# A Novel Palladium Stripping Solution-Its Performance & Maintenance

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Palladium finishes have become widely established in electronic and decorative applications. A reliable stripping solution for rework and metal recovery has not been commercially available, however. A threecomponent system has been developed that provides satisfactory and economical processing of palladium, gold-flash palladium or palladium-nickel finishes. The system is exceptionally selective for palladium and palladium-nickel vs. copper, and can be applied in rack, barrel or reel-to-reel operational modes. Formulation data, etch rates, performance, maintenance, metal recovery, and analytical procedures associated with the process are presented. Ways of recovering precious metal from the spent stripper solution are discussed, both for in-house recovery and for costeffective shipment to outside refining.

In the fabrication of electronic devices and in the decorative industry, palladium and its alloys are often used to replace gold.1-6 They are sometimes finished with a thin overlayer of gold. Palladium and its alloys, notably with nickel or cobalt, afford corrosion protection and superior wear, combined with excellent electrical properties.7-11 Palladium is also useful for providing a barrier against diffusion (e.g., between gold and nickel). It is economically favorable because it costs significantly less than gold. But even though the metal cost is reduced, a reliable palladium and palladium alloy stripping process is highly desirable for two reasons: It will permit recovery of precious metal from discarded or worn-out parts, and rework of expensive parts after faulty plating. In the latter case, especially, it is important that the substrate be fully preserved. Therefore, a stripping method is desirable that functions with a minimum of substrate corrosion, that is, with pronounced selectivity for the precious metal.

While the stripping of gold from base metal substrates is in common use, the stripping of palladium and its alloys is much less well known. One reason may be that the available processes lack selectivity. The lack of a feasible stripping method presents an obstacle for the otherwise commercially attractive conversion from gold to palladium.

The stripping solution<sup>12</sup> to be described is selective for palladium with regard to nickel, copper, copper bronzes, and steel substrates. The proposed process easily dissolves any pure or hard gold finish on top of palladium or a palladium alloy. If palladium is plated over nickel, both layers can be dissolved in the same solution, but nickel is removed more slowly than palladium by a factor of 10 or more. If the nickel layer is thick, it may be preferable to strip the nickel separately. On the other hand, the large difference in stripping rates permits selective stripping of palladium from nickel. The corrosion of copper or copper bronzes is so inhibited that a clean removal of palladium or palladium alloy can be achieved virtually without loss of substrate material. This leaves expensive work pieces reusable after palladium stripping.

Although many procedures can be used, a chemical salting-out of the complexed precious metals has been found preferable for safe and efficient precious metal recovery from the spent solution. The cyanide-containing supernatant liquid can then be treated by conventional means (*e.g.*, reaction with sodium hypochlorite solution to form carbon dioxide and ammonia).

# Prior Developments

Palladium Stripping and Related Information Both electrochemical and chemical stripping methods have been proposed for palladium removal. E.B. Saubestre proposed anodic stripping in a solution of NaCl and NaNO<sub>2</sub> at pH 4-5, 2-4 V;<sup>13</sup> similar methods are also given by N. Hall *et al.*<sup>14</sup> It appears, however, that most electroplaters prefer chemical methods in which an oxidizing chemical is used to dissolve the metal. T.A. Shankoff proposed the use of dichromate ion as the oxidizing agent and chloride ion as the complexing agent.<sup>15</sup> Concentrated sulfuric acid has been suggested as a solvent for chemical stripping with nitric acid added as an oxidant, as well as an electrolyte for anodic stripping.

Another group of oxidants in use for precious metal stripping includes "nitro-substituted aromatic compounds," which have been suggested for "dissolving metals of the class consisting of nickel, copper, cadmium, silver, zinc, and gold by chemical action alone, etc." in 1949 by R. Springer and W.R. Meyer.<sup>16</sup> This class of oxidants is used in combination with ammonium and alkali cyanides, which, as the inventors point out, are rendered unstable or even explosive by inorganic oxidizing agents of high oxidizing potentials. J.J. Grunwald<sup>17</sup> proposed the use of complex tetracyanide ions, such as  $[Zn(CN)_{4}]^{-2}$ , in combination with nitro-substituted aromatics, for gold stripping with the aim of diminishing corrosion of the substrate, especially copper. L.R. Fountain<sup>18</sup> used a solution of alkali cyanide and a nitro-substituted aromatic compound for removing a gold alloy braze having palladium or niobium in combination therewith. H.M. Solidum and R.C. Zobbi19 recommended use of a dry powder containing cyanides and nitrobenzene derivatives with an auxiliary agent for making up and replenishing stripping solutions for gold and silver (palladium is not mentioned). Nitrobenzoate derivatives as oxidant and alkali cyanide as ligand are also used in a palladium stripping solution proposed by A. Fletcher and W.L. Moriarty.20

