




View metadata, citation and similar papers at core.ac.uk

brought to you by  **CORE**

provided by Illinois Digital Environment for Access to Learning and Scholarship Repository

Waste Management and Research Center

Non-Cyanide Silver As a Substitute For Cyanide Processes

CMFI

The Chicago Metal Finishers Institute

**RR-94
July 2002
Electronic Version**



Non-Cyanide Silver As a Substitute For Cyanide Processes

CMFI

Chicago Metal Finishers Institute
Chicago, Illinois

July 2002

Submitted to
The Illinois Waste Management and Research Center
One E. Hazelwood Dr.
Champaign, IL 61820
www.wmrc.uiuc.edu

About WMRC's Electronic Publications:

This document was originally published in a traditional format.

It has been transferred to an electronic format to allow faster and broader access to important information and data.

While the Center makes every effort to maintain a level of quality during the transfer from print to digital format, it is possible that minor formatting and typographical inconsistencies will still exist in this document.

Additionally, due to the constraints of the electronic format chosen, page numbering will vary slightly from the original document.

The original, printed version of this document may still be available.

Please contact WMRC for more information:

**WMRC
One E. Hazelwood Drive
Champaign, IL 61820
217-333-8940 (phone)**

www.wmrc.uiuc.edu



WMRC is a division of the
Illinois Department of Natural
Resources

This report is part of WMRC's Research Report Series. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ACKNOWLEDGMENTS

The authors would like to thank the following for their assistance, patience and guidance as we conducted this study:

Perfection Plating, Mr. Lou Delmonte

Nobert Plating Company, Mr. Todd Smith

Reinewald Plating Company, Mr. Ted Reinewald, President

The Chicago Metal Finishing Institute, Mr. Bill Suzuki, President and Ms. Evelyn Hallberg, Secretary

Chris Hayes, Pollution Prevention Technical Assistant, WMRC

Tim Lindsey, Manager, Pollution Prevention Program, WMRC

Nandakis hore Rajagopalan, Sr. Research Engineer, WMRC

TABLE OF CONTENTS

	<u>Page Number</u>
Acknowledgments	iii
Table of Contents	iv
List of Figures	v
Abstract	vi
Executive Summary	vi
Body of Report	
Introductory Material	1
Methodology	5
Results	8
Discussion of Results	9
Conclusions	9
Recommendations	10
References	11
Appendices	
Appendix: Figures	A1-A7

LIST OF FIGURES

<u>Figure</u>	<u>Title</u>	<u>Page</u>
Figure -1	Commercially plated silver-1	Page A-1
Figure -2	Commercially plated silver-2	Page A-1
Figure -3	Hull Cell Apparatus	Page A-2
Figure -4	Contamination Test-Supplier-1	Page A-2
Figure -5	Contamination Test-Supplier-2	Page A-3
Figure -6	Appearance, Silver Over Bright Nickel, Supplier-1	Page A-3
Figure -7	Appearance, Silver Over Polished Brass, Supplier 2	Page A-4
Figure -8	Appearance, Silver Over Bright Nickel, Supplier 2	Page A-4
Figure -9	Adhesion, Silver Over Bright Nickel, Supplier-1	Page A-5
Figure -10	Adhesion, Silver Over Bright Nickel, Hull Cell, Supplier-1	Page A-5
Figure -11	Adhesion, Silver Over Brass, Supplier-2	Page A-6
Figure -12	Adhesion, Silver Over Nickel, Supplier-2	Page A-6
Figure -13	Adhesion, Silver Over Silver Strike Over Nickel, Supplier-1	Page A-7
Figure -14	Adhesion, Silver Over Silver Strike Over Nickel, Supplier-2	Page A-7

ABSTRACT

Since the mid 1800s, silver has been deposited from a cyanide-based formulation on a commercial basis. Commercial non-cyanide silver plating solutions were first made generally available in the late 1970s, and yet today the vast majority, and nearly all commercial silver plating is conducted in formulations that contain cyanide.

This study was conducted to determine if non-cyanide silver plating processes that have been developed in the last few years would be suitable replacements for cyanide based formulations.

The study was to be co-sponsored by a Chicago area plater, who originally agreed to work with us in resolving commonly encountered complaints about these processes. Unfortunately, after a short period of time, this plater withdrew from the project, citing severe doubts about the potential for success. We were not able to interest any other silver plater to co-sponsor this project. We therefore conducted laboratory experiments on two commercially available processes to gather enough data that we could use to convince a plater to give the process a try.

Our laboratory experiments failed to resolve the major problems associated with non-cyanide silver:

- a. Susceptibility to contamination by base metals due to immersion deposition
- b. Failure to yield a bright, white deposit
- c. Failure to provide adequate adhesion on bright nickel and copper substrates

EXECUTIVE SUMMARY

Commercial non-cyanide silver plating solutions were first made generally available in the late 1970s, and yet today the vast majority, and nearly all commercial silver plating is conducted in formulations that contain cyanide.

This study was conducted to determine if non-cyanide silver plating processes that have been developed in the last few years would be suitable replacements for cyanide based formulations.

The study was to be co-sponsored by a Chicago area plater, who originally agreed to work with us in resolving commonly encountered complaints about these processes. Unfortunately, after a short period of time, this plater withdrew from the project, citing severe doubts about the potential for success. We were unable to interest any other silver plater to co-sponsor this project. We therefore conducted laboratory experiments on two commercially available processes to gather enough data that we could use to convince a plater to give the process a try.

Our laboratory experiments failed to resolve the major problems associated with non-cyanide silver:

- a. Susceptibility to contamination by base metals due to immersion deposition
- b. Failure to yield a bright, white deposit
- c. Failure to provide adequate adhesion on bright nickel and copper substrates

However, we were able to identify a process for deposition of bright-white silver deposits over brass parts. We tested each of two commercially available processes:

1. Sensitivity to Metallic Contamination

Each silver plating solution was made up in accordance with the manufacturers instructions. We then immersed strips of polished brass and bright nickel plate over polished brass into each solution for 10 and 20 seconds. The strips were then examined for the presence of immersion deposits (which would indicate susceptibility to metallic contamination).

2. Appearance

A. Appearance of two commercially available silver plating processes

The appearance of the plated deposit from each solution was evaluated using a Hull Cell. Plated panels were visually inspected for appearance, using reflection of text printed on standard white photocopy paper that had black text, as illustrated in the photographs in the appendix.

B. Modification of appearance of non-cyanide silver deposit with flash over-plate

We evaluated an electroless silver deposition process per US PAT 5,322,553, along with nine other silver flash plating processes.

3. Adhesion Over Copper and Bright Nickel

Adhesion over copper (brass) and bright nickel was evaluated qualitatively by bending the high current density portion of a Hull Cell panel back and forth at 90 degrees twice and examining the deformed panel areas for signs of cracking, blistering and/or peeling.

We also attempted to produce a silver strike plating solution in an effort at eliminating immersion deposits. We mixed the ingredients so that the silver concentration was reduced by 90%.

We came to the following conclusions that the non-cyanide silver plating process from supplier No.1 at the present time does not appear to meet appearance requirements and adhesion over bright nickel. While the supplier has successfully plated copper and copper alloy substrates, as is evidenced by the parts supplied to us for examination, we were not able to obtain good adhesion in our Hull Cell experiments.

The process from this supplier yields immersion deposits, which can, over time, yield metallic contamination problems.

Process supplier No. 2 yields a silver deposit over brass that is both fully bright and adherent. However, the fact that this process does produce immersion silver deposits via electrochemical potential differences, indicates that over a long term of use, the solution would be progressively contaminated and may become unsuitable for bright silver plating.

This process does not produce the adhesion qualities over bright nickel that most platers require. Further, we were unable to produce a bright white finish over bright nickel, as we did over polished brass.

We were able to produce a dull white flash silver deposit over bright silver to eliminate the yellow, but we were unable to keep the bright finish.

A possible process for future research was identified.

INTRODUCTORY MATERIAL

Essentially all commercial silver electroplating solutions are formulated using cyanide salts. Typical solution formulations¹ (g/L) are:

	<u>Bright</u>	<u>High Speed</u>	<u>Strike</u>
Ag (as metal)	20 - 45	35 - 115	3.0 - 4.0
AgCN	25 - 56	44 - 143	3.7 - 5.0
KCN (total)	50 - 78	68 - 235	62 - 78
KCN (free)	35 - 50	45 - 160	60 - 75
K ₂ CO ₃	0 - 90	15 - 90	—
KNO ₃	—	40 - 60	—
KOH	—	4 - 30	—

The data above indicates that a silver plating solution may contain over 100,000 ppm of cyanide, while wastewater discharge regulations prescribe maximum cyanide content of under 1ppm, and solid waste (F-006) is regulated at 590 ppm CN (total). These environmental regulations, plus the obvious safety hazards involved in working with cyanide produce a high incentive for a plater to substitute a non-cyanide process, if at all possible. Yet because the cyanide process has distinct operational advantages over other non-cyanide formulations, even these incentives have not caused substitutions to occur to any great extent. The reasons for staying with cyanide for silver plating are many:

1. Cyanide is an excellent complexing agent, which complexes impurities, allowing operation with metal contamination levels that non-cyanide silver processes can not tolerate.
2. Cyanide silver plating solutions produce a pleasing pure white, fully bright deposit, which is in demand by the customers.
3. Cyanide solutions can be formulated into “strike” processes. Such strike processes allow for the deposition of a very thin adherent layer of (relatively dull) silver over most any metal substrate. A second layer of bright silver is then plated over the silver strike. The result is a part exhibiting excellent adhesion and appearance properties.
4. Cyanide silver plating processes are easy to chemically control, and have a broad range of concentrations that will yield successful deposits.

In 1978 and 1981, E. Hradil et al.,⁴ patented a non-cyanide silver plating solution based upon a succinimide complex. As recently as 1997² this non-cyanide silver process was compared against cyanide silver and found to contain 10-25 times as much carbon, 7-10 times as much hydrogen, more than 10 times as much oxygen, and 300 times as much nitrogen. The researchers concluded that the process can produce sound, thick deposits, but has a higher

electrical resistivity (as much as 100% higher for dull cyanide vs. the non-cyanide) and higher stress (165 MPa in the as deposited condition vs. 10 MPa for the cyanide deposit) than silver deposits from the cyanide process. The non-cyanide process was found to offer better wear characteristics, but this is not often required of a silver deposit, while low electrical resistivity is highly desirable. No information was provided as to adhesion or appearance properties. S. Sriveeraraghavan⁸ described a non-cyanide silver plating solution based upon thiosulfate chemistry in 1989. This solution is described as “fairly stable” (for several months) and yielded adherent deposits only over copper. Adhesion on nickel is obtained only after anodic and cathodic treatment in a “strike” containing approximately 3 g/L silver (as silver chloride) and 300 g/L sodium thiosulfate. No mention is made of appearance.

In 1991, Kondo⁶ reported on a non-cyanide silver plating solution based upon methanesulfonate-potassium iodide. Kondo confirmed that the previously reported non-cyanide silver plating solutions such as those based upon silver chloride-potassium iodide, silver chloride sodium thiosulfate, silver nitrate-tartaric acid, silver chloride-potassium ferrocyanide, and thiocyanate produced coarse grain structures and deposits that were not silver white. Kondo found “little” immersion plating over copper and “almost” indistinguishable color difference. He also reported yellow spotting that required soaking in potassium iodide to remove. The deposit was not bright (just “white”). To our knowledge, no commercially available process has been developed using this type of chemistry to date.

In 1996, Jayakrishnan⁵ provided information on an alkaline non-cyanide silver plating solution based upon a succinimide complex. This solution contained 0.5-1.0 M silver, 0.2 M potassium carbonate and 0.5-0.7 M succinimide. A typical current density was 0.75 A/dm². Hull Cell experiments indicated that a smooth, white silver deposit over an “appreciable range” of current density and at a pH range of 8-12 was possible with this formulation. The deposit was not bright, however, and there was no investigation into adhesion over a variety of substrates.

In 1998, Masaki⁹ et. al., reported on a bright silver plating deposit that could be obtained by the addition of polyethyleneimine (PEI) to a formulation similar to Jayakrishnan, but stabilized at pH 10 with boric acid. This solution operates at 2 A/dm² and yields a mirror bright surface. Masaki conducted Hull Cell experiments that showed that PEI at 0.5 g/L yielded a bright deposit, no matter what molecular weight PEI was used, but a molecular weight of 600 produced the brightest surface over the broadest current density range. The deposit exhibited soldering properties similar to deposits from cyanide solutions and contact electrical resistance and hardness better than cyanide solution deposits. The PEI solution had a current efficiency of about 100%. No data on adhesion over various substrates was reported/investigated. No information on adhesion over various substrates is given in this paper, and we are not aware that the process is commercially available in the USA, at this time.

The literature indicates that there is no non-cyanide silver plating process currently available that resolves all of the major problems associated with these processes.

The original intent of this study was to enlist a job shop electroplater that utilizes cyanide silver plating processes and have them add a commercially available non-cyanide process to their

facility. We then could evaluate plating problems and attempt to resolve them. Identified problems that silver platers have with non-cyanide processes are:

1. Sensitivity to metallic contamination
2. Poor color (yellow tint, see Figures 1 and 2)
3. Poor adhesion, especially over bright nickel

Our original volunteer company had discussions with other silver platers after volunteering participation in this project and was so convinced that the above problems could not be worked out, that he withdrew support of this project. We then decided to obtain sample plating solutions from two suppliers of non-cyanide silver plating chemistries, in an effort to demonstrate to this plater and possibly other potential volunteer companies, that newer non-cyanide silver plating processes can be operated in a manner that avoids/eliminates the above problems. The two non-cyanide processes were obtained with the permission and full knowledge of our intent/activities of the suppliers. We have identified each supplier only as No-1 and No-2. Since we may have terminated this project before all potential remedies to the above problems were investigated, we will not identify these suppliers.

The following was our approach to investigating remedies to the above problems:

1. Sensitivity to metallic contamination

Silver is commonly plated over copper/copper alloys and over bright nickel. The simple act of immersing copper or nickel coated substrates into a silver plating solution can cause contamination of the solution, even if current connections are made prior to immersion. Such contamination results from a chemical reaction between the solution and the surface, before deposition of a pore-free layer of silver is deposited. Contamination also results from contact between non-plated part surfaces such as blind holes and faying surfaces and the plating solution. If the plating solution contains a complexing agent that binds up metallic contaminants, suitable silver deposits can still be produced in the presence of metallic contaminants such as copper and nickel. Cyanide is an excellent complexing agent for these and numerous other metals, and therefore cyanide-based solutions can contain a significant amount of metallic contamination without affecting the quality of the deposit.

Silver is electrochemically a very noble metal, $E^{\circ} = +0.8$ V, while copper has a standard potential of +0.34 V, and nickel has a standard potential of -0.25 V. When a less noble metal such as copper is immersed into a solution containing a more noble metal such as silver, a displacement reaction occurs, causing the less noble metal (copper or nickel) to dissolve into the chemical solution, while the more noble metal (silver) is precipitated out of the solution, usually in a non-adherent spongy deposit. Thus the same electrochemical reaction produces a non-adherent silver deposit and at the same time contaminates the chemical solution with metal ions from the substrate.

Clearly, the largest potential difference (copper vs. nickel) is between silver and nickel, and therefore plating onto a nickel surface poses the most challenging problem. Further, bright nickel is more “active” (has a more negative standard electrochemical potential) than dull nickel and therefore is even more difficult to plate onto in solutions containing free silver ions.

Non-cyanide silver solutions often contain weak chelates or may contain chelates that do not adequately tie up metallic contamination. The result is a deposit that has a poor appearance, as metallic contaminants are plated along with the silver. Further, some formulations utilize chelates for silver that are so weak that free silver ions remain in the solution at high population densities, resulting in chemical displacement reactions, which further contaminate the plating solution and produce non-adherent coatings.

One remedy is to employ a silver strike solution that covers the surface of the object plated with a thin silver deposit. This strike solution must contain a higher than normal level of chelate to tie up metallic impurities and eliminate the presence of free silver ions. This higher chelate content renders the solution highly ineffective at depositing silver, but the solution is used only for a very thin coating, and is normally followed by deposition of the desired silver thickness in a “full strength” silver plating solution. Even cyanide silver plating solutions are typically operated using silver strike solution immediately before “normal” silver plating to assure that no immersion silver deposits occur, and to keep the full strength solution more free of contaminants.

We attempted to produce a strike solution from the main ingredients used to make up the full strength plating solution in an effort at solving the metallic contamination problem. This was done, by mixing the ingredients, so that the solution contained $1/10^{\text{th}}$ the silver concentration and 10 times more complexing agent. Using such a strike ahead of each of the two processes did not result in improved adhesion properties over a bright nickel surface. One of the two solutions provided adequate adhesion over the brass Hull Cell surface, but not over nickel.

One of the non-cyanide silver process suppliers, in recognition of the adhesion/contamination problems associated with non-cyanide silver did supply us with specially formulated copper and nickel strike solutions that were described as processes that reduced or eliminated the problem. We were not successful in avoiding adhesion or contamination problems in using the special nickel strike solution and we did not need the special copper strike, since we obtained adequate adhesion without it.

2. Poor Color

The companies that were potential sponsors of this project had strong objections about the color of the silver deposit delivered by non-cyanide processes. Their clients did not accept anything but a pure white or pure bright-white silver plated surface. We believe this is due to consumer objection for decorative plated parts, and a perception that anything looking out of the ordinary is undesirable on the part of buyers of non-consumer silver plating. As reported by Dini et. al. and other researchers silver from a non-cyanide process can offer similar physical and electrical

properties despite the slightly yellow appearance. The reality of the market, however, dictates what can be applied by a commercial plater.

We investigated the possibility of leaching the yellow silver color from the deposit using ammonium hydroxide-peroxide and sulfuric acid-peroxide solutions and found that the color could not be leached out and was not a surface effect. The color permeated throughout the deposit.

We then attempted to resolve the color problem, by the application of a very thin electroless silver deposit over the yellow silver. Electroless silver plating has been described by Pearlstein¹⁰ in 1974. However, this process utilized a solution formulated with cyanide. Use of this solution would be counter-productive in resolving a cyanide elimination problem, so we sought a non-cyanide electroless silver plating solution.

Djokic³ described an electroless silver process based upon a silver-ammonia complex, but the process is described as producing a combination of a “displacement and reduction types of reactions”, which indicate no long-term stability.

Mandich⁷ described a non-cyanide silver plating solution based upon a thiosulfate-sulfite chemistry. The process is described as yielding white deposit, which we intended to use as a thin deposit over the yellow silver, to produce an acceptable white silver plate. We hypothesized that a very thin deposit over a bright (yellow) silver plate might produce bright or semi-bright white silver as well.

3. Poor Adhesion Over Bright Nickel

We attempted to resolve the poor adhesion over bright nickel by utilizing a workable strike formulation or by use of the proprietary nickel strike from supplier No.2.

METHODOLOGY

This section will discuss the methodologies used to investigate possible solutions to identified problems with non-cyanide silver plating.

1. Sensitivity to Metallic Contamination

Each silver plating solution was made up in accordance with the manufacturer’s instructions. We then immersed strips of polished brass and bright nickel plate over polished brass into each solution for 10 and 20 seconds (see Figures 4 and 5). The strips were then examined for the presence of immersion deposits (which would indicate susceptibility to metallic contamination).

2. Appearance

A. Appearance of two commercially available silver plating processes

The appearance of the plated deposit from each solution was evaluated using a Hull Cell as illustrated in Figure 3. We used a magnetic stirring bar for agitation, and a solid platinum mesh anode. A Kocour Hull Cell rectifier was used as the power supply. Current applied was in accordance with the manufacturers recommended current density/voltage range. Cathodes were made of polished brass, as supplied by The Kocour Company. Prior to plating in the Hull Cell, each brass panel was cathodically electrocleaned in an aqueous alkaline cleaner, rinsed in tap water, dipped for 30 seconds in a solution of 10% volume sulfuric acid, and rinsed in tap water.

Plated panels were visually inspected for appearance using reflection of text printed on standard white photocopy paper that had black text, as illustrated in the photographs in the appendix.

B. Modification of appearance of non-cyanide silver deposit with flash over-plate

We evaluated the electroless silver deposition process by producing an electroless silver plating solution in accordance with US PAT 5,322,553, with varying concentrations of sodium thiosulfate, sodium sulfite, EDTA, and silver, including:

Solution a

20 g/L sodium thiosulfate
20 g/L sodium sulfate
0.1 g/L EDTA
6 g/L silver as silver sulfate
pH 8
100°F

Solution b

200 g/L sodium thiosulfate
20 g/L sodium sulfite
10 g/L EDTA
15 g/L silver as silver sulfate
pH 9
165°F

Solution c

200 g/L sodium thiosulfite
10 g/L EDTA
15 g/L silver as silver sulfate
pH 9
165°F
DC current at 4 volts

We also tried other flash electroplating chemistries we developed independently based our own knowledge:

Solution d (independently developed formulation)

75 g/L silver as silver oxide
25 g/L boric acid
45 g/L ammonium bifluoride
pH 1
Room temperature

Solution e (formulation from Chemical Formulary)

45 g/L Silver as silver nitrate
45 g/L ammonium hydroxide
75 g/L sodium hydrosulfite
75 g/L calcium carbonate

Solution f

10 g/L silver as silver nitrate
50 g/L potassium nitrate
4 g/L boric acid

Solution g

10 g/L silver as silver nitrate
75 g/L ammonium sulfamate

Solution h

5 g/L silver as silver nitrate
45 g/L ammonium sulfamate
75 g/L barium carbonate

Solution i

5 g/L silver nitrate + excess of ammonium hydroxide (enough to dissolve precipitate that forms upon addition)
45 g/L ammonium sulfamate
45 g/L potassium nitrate

Solution j

Same as solution I plus 2 g/L EDTA

Solution k

3 g/L silver as silver nitrate
75 g/L ammonium sulfamate
potassium hydroxide to pH 9

Solution 1

1 g/L silver as silver nitrate

75 g/L potassium nitrate

potassium hydroxide to pH 9

3. Adhesion Over Copper and Bright Nickel

Adhesion over copper (brass) and bright nickel was evaluated qualitatively by bending the high current density portion of a Hull Cell panel back and forth at 90 degrees twice and examining the deformed panel areas for signs of cracking, blistering and/or peeling.

We also attempted to produce a silver strike plating solution in an effort at eliminating immersion deposits. We mixed the ingredients so that the silver concentration was reduced by 90%.

RESULTS

1. Sensitivity to Metallic Contamination

The commercially available plating processes rapidly produced immersion deposits, indicating a great degree of susceptibility to contamination effects. Further, as we used the solutions in our Hull Cell experiments, the appearance of the deposit gradually degraded, which indicated to us that electrochemical effects were reducing the quality of deposit achievable as the solutions were used.

Figures 4 and 5 show immersion deposition effects obtained when clean strips of brass and bright nickel plated brass were partially immersed in the test solutions. An immersion silver deposit was visible on brass immediately upon immersion and on nickel after only a few seconds of immersion. We suspect that the failure to see immersion deposits immediately over bright nickel has to do with the similar colors of silver and bright nickel.

2. Appearance

A. Commercially available processes

The deposit from commercial supplier No.1 was very bright, with a faint yellow haze (Figure 6). The deposit from manufacturer No. 2 was very bright and white, when deposited over brass (Figure 7). When deposited over a bright nickel (Watts formulation, two class, saccharin brightened), the deposit was not quite as bright, and with a yellow tint. We tried plating this silver over the manufacturer's nickel strike and obtained the same results (Figure 8).

B. Commercially available processes with flash over-plate

None of the formulations tried yielded a bright deposit when applied over the commercial silver deposits. The electroless silver was highly unstable and failed to produce a white deposit as claimed by the patent. Of the alternate solutions i and j produced a dull white deposit over the bright silver, eliminating the yellow, but we were unable to plate the silver thin enough to yield a bright white finish over-all. Discussion with one potential plater-sponsor indicated that they had no interest, unless the deposit was both white and bright.

3. Adhesion Over Copper and Bright Nickel

The deposit from commercial supplier No.1 was of poor adhesion over both brass and nickel. The adhesion over nickel was so poor, that silver could be seen peeling off the nickel surface during deposition in the Hull Cell (Figures 9 and 10).

The deposit from commercial supplier No. 2 yielded adequate adhesion over brass (Figure 11), but poor adhesion over bright nickel and poor adhesion over their own nickel strike (Figure 12).

When plated over silver strike formulations produced by reducing the silver content by 90% as described above, no difference in adhesion of silver over nickel was obtained. Both processes yielded poor adhesion over bright nickel (Figures 13 and 14).

DISCUSSIONS

We emphasize that all avenues of experimentation were not pursued, as the project was cancelled due to lack of a sponsor interested in field testing any of these processes. It appears that bright, adherent non-cyanide silver can be obtained from one commercial process, but only if deposited over brass. In our discussions with the supplier representative, he indicated that he was experiencing the reverse problem (acceptable appearance over nickel but not over brass). We did not investigate these differing findings further.

CONCLUSIONS

Process Supplier No.1

The non-cyanide silver plating process from this supplier does not at the present time appear to meet appearance requirements, and adhesion over bright nickel. While the supplier has successfully plated copper and copper alloy substrates, as is evidenced by the parts supplied to us for examination, we were not able to obtain good adhesion in our Hull Cell experiments. The

process from this supplier yields immersion deposits, which can, over time, yield metallic contamination problems.

Process Supplier No. 2

Process supplier No. 2 yields a silver deposit over brass that is both fully bright and adherent. However, the fact that this process does produce immersion silver deposits via electrochemical potential differences, indicates that over a long term of use, the solution would be progressively contaminated and may become unsuitable for bright silver plating.

This process does not produce the adhesion qualities over bright nickel that most platers require. Further, we were unable to produce a bright white finish over bright nickel, as we did over polished brass.

We were able to produce a dull white flash silver deposit over bright silver to eliminate the yellow, but we were unable to keep the bright finish.

RECOMMENDATIONS

It is possible that the solution described by Masaki⁹ produces adherent, bright (and presumed white) deposits over bright nickel from succinimide complex with polyethylene as a brightening agent. Masaki did not evaluate the process to see if his process solves the problems discussed in this report. An evaluation of this process is warranted.

We found mention in the paper by Sriveeraraghavan⁸ of a treatment of bright nickel consisting of anodic electrolysis in a solution of 300 g/L sodium thiosulfate containing 3 g/L of silver followed by cathodic treatment in the same solution. Such treatment was found to be necessary for adhesion over bright nickel.

It may be possible that a combination of the above-described treatment of bright nickel followed by a bright deposit from the Masaki process would yield suitable results for the successful replacement of cyanide silver plating with a non-cyanide process. Further work in this direction is recommended.

REFERENCES

1. Altmayer, F., "Silver Plating", American Electroplaters & Surface Finishers Society, Inc. training lesson, part of "Precious and Related Metals Plating Training Course."
2. Dini, Dr. J. W., Morrissey, R. J., and Pacheco, D. R. "Materials Characterization of a Non-Cyanide Silver Electrodeposit", *Plating & Surface Finishing*. vol. 84, Dec. 1997, p. 62-67.
3. Djokic, Dr. S., "Electroless Deposition of Silver onto Copper Particles" National Metal Finishing Resource Center NMFRC.org Internet download.
4. Hradil, E. Hradil, H., and Weisberg, A. US pat. 4126524 and 4246077.
5. Jayakrishnan, S., Natarajan, S. R., and Vasu, K.I., "Alkaline Noncyanide Bath for Electrodeposition of Silver", *Metal Finishing*. vol. 94, May, 1996, p. 12-15.
6. Kondo, T., Masaki, S., Inoue, H., and Yamakawa, K., "Silver Plating from Silver Methanesulfonate-Potassium Iodide Bath", *Metal Finishing*. vol. 89, October, 1991, p. 32-36.
7. Mandich, Dr. N., Krulik, G., Singh, R., US Pat 5,322,553, June 21, 1994.
8. Sriveeraraghavan, S., Krishnan, R. M., and Natarajan, S. R., "Silver Electrodeposition from Thiosulfate Solutions", *Metal Finishing*. vol. 87, June 1989, p. 115-117.
9. Masaki, S., Inoue, H., and Honma, H. "Mirror Bright Silver Plating from a Cyanide-Free Bath", *Metal Finishing*. vol. 96, Jan. 1998, p. 16-20.
10. Pearlstein, F., and Weightman, R. F., "Electroless Deposition of Silver Using Dimethylamine Borane", *Plating*. vol. 61, Feb. 1974, p. 154.

Appendix-Figures



Figure 1
Photo of commercially plated non-cyanide silver exhibiting yellow tint



Figure 2
Parts plated in non-cyanide silver by Supplier No. 1

Appendix-Figures



Figure 3
Hull Cell Apparatus, Brass panel being plated with non-cyanide silver from supplier No. 2.
agitation is via a magnetic stir bar, anode is made of solid platinum mesh.



Figure 4
Immersion silver deposits on brass (upper two strips) and bright nickel after 10 and 20 seconds
immersion in non-cyanide process from Supplier-1

Appendix-Figures

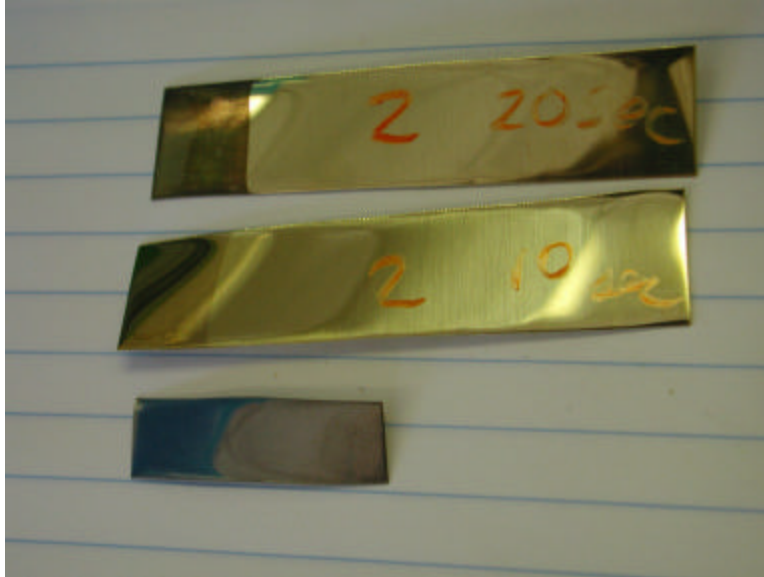


Figure 5
Immersion silver deposits on brass (upper two strips) and bright nickel after 10 and 20 seconds immersion in non-cyanide process from Supplier-2

