A New Alkaline CN-free Silver Process for Electronic, Industrial & Decorative Plating Applications

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A new CN-free silver plating process that can be utilized in barrel and rack applications has been in production use for more than a year. A discussion on the bath parameters, plating characteristics and the properties of the silver plate will be presented. Platers who are currently using this process have found it to be easy to operate and say it has many advantages over other alkaline CN-free silver plating processes. It offers brilliant white color, very stable chemistry, and a wide operating window. Some platers have even found advantages over CN-silver plating processes. By switching to this process, the plater can meet requirements of EPA's Common Sense Initiative by eliminating or reducing their cyanide use, which would lower the plater's hazardous waste.

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Now you can replace a cyanide silver bath with an alkaline non-cyanide silver. Switching a cyanide bath to an alkaline non-cyanide silver bath is one step of meeting the Common Sense Initiative (CSI) hazardous waste reduction requirement. This paper will discuss the alkaline non-cyanide silver bath parameters and silver plating characteristics.

Silver plating is used on coinage, photography, tableware, decorative, jewelry, and electrical/electronic components. At the writing of this paper, the alkaline non-cyanide silver bath is considered more of an industrial silver than decorative silver because it does not use a brightener. The plated silver will plate as bright as the surface. If you have a polished surface, the silver will be bright. If you have a dull surface, the plated silver appearance will be dull. The alkaline non-cyanide silver process does not offer the leveling characteristics of cyanide silver with a proprietary cyanide silver brightener. If a silver plater wishes to have a bright-leveled surface, then a bright-leveled acid copper underplate is required.

Electrochemistry Challenge

Cyanide silver complex $KAg(CN)_2$ provides a very stable complex/chelation. The cyanide serves as chelator and the anode corroder. The excess free cyanide serves as the anode corroder and increases the conductivity of the bath. The breakdown products of the cyanide process are carbonate and ammonia. Potassium carbonate levels will slowly rise in a silver cyanide bath.

Above 14 oz/gal (100g/L), carbonates will cause precipitation in the bath resulting in rough silver plate. The option for the silver plater is bath dilution or chemical treatment. Switching to the alkaline non-cyanide silver eliminates the concern and cost of having to treat for carbonates. This is another consideration for meeting the EPA's CSI.

The alkaline non-cyanide silver bath contains proprietary complexing agents that form a stable silver complex. The stability of this alkaline non-cyanide bath is one of its strong selling points. Other alkaline non-cyanide baths precipitate out over time because of the unstable chemistry and thus have a high cost because they have to be made up new on a regular basis.

This alkaline non-cyanide silver does not contain any EDTA or ammonium hydroxide which means it will not cause any waste treatment problems.

Bath Parameters (see Table 1)

Equipment and Operation

Anode: Pure silver anodes 99.95%

Anode/Cathode Ratio: 2:1
Note: Calculate the maximum cathode area before setting up the process and insure the anode area is two times the maximum cathode area.

Filtration: 2-3 tank turnover per hour.
Continuous carbon filtration with 2 micron filtration rating is recommended. Use sulfur-free carbon. Change carbon weekly to remove organic contamination.

Tank: Plastic tanks can be used. Large polypropylene tanks must be reinforced.

Best conversion results occur with a new tank or new flexible liner in a tank that has cyanide silver solution. New silver anodes are recommended also.

Agitation

Air agitation at the anodes, plus cathode rod agitation.

pH Control

pH range: 8.5 to 9.5.

pH below 8.5 add 45% by volume KOH to pH 8.8 (too low of pH results in immersion silver).

pH above 9.5 add 50% by volume nitric acid to pH 8.8.

Replenishment

Liquid concentrate electrolyte added by amp hour and every day to the silver bath is used. Prior to plating, add 0.1-0.5% by volume electrolyte and adjust pH to 8.8.

Table 1
Bath Parameters

	Rack Plating		Barrel Plating	
	Optimum	Range	Optimum	Range
Silver Metal	2.0 oz/gal	1.5 – 2.5 oz/gal	2.4 oz/gal	2 – 2.5 oz/gal
pH	8.8	8.5 – 9.5	8.8	8.5 – 9.5
Temperature	68°F	60 – 75°F	68°F	60 – 75°F
Cathode current density		5 – 20 ASF		5 – 15 ASF
Anode current density		2 – 10 ASF		2 – 10 ASF

Table 2
Charging a New Bath

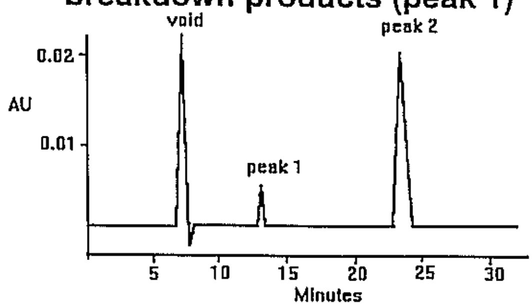
	Rack Plating (% by volume)	
	Optimum	Range
Liquid silver concentrate	50%	40 – 60%
Liquid electrolyte	5%	0 – 10%
D.I. water	45%	60 – 30%
Add 45% KOH to adjust pH to 8.8.		
	Barrel Plating (% by volume)	
	Optimum	Range
Liquid silver concentrate	60%	50 – 70%
Liquid electrolyte	10%	5 – 15%
D.I. water	30%	45 – 15%
Add 45% KOH to adjust pH to 8.8.		

Silver liquid concentrate has a silver concentration of 4.0 oz/gallon. If the silver concentration in the bath decreases, add the silver concentrate to replenish silver.

Bath Control

- pH
- Silver metal by titration
- Running Hull Cell
- Electrolyte determined by EPI

Figure 1
HPLC of Electrolyte (peak 2) and its breakdown products (peak 1)



A HPLC (high performance liquid chromatography) method was developed to independently monitor the additives and their breakdown products with respect to their stability and consumption rate. Monitoring the additive system by HPLC is shown in Figure 1. The Y-axis represents the UV absorption of the electrolyte and its breakdown products. X-axis is the retention time or the time it takes for the mobile phase to elute a particular compound.

It is noteworthy that even though breakdown products did form and accumulate, it did not adversely affect the performance of the plating chemistry. This might suggest a synergistic mechanism between electrolyte and its breakdown products resulting in brightness and grain refinement. The consistent performance of non-cyanide silver bath is fully supported by HPLC, TOC (total organic carbon) and AA (atomic absorption).

Material Properties of Non-cyanide Silver Coatings:

The silver coatings are electroplated at 10 ASF with thickness of 300-500 µinches. The substrate is brass, which is degreased in standard alkaline soak and electrocleaner and activated by 5-10 % H_2SO_4. The test performed in this study is focused on the material properties of non-cyanide silver coatings for electronic applications.

Here is the summary of some of the properties of non-cyanide silver coating:

The crystal structure of silver coating is characterized by X-ray diffraction. The broader diffraction peak of non-cyanide silver suggests the finer grain than the cyanide silver deposit.

The hardness of non-cyanide silver coating is around 95-110 KHN_{25}, which is harder than the cyanide silver deposit from solution with no additives. The hardness is measured on cross section sample with a Knoop diamond indenter at a load of 25 grams.

The electrical resistivity of non-cyanide deposit is around 3.0-3.5 micohom-cm, which is higher than those of cyanide deposit, but still a very low number and suitable in electrical applications.

The wear resistivity for non-cyanide silver deposit is superior to the cyanide silver deposit. The wearing test is performed by Taber Abrader by abrading the silver deposit. The load is 250 grams.

The purity of non-cyanide coating is characterized by Auger Emission Spectroscopy. The purity of silver deposit is around 99.8 %.

Plating Process on Various Substrates

Only one bath, no strike tank necessary, plates directly to copper, brass, any other copper alloys.

Steel, nickel, and electroless nickel substrates:

- Copper strike – alkaline non-cyanide copper

Aluminum substrates such as aluminum wave-guides can go non-cyanide by:

- non-cyanide zincate (double process)
- non-cyanide alkaline copper strikes

non-cyanide alkaline silver plate

Alkaline non-cyanide copper has been in production for six years. Many silver platers have been hesitant to switch the copper cyanide only because it is difficult to realize all the economic and intangible benefits.

Now the silver platers can eliminate cyanide from their facility.

Color

- Produces an excellent color like cyanide silver in rack plating.
- Extreme low current densities in barrel plating may produce a <u>very</u> <u>slight</u> yellow hue. Increasing the current density and/or solution movement reduces this phenomenon.
- Rinsing is important for excellent color of the alkaline non-cyanide silver bath.

  Recommend:
  - silver drag-out
  - cold water rinse
  - cold water rinse
  - 10-20% sulfuric acid
  - D.I. water rinse
  - Anti-tarnish solution
  - Hot water
  - Dry

Anti-Tarnish Properties

- To pass potassium sulfide drop test, need chromate base anti-tarnish inhibitor.
- Triazole compounds work well but do not pass the potassium sulfide drop test.

Eliminating Cyanide Silver Advantages

Municipal Fire Departments usually do not fight fires when cyanide is in a facility. They will let the facility burn than risk a fireman's life.

Insurance companies offer lower insurance premiums.

Eliminate chlorine or bleach from facility.

Eliminates the costs of cyanide destruct.

Reduction in TRI Form R reporting and data recording.

Potential new regulations (new EPA regulation that is under study) of 0.02 ppm cyanide would make it very expensive to treat cyanide. Alkaline non-cyanide silver would cost less to install than improve cyanide destruction to new proposed limit.

EPA's CSI is looking for reduction in hazardous waste generated. A plating facility that eliminates cyanide by switching to alkaline non-cyanide silver would qualify and meet the CSI requirements.

Advantages to Meeting CSI Requirements

Raise tier status (presently four tiers) with Tier I enjoying EPA rewards for minimizing waste. Such rewards might include longer storage time of hazardous waste, less paper reporting, and others determined by the EPA.