# Corrosion Problems with Copper Substrates

Inhibitors are commonly in use for selective stripping of nickel or gold from copper substrates. M. Weisberg and F.P. Butler<sup>21</sup> claimed a long list of compounds of sulfur in the -2 oxidation state in combination with a nitro-substituted organic compound and an amine for removing metals, especially nickel, from bases, especially copper and its alloys. E.H. Too and D.R. Marx<sup>22</sup> proposed addition of an organomercapto compound for selectively stripping gold from a



Fig. 1-Etch rates vs. Immersion time for individual metals.

metal substrate, especially copper, in a solution also containing a ring-substituted nitrobenzoic acid compound, a bathsoluble cyanide, and a lead or bismuth compound. C.H. Huang<sup>23</sup> described the function of benzotriazole as a corrosion inhibitor for copper in a sodium chloride solution. None of these corrosion inhibitors, however, has yet been applied for stripping palladium from copper. We tested solutions as proposed by Too and Marx<sup>22</sup> for selective gold stripping, for removal of palladium from copper substrates. The attack rates were 0.18 to 0.30 µm/min for palladium, and 4.5 to 4.8 µm/min for copper, at 40-43 °C. These initial findings suggest that conventional copper inhibitors may be ineffective in palladium stripping.

## Process Description

## Palladium Stripping with Copper Passivation

While corrosion inhibitors for copper do not appear to be useful by themselves, it was found that a suitable combination of additives with synergistic action can provide a good palladium stripping rate, as well as very satisfactory copper protection. The resulting stripper meets all practical demands with regard to speed of operation, selectivity, safety, and metal recovery. It is freshly prepared prior to each use from two liquid concentrates and a salt mixture containing cyanide.

Preparation and Operation of the Stripping Solution The stripping solution is prepared by dissolving 150 g of a salt mixture in water, followed by the addition of 250 mL of



Fig. 3—Etch rate vs. Pd conc. as illustration of "aging" of stripping Fig. solution with use.



Fig. 2—Etch rate vs. shelf-life as indication of stability of the stripping solution.

oxidant solution and a small amount of inhibitor. Ten mL of inhibitor solution per liter has been found optimal for most decorative and electronic components. For components with discrete geometries and/or uneven deposit thickness, however, such as electronic packaging lead-frames, high inhibitor concentrations (as high as 80 mL/L) have been found advantageous to avoid attack on even the thinnest of leads. The solution may become turbid when inhibitor is added, but will clear on heating. Just before use, the solution is heated to 40 to 50 °C; temperatures above 55 °C should be avoided, because solution decomposition, with loss of stripping activity, may set in. Before immersion, the parts are cleaned thoroughly and rinsed. Good agitation during stripping is essential. After stripping, the parts are rinsed repeatedly; water from the first rinse can be used to prepare more fresh stripper, or added to the spent stripping solution for eventual metal recovery. Cathodic cleaning of the parts is recommended before re-plating.

## Performance Tests

## Individual Metal Stripping Rates

Selectivity for palladium in the proposed stripping solution was evaluated by testing etch rates for individual metals, as well as for multilayer finishes. For the individual metal tests, electroplated palladium, nickel, cobalt-hardened gold, and rolled copper foil and unplated Alloy 725 were used. The workpieces were immersed in the stripper for five subsequent periods of 30 sec each, at 42 °C, with moderate agitation. After each interval, the pieces were rinsed, dried, weighed,



Fig. 4—Effect of salt replenishment on etch rate.



Fig. 5—Scrap Pd stripping trial.

and immediately re-immersed for the next interval. The etch rates are expressed in  $\mu$ m/min and plotted at the end of each interval (Fig. 1).

