Alternatives to the Use of Cyanide Solutions in Electroplating

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As part of its efforts to promote pollution prevention in Minnesota, the Minnesota Office of Waste Management (OWM) contracted with Braun Intertec Environmental to investigate available pollution prevention alternatives to cyanide-based solutions in electroplating, and to determine the extent of implementation of these alternatives in Minnesota. The study entailed a literature search investigating the alternatives for the different plating solutions, a telephone survey of 58 Minnesota electroplaters and the development of four case studies recording industry experience in implementing non-cyanide plating solutions and rinsing modifications. Sources contacted for information on alternative solutions and rinsing modifications included the Minnesota Technical Assistance Program (MnTAP), American Electroplaters and Surface Finishers Society, Sandia National Laboratories, a chemical supplier and Minnesota Metal Finishers.

Zinc, copper, cadmium, silver, gold, brass and nickel are commonly plated using cyanide solutions. Although cyanide solutions arc extremely toxic, their use has become widespread due to their intrinsic cleaning ability and effectiveness in keeping metals in solution during the plating process. Motivation for eliminating cyanide solutions stem from cyanide's toxicity, potential liability, public distrust, increasing regulation and rising waste treatment and disposal costs.

A cable listing alternative solutions for the various cyanide placing solutions, along witch their advantages and disadvantages, can be found at the end of this fact sheer. Zinc and, to a certain extent, copper cyanide solutions are the most commonly replaced. Alternatives for cyanide silver, cadmium, nickel and gold are currently limited in application.

Rinsing is vital in the plating process because it ends the chemical reactions char occur as part of the process and prevents cross-contamination of the subsequent placing tanks. Poor rinsing can cause staining, sporting, blistering or peeling of the coating on the plated parts. The purpose of alternative rinsing practices is to control dragout of the various plating solutions from the baths and to minimize water use. Proper design, operation and maintenance arc vital to the success of-the various alternative rinsing methods.

Methods to control dragout include:

- Decreasing withdrawal rate of the parts from the plating baths.
- Increasing drip time over the solution ranks.
- Racking parts to avoid cupping solution within the part cavities.
- Shaking, vibrating or passing the parts through an air knife.
- Angling drain boards between the ranks.
- Using wetting agents to decrease surface tension in the tank.
- Increasing bath temperacures.

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Water conservation methods include the use of:

- Flow restrictors on flowing rinses.
- Flow control valves on each tank.
- Agitation to assure adequate rinsing and homogeneity within the rinse tank.
- Conductivity controllers.
- Dead rinses.
- Counter-current rinsing systems.
- Fog or spray rinsing.
- Reactive rinses which allow reuse in compatible rinsing systems.
- Purified or softened water.

The telephone survey indicated that most platers are aware of the existence of cyanide plating alternatives and have done at least some research into the alternatives. The reasons most often provided for investigating the alternatives include increasing environmental regulations, higher waste management and disposal costs, and process cost savings. The primary barrier appears to be the high capital costs associated with converting to non-cyanide solutions, followed by the lack of customer acceptance of the alternatives.

Most platers surveyed have done some modification of their rinsing systems. Most zinc electroplaters have performed pilot testing on non-cyanide solutions, or at least partially replaced their zinc cyanide plating. Most copper cyanide platers have investigated alternative solutions, while a few have run pilot testing on or converted to non-cyanide solutions. Brass, cadmium, gold, nickel and silver platers surveyed felt that there were few, if any, viable alternatives to cyanide solutions for their processes.

The most common response by the platers regarding the type of assistance needed from the OWM was that the OWM could strive to foster a better relationship with industry. Some survey respondents felt that OWM is not patient enough with industry, does not recognize the good faith efforts by industry and needs more input from industry. Another common response was confusion regarding the roles the various governmental agencies play, and the need to make environmental compliance within Minnesota more streamlined and uniform. Concern was also expressed that information provided to OWM and MnTAP may result in either enforcement actions or increased regulation. There also appears to be a lack of awareness of the assistance available to industry from OWM and MnTAP. Other needs expressed by survey respondents include tax incentives for pollution prevention, training focused specifically on the plating industry, customer/ consumer education and continued research into alternatives.

A series of four case studies were developed as part of this report. The first recorded one company's experience in converting from cyanide zinc electroplating to alkaline non-cyanide zinc. The other three case studies discuss the implementation of rinsing modifications in three other plating facilities.

For more information

Copies of the full report and the case studies are available upon request. For a copy of the full report, the alkaline non-cyanide zinc plating or rinsing case studies, or for more information on the Pollution Prevention Research Award Program, please contact the OWM at 6120-649-5750, or 800-657-3843 toll-free in Minnesota, or write:

Pollution Prevention Research Award Program
Minnesota Office of Waste Management
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St. Paul, MN 55108-5272

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Cyanide Eletroplating Solution Alternatives

Summary of options

Alterntive solution	Advantages	Limitations	Application potential
Alkaline zinc	• Good coverage in low-current density areas • Bright deposits • Throwing power similar to cyanide solutions • Use of existing tanks • Allows for gradual phase-out of cyanide solutions • Chemical costs simlar to cyanide solutions	• Loss of intrinsic cleaning ability of cyanide • Harder to plate on cast iron and carbonitrided steel. • Generally requires additional filtration.	Promising for plating under 0 5 mils. Firms using solution must compensate for loss of intrinsic cleaning ability of cyanide and control post-blistering problems
Acid zinc	• Faster deposition speed than alkaline zinc solutions. • Yield bright deposits that level surface irregularities. • Plate readily on cast iron and cabronitrided steel. • Less prone to post-blistering than alkaline zinc solutions. • Less sensitive to make-up water than alkaline zinc solutions. • Better able to accept chromate sealers than alkaline zinc solutions.	• Loss of intrinsic cleaning ability of cyanide. • Corrosive nature of solutions may require modifications to plating equipment. • Higher maintenance costs. • Additional cooling and filtration equipment may be necessary. • Cannot be gradually phased in. • Poor throwing power in low-current density areas. • Make-up water may require iron removal.	Promising for firms willing to provide the necessary modifications and investments in their lines.
Acid sulfate copper	• Superior leveling and brightness. • Pretreatment is relatively easy and inexpensive. • Make-up costs are inexpensive. • High plating current densities are possible. • High line speeds are possible • Only bright copper works well on plastic.	• Corrosivity of solution is hard on plating equipment. • Hard to recover dragout. • Poor macro-throwing power. • Solution may attack base metal (strike coatings may be necessary) • Additional cooling equipment may be necessary. • Acid-resistant ventilation systems may be necessary.	Promising; has been used since 1950s and accepted in a wide variety of plating applications
Pyrophosphate copper	• Excellent throwing power. • Does not attack base metal or plating equipment • Dragout recovery is possible. • Pretreatment is relatively easy. • Excellent subsequent plating adhesion. • Anode bags are not needed. • High deposition of metals.	• High initial solution costs. • May require longer plating times. • Steel and zinc parts require copper cyanide strike. • May contain significant amounts of ammonia that may pose pretreatment problems. • Life of solution is limited.	Promising; provided the loss of the intrinsic cleaning ability of cyanide is compensated for and production speed can be lowered to compensate for the longer plating time required.
Alkaline copper	• Works well on steel, brass, white metal, zinc die cast and zincated aluminum surfaces. • Good throwing power. • Good coverage capability.	• Additional cleaning and process controls may be necessary.	Less promising – more difficult and expensive to operate
Copper fluoborate	• Can accommodate higher line speeds. • More soluble than sulfuric acid.	• May be more expensive to operate and difficult to control	Less promising – more difficult and expensive to operate

Alternative solution	Advantages	Limitations	Application potential
Electroless nickel	• Eliminates need for a copper strike on zinc parts. • Improved coverage capability. • Improved corrosion protection of zinc substrates. • Lower reject rates.	• Plating process much more complex.	Limited application – tested as an alternative to copper/nickel plating on zinc die casts.
Ammonium silver		• Bath generates ammonium hydroxide, which poses an exposure concern for line operators. • Limited information is available on solution.	Not promising due to worker health and safety concerns.
Halide silver	• Very stable and easy to operate.	• Light-sensitive solution. • Initial cost high for electronic and decorative applications. • Solution is toxic.	Limited application since solution is fairly unstable
Methanesulfonate-potassium iodide silver	• Yields fine-grained structured deposits similar to cyanide solutions.	• Not yet developed on a commercial scale.	Only tested on a laboratory scale. No tests in commercial setting have been performed.
Amino- or thio-complex silver		• Readiness of thiosulfate ions to be oxidized. • Low current density areas may be discolored. • Limited information is available on solution.	Not promising. At one time the solution was widely marketed, but has since been withdrawn.
No free cyanide silver	• Developed specifically for electronics industry. • Good contact properties. • Less susceptible to tarnishing. • Silver can be precipitated as AgCN and reused. • Neutral pH and no free cyanide allows for free rinsing.		Limited test application. Developed for high speed electronics plating
Cadmium chloride		• Limited information is available on solution.	Not promising. Cadmium plating likely to be phased out due to the toxicity of cadmium.
Cadmium sulfate	• Can produce deposits up to 0.02 inches with good adhesion and density properties.		Not promising. Cadmium plating likely to be phased out due to the toxicity of cadmium
Cadmium fluoborate		• Limited information is available on solution.	Not promising. Cadmium plating likely to be phased out due to the toxicity of cadmium
Cadmium perchlorate		• Limited information is available on solution.	Not promising. Cadmium plating likely to be phased out due to the toxicity of cadmium.
Gold sulfite	• Excellent throwing power. • Can plate on complex parts. • Performs as well as gold cyanide solutