion Science*, **29**, 1179 (1989).
7. P.L. Cavallotti, M. Bestetti, L. Magagnin & A. Vincenzo, *Proc. Workshops on Education, Training, Transfer and Future Research*, European Jewellery Technology Network, Milan, Italy, 2000.
8. J.P. Randin, *Rapport étude du Laboratoire du groupe de recherche de Suisse*, Microélectronique et Horlogerie de Neuchâtel, Switzerland, 1992.
9. L.E. Price & C.J. Thomas, *Journal Inst. of Metals*, S.C. Guillan edition, **63**, 29 (1938).
10. H.F. Feshe, E. Wend, H. Dimigen & T. Jung, Rapport WMF Wuerttembergische Metallwarenfabrik AG, European patent, *Allemagne* (1996).
11. F.H. Rezsó, *et al.*, *Galvanotechnik*, **11**, 884 (1968).
12. W.H. Safranek, *The Properties of Electrodeposited Metals and Alloys*, AESF, Orlando, FL, 1986.
13. H.H. Uhlig, *Corrosion Handbook*, J. Wiley & Sons, Hoboken, NJ, 2000.
14. D. Davitz, U.S. patent 4,895,701 (1990).
15. H. Sasaki & M. Nishiya, Kabushiki Kaisha Zero One, Japanese patent (1990).
16. M. DeBonte, J.P. Celis & J.R. Roos, *Plating and Surface Finishing*, **80**, 43 (July 1993).
17. M. Rateau, *Matériaux & Techniques*, **10-11**, 53 (1995).
18. J.C. Puipe, Swiss patent, 1988.
19. S. Lohmeyer, *Galvanotechnik*, **84**, 762 (1993).
20. P.A. Angevaere & R.G. Gary, U.S. patent 5,468,410 (1995).
21. H. Moeller, H. Blum & C. Nitsch, European patent, *Allemagne* (1997).
22. J.P. Franey & K. Donaldson, *Proc. MRS Symposium*, Materials Research Society, Warrendale, PA, 1992.

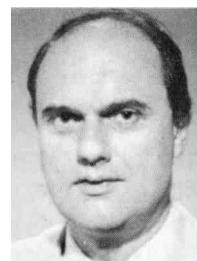
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