The plot shows that cobalt-hardened gold and the base metals were much more slowly etched than palladium; moreover, it shows that the palladium etch rate stayed constant over the whole 2.5-min period, during which a total of 1.65  $\mu$ m was stripped, while the nickel etch rate increased, and the copper etch rate decreased over the same period. Palladiumnickel alloy (20% Ni) behaves like palladium. That hard gold could be etched, even though the rate is slow, demonstrates that gold-flashed palladium and palladium nickel finishes are amenable to treatment. Initial and final (after 2-min immersion) etch rates were as shown in Table 1.

		Table1 EtchRates µm/min	
A	Metal	<b>Initial</b>	<b>Final</b>
	Hd. Au	0.125	0.125
	Pd	0.67	0.67
	Ni	0.075	0.35
	Cu	0.109	0.019
	Alloy 725	0.094	0.043

### Table 2

	Immersion	Weight	
Metal	Time	Loss	Comments
Pd	0.5 min	6.8 mg	Palladium layer totally removed
Ni	1.5 min	11.5 mg	Nickel layer totally removed
Alloy 725	>2.5 min	≤0.5 mg	No visible attack on lead-frame
			pattern

### Table 3

Fresh stripper Unused stripper aged 40 days	<b>Pd</b> g/L 0 0	Complexing Salt g/L 150 132	Stripping Rate µm/min 0.75 0.54
Used stripper, after 1 day	13.5	80.3	0.36
Used stripper, after 13 days	13.5	80.3	0.32
Same stripper, replenished	13.5	150	0.60



Fig. 6-Scrap Pd-Ni stripping trial.

Applying these rate figures to a multilayer finish, where palladium is plated over nickel on a copper substrate, the following can be expected: If only palladium stripping is intended, with the nickel underplate to be left intact, the low initial nickel etch rate offers clean palladium removal with little loss of nickel. On the other hand, if the nickel layer is to be removed, the autocatalytic acceleration of nickel etching, as expressed in Table 1, is favorable; moreover, the nickel stripping rate can be increased by adding nickel salt to the stripper. The simultaneous removal of the nickel layer has been found especially advantageous in lead-frame applications. Finally, the slight initial corrosion of the copper or copper-based substrate will be further diminished with time.

## Stripping of a Multilayer Finished Workpiece

The above considerations were demonstrated on a multilayer finished lead-frame strip with 50 to 100  $\mu$ in. of nickel and 5 to 10  $\mu$ in. of palladium plated over Alloy 725. The results of this experiment are shown in Table 2.

This experiment shows how important a high degree of selectivity is in the stripping of pieces with coatings of uneven thickness, because in such cases two layers of metal may be exposed simultaneously for relatively long periods. In the above instance, consideration might also have been given to switching to a substrate-protecting nickel stripper after all palladium had been removed. No general preferences can be given here, for each application must be judged on its own merits.

## Stability of the Stripper Solution

The made-up stripper solution is stable at room temperature. We also tested the palladium stripping rate in a solution kept at 42 °C, after 1, 2, 4, and 8 hr. The results are shown in Fig. 2. Over long periods, a slight drop in the etch rate is expected as a result of the loss of free cyanide.

## Aging of the Stripping Solution with Use

Because of the variety of stripped materials and stripping operations, the aging behavior of the stripping solution cannot be exactly predicted. In an attempt to obtain a useful simulation of actual operating conditions, incremental amounts of palladium metal powder were added to the stripping solution and permitted to react completely before the etch rate was determined. The results (Fig. 3) show a decline in the etch rate with depletion of the reagents, caused by complexing of free cyanide with palladium, and reduction of the oxidant.

A connection between the etch rate of palladium and the availability of cyanide in the solution can also be seen in Fig.

3, where the "free" cyanide content has been plotted against the amount of palladium metal dissolved; the curves for the etch rate and free cyanide run parallel to each other.