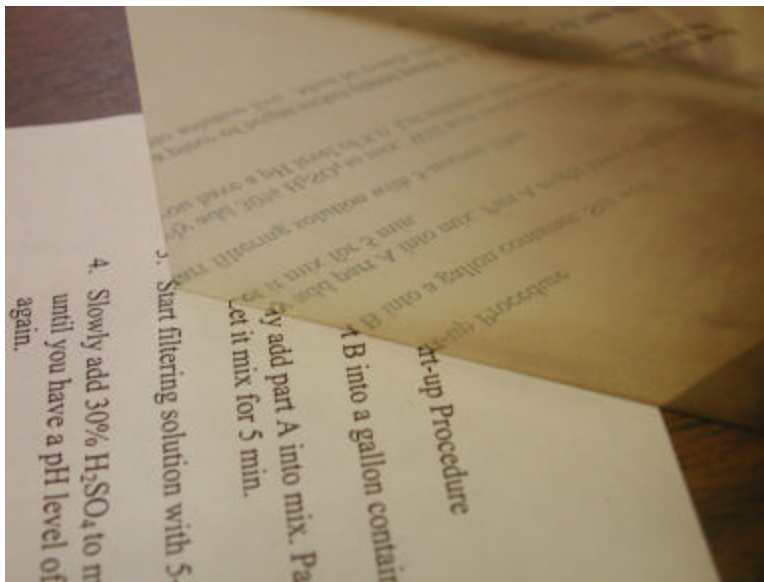


Figure 6 Bright silver deposit from supplier 1 over bright nickel. Deposit has definite yellow tint.

Appendix-Figures

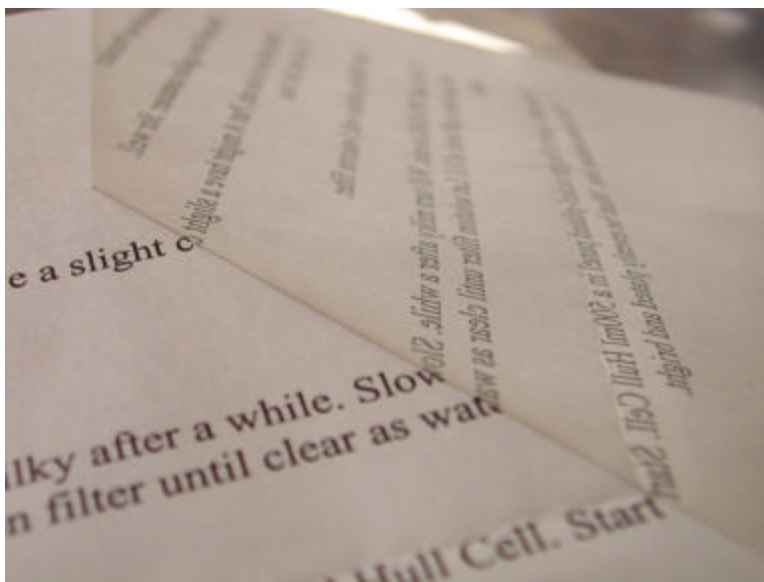


Figure 7
Photo of bright silver over polished brass. Solution from Supplier No. 2

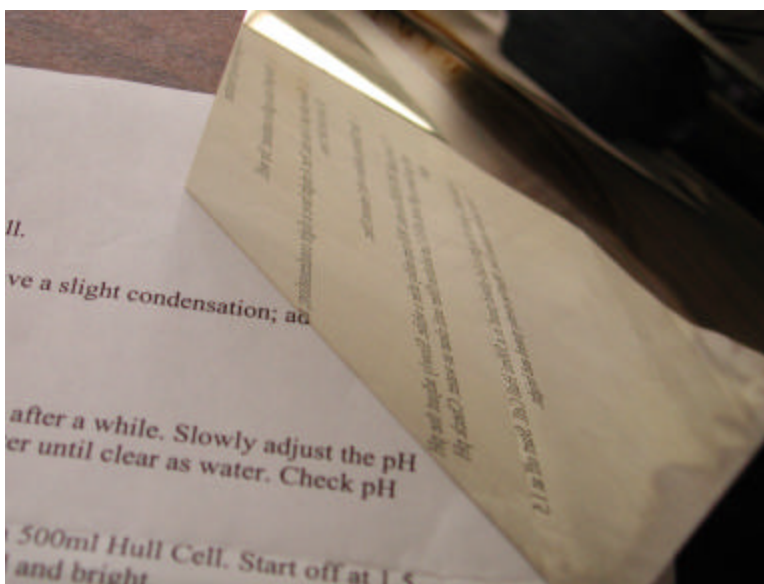


Figure 8
Bright silver over nickel strike from Supplier No.2. Silver solution from Supplier No. 2

Appendix-Figures

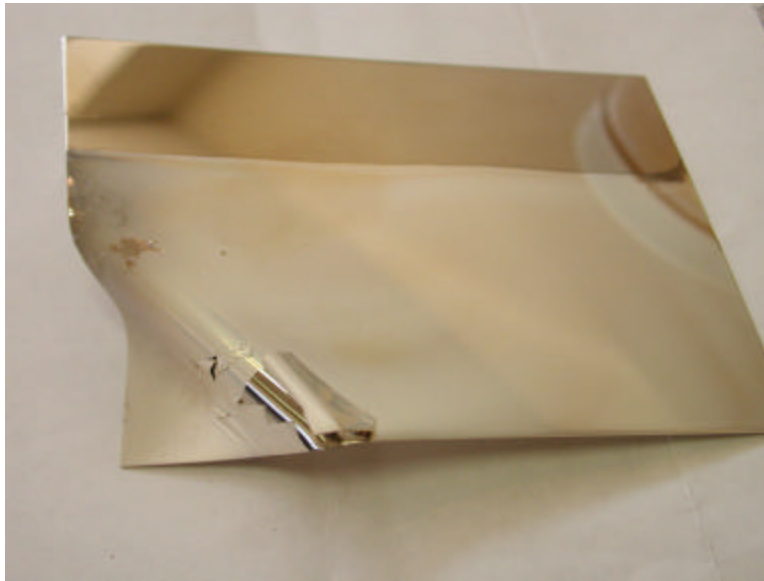


Figure 9
Adhesion test (fail) of bright silver over bright nickel. Solution from Supplier No. 1



