Noncyanide Silver Plating

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Abstract

This paper reviews the chemistry of the Techni-Silver Cy-Less process, and also some of the mechanical and physical properties of the silver deposits obtained.
Silver forms a number of water-soluble species, both simple and complex, any of which in principle might serve as the basis for electroplating solutions. A selection of these are shown, together with their formula weights and approximate silver solubilities, in Table I.

The first group of compounds in Table I are simple salts (compounds in which silver is the sole cation.) In general, silver salts are stable only up to a pH of about 4. Above that, hydroxides or other species precipitate. Additionally, acid solutions are often corrosive; and since silver is noble with respect to other metals in the electromotive series, it is very prone to immersion deposition. Silver salt solutions are often photosensitive as well. Nonetheless, silver plating solutions based on the nitrate, and more recently on the methane sulfonate, have been attempted. The famous Brashear process for silverying mirrors is also based on the nitrate, although in that process an ammonia complex is actually formed.

Silver complexes (forms in which silver is in the anion) are generally more stable than the simple salts, and thus less susceptible to photosensitivity and immersion deposition. They are also usable over wider ranges of solution pH. Some representative silver complexes are also shown in Table I. As you can see, the formula weights of the complexes (except, notably, the cyanide) are higher than those of the simple salts. This has important implications regarding solubility, and also regarding the ionic mobility of the dissolved species.

The silver complex in Technic noncyanide solutions is based on succinimide (see Figure 1.) The plating system was originally developed in the middle-to-late 1970's, and was the subject of two patents (1,2). The silver complex is available either as liquid concentrates or as a solid containing 50 percent silver by weight.

The general operating characteristics of the Technic Silver Cy-Less plating solutions are shown in Figure 2. Over the years we have made extensive changes in electrolyte configurations for various applications, but the silver complex has remained the same; so that operating parameters such as pH, current density, and anode-to-cathode ratio have remained close to their original values.

One of the characteristics of the Cy-Less solutions is that succinimide is subject to slow hydrolysis at the operating pH, as shown in Figure 3. The hydrolysis proceeds in stages, first to succinamic acid and then to (mono) ammonium succinate. It is thus necessary to replenish succinimide to the plating solution from time to time. Since the hydrolysis process consumes hydroxyl ions, it also follows that the pH of the plating solution falls slowly, and this is true whether the solution is used or not.

Deposits from the Silver Cy-Less solutions are adherent to copper and copper-based alloys. Adhesion to ferrous and to passive-prone materials is poor, and it is common to use a copper strike on such materials prior to noncyanide silver plating. Early versions of the noncyanide silver were prone to cracking at deposit thicknesses above about 20 micrometers. More recent modifications have allowed us to achieve coherent thicknesses in excess of 200 micrometers, although formulation of nodules at edges is often observed above about 90 micrometers. As part of the effort to develop solutions suitable for very heavy deposition, Technic entered into a cooperative agreement (CRADA) with Lawrence Livermore National Laboratory to determine physical properties of deposits plated under various conditions using several chemistries. Much of what follows was developed from that program, some of the results of which have been published (3).
Deposits from the Silver Cy-Less process are bright-to-semibright in appearance, even when a chemical brightener is not used. Figure 4 shows cross-sections at 500x magnification of deposits from the cyanide and noncyanide systems. The grain structure of the cyanide deposit is large and well developed, whereas at this magnification the noncyanide deposit is almost featureless.

In the as-plated condition, the Knoop hardness of non-cyanide silver deposits at 25 grams load is in the range of 115-130, as against 50-60 for unbrightened cyanide deposits. Aging of the noncyanide deposits for short periods (2-5 min) in hot (60 to 70°C) water is sufficient to reduce the Knoop hardness to the range of about 90-100. Similarly, the as-deposited stress of the noncyanide deposits is higher than for unbrightened cyanide deposits. Table II shows some representative values. The value marked "aged" is for a deposit plated from a solution which had been worked for about 1.8 ampere-hours per liter. The "as-is" value was for a sample plated from a new, previously unworked solution. Stress also decreases in deposits warmed after plating. In this case, the post-warming was at only 38°C, which is about 100°F.

Electrical resistivities of various silver deposits are shown in Table III. Resistivities of the noncyanide deposits in the as-plated condition are higher than those of cyanide deposits, and appear to be reduced by thermal aging in a fashion similar to that exhibited by the hardness and stress data. It should be pointed out that all of these data are very low numbers. Silver is among the most conductive of metals, and the resistivity of wrought silver, by way of comparison, is 1.8 microohm-centimeters. Even though the values for as-deposited noncyanide silver are about twice this, the major usage of the noncyanide deposit has been in electrical switchgear.