# Effect of Replenishing and Storage

Etch rates approximating the initial conditions can be attained by replenishment of the components, even if the stripping solution is used infrequently. A "spent" stripping solution containing 15 g/L of palladium and 54 g/L of free cyanide salt had an etch rate of  $0.32 \mu$ m/min after being used intermittently for 15 days. The solution was replenished twice during this period, with 70 g/L salt mixture, 100 mL/L oxidant solution, and 5 mL inhibitor solution. After each replenishment, the etch rate was found to be  $0.65 \mu$ m/min, and  $0.6 \mu$ m/min, respectively, demonstrating a recovery of 80 percent of the initial rate. The results are presented graphically in Fig. 4.

The stripping solution was also found to be quite stable in storage, with only marginal losses in etch rate after 40 days, which is particularly advantageous. The results are listed in Table 3.

# Production Scale Application of the Stripper

The stripping solution described above was successfully applied in refining approximately 4,000 lb of low-grade, precious-metal scrap etched in 50-lb batches for the purpose of precious metal recovery. The parts had been plated with 20 to 50 µin. of Pd-Ni alloy. The solution volume was 160 gal (approx. 600 L) and the temperature was maintained between 40 and 50 °C. The parts were loaded into a stainless steel wire-mesh basket prior to immersion in the solution. Solution agitation was approximately 50 gal/min, and the exit nozzle from the pump was aimed directly at the bottom of the basket to ensure exposure of all parts to the etching solution. After 15 min, the innermost parts were spot-tested for Ni underplate exposure, using nitric acid. A drop of concentrated nitric acid placed on a well-rinsed part turns green immediately if the nickel underplate is exposed. If Pd or Pd-Ni alloy remains, the spot turns yellow after approximately 30 sec. If the test indicated that Pd-Ni remained on the surface, the basket was immersed for an additional 15 min and retested. The parts were rinsed twice with water before being discarded for base metal refining. The results are shown in Figs. 5 and 6.

The conducting salts and oxidant solution were replenished only once after 2,000 lb had been processed. Replenishment was required because, after 30 min of etching, the spot test still showed Pd remaining on the surface of the parts. The inhibitor solution was not replenished, because the parts were not destined for reuse.

# Metal Recovery

# Choice of Recovery Methods

Most of the precious metal in the spent stripping solution (including gold) is present in the form of its cyanide complex(es). The simplest way to recover palladium from spent stripping solutions is to return the solutions to the manufacturer for refining. Existing regulations for the shipment of "hazardous waste," however, may render that option financially unattractive. In such cases, it is preferable to recover the precious metal as a medium- to high-purity metal or sludge that is more easily transported. The decision whether to ship the solutions to the refinery as such, or to send the recovered precious metal for refining, depends on a variety of economic and engineering factors that must be weighed, such as:

- 1. Proximity of a precious metals refinery.
- 2. Volume and precious metal concentration of stripping solution to be refined.
- 3. Cost of state and local government hazardous waste transportation permits.
- 4. Availability of chemical or electrochemical process equipment, air-borne emission exhaust system and wastewater treatment facility.

In-plant recovery of palladium can be effected primarily by chemical or electrochemical methods; possibly also by a combination of them. Because of the extreme stability of the palladium cyanide complex, cyanide ions must be removed, precipitated or destroyed in all cases. A chemical method has been found to precipitate the bulk of the complexed palladium. The solids can then be filtered, dewatered and shipped for refining as a dry cake, which would ease hazardous waste management and reduce shipping costs. The resultant filtrate is then treated with sodium hypochlorite solution, a wellknown reagent for cyanide destruction,<sup>24</sup> which precipitates the remaining nickel as oxide and destroys the free cyanide. Any trace of metal left in the filtrate is then removed with sodium borohydride, after which Pd, Ni and cyanide are reduced to undetectable levels. The resulting filtrate can then be evaluated, further treated, (e.g. neutralized) and discarded as per local environmental regulatory agency guidelines.

# Summary

A reliable stripping solution for rework and metal recovery has been developed, comprising a three-component system. This formulation provides satisfactory and economical processing of palladium, gold-flash palladium or palladiumnickel finishes. The system has been demonstrated to be exceptionally selective for palladium and palladium-nickel vs. copper. Electrolytic recovery of the precious metal, using standard equipment, is described. The relationships between the etch rate, dissolved metal and free cyanide concentration were also established, along with analytical methodologies useful for process control.

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