Figure 10
Adhesion failure during silver plating of non-cyanide silver over bright nickel. Silver solution from Supplier No. 1

Appendix-Figures



Figure 11
Adhesion test (pass) of bright silver over polished brass. Solution from Supplier No. 2

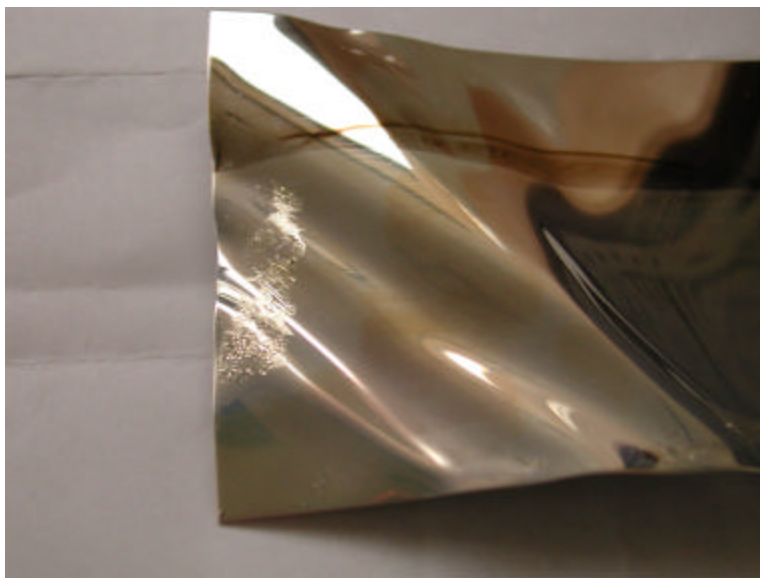


Figure 12
Adhesion test (failure) of bright silver over bright nickel. Silver solution from Supplier No. 2

Appendix-Figures

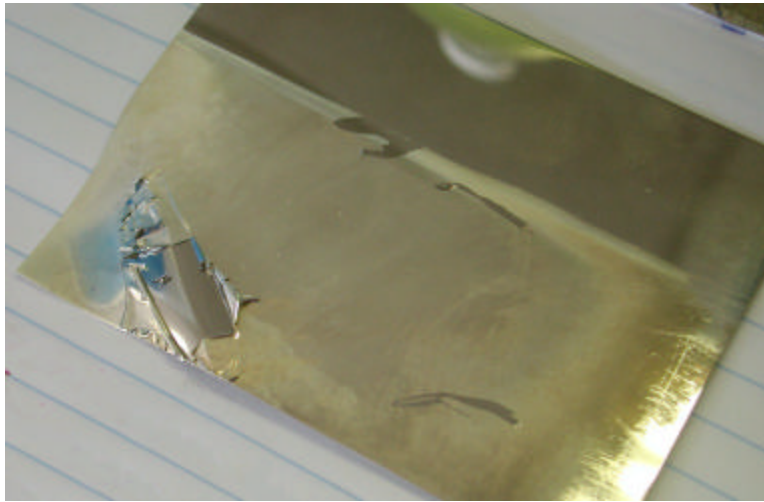


Figure 13
Adhesion test (fail) of bright silver over silver strike over bright nickel.
Solution from Supplier No. 1

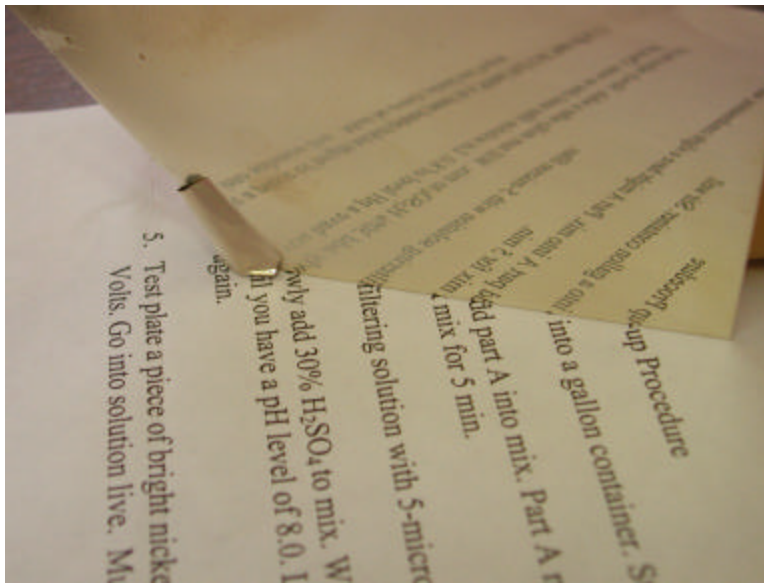


Figure 14
Adhesion test (fail) of bright silver over silver strike over bright nickel.
Solution from Supplier No. 2

ILLINOIS



**DEPARTMENT OF
NATURAL
RESOURCES**