Figure 5 is a bar-graph representing mass loss for various electrodeposits when abraded for 1000 cycles by a coated wheel (4) rotating at 70 rpm. Load was 100 grams. With the exception of one sample plated at 0.32 A/dm², the noncyanide deposits exhibited less loss than the average of the silver deposits tested, and considerably lower than the average of four hard acid golds. In pin-on-disk testing (5), noncyanide deposits showed significantly lower mass losses than cyanide deposits, even though the coefficients of friction measured were about the same.

As might be expected from a fine-grained, relatively highly stressed deposit, the rate of tarnishing of the noncyanide deposits, if no preventive means are employed, is more rapid than that of deposits from cyanide solutions. It has been known for many years that light polishing of the noncyanide deposit greatly reduces the rate of subsequent tarnishing. Similarly, use of a hot (60-70°C) final rinse has also been shown to reduce the tarnish rate. Both of these methods presumably operate by stress-relieving the deposit. More recently, however, we have found that by chilling the plating solution to about 10-15°C (50°-60°F) it is also possible to reduce the postplating tarnish rate. The mechanism for this latter effect is still unknown.

Figure 6 shows a transmission electron micrograph at about 200,000x magnification of a noncyanide silver deposit plated at 10 A/dm². The deposit is microcrystalline, and the distribution in grain sizes is fairly wide. If one defocuses this image slightly, a pattern of voids in the crystallities is revealed as in Figure 7. This arrangement of void-bearing microcrystallities is highly unusual in silver, and more closely resembles the structure of a hard gold. The observed void density for these deposits is about 10¹⁷ per cubic centimeter.

The existence of voids in the deposit immediately raises a question as to what, if anything, they contain. A number of deposits were analyzed for carbon, hydrogen, oxygen and nitrogen, with results as shown in Table IV. It could be shown that an apparent correlation existed between the impurity content and the electrical resistivity. Of further interest, if one
normalizes the impurity contents (by setting the total parts per million for each deposit to 100 percent and then determining the relative percentages of each impurity) one obtains a set of relative abundances as shown in Table V. The data in Table V indicate that the relative abundances of carbon, hydrogen, oxygen and nitrogen in deposits plated at 3, 5 and 10 mA/cm² are approximately constant. This in turn indicates that the included material may be a compound. We then calculated the relative percentages in a number of compounds related to succinimide. Of these, the closest match to the material actually found appears to be (mono) ammonium succinate, which we noted previously to be the second hydrolytic product of succinimide.

The silver succinimide process has at this point been in successful commercial usage for almost twenty years. Over time we have learned how to control many of the parameters which affect the operation of the solution, some of which are not at all obvious; and we have learned how to optimize the process for applications not originally envisioned for it. We are still seeking to increase plating speed and broaden substrate compatibility for non-cyanide process.

References

4. Taber Wear Test, ASTM D 4060
5. Falex Wear Text, ASTM G 99
Table I

Soluble Salts and Complexes of Silver

<table>
<thead>
<tr>
<th>Formula</th>
<th>Silver Weight, Grams</th>
<th>Solubility gm/l</th>
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<tbody>
<tr>
<td>Nitrate</td>
<td>Ag NO₃</td>
<td>169.87</td>
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<tr>
<td>Acetate</td>
<td>Ag C₂H₃O₂</td>
<td>166.92</td>
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<tr>
<td>Lactate</td>
<td>Ag C₃H₅O₃.H₂O</td>
<td>214.96</td>
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<tr>
<td>Sulfamate</td>
<td>Ag SO₃.NH₂</td>
<td>203.83</td>
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<td>Mesylate</td>
<td>Ag SO₃.CH₃</td>
<td>202.88</td>
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<tr>
<td>Cyanide</td>
<td>K Ag (CN)₂</td>
<td>198.9</td>
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<td>Thiosulfate</td>
<td>Na₃ Ag (S₂O₃)₂</td>
<td>400.88</td>
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<tr>
<td>Succinimide</td>
<td>Ag (C₄H₅NO₂)₂</td>
<td>306.06</td>
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<tr>
<td>Dimethyl-Hydantoin</td>
<td>Ag (C₅H₈N₂O₂)₂</td>
<td>368.04</td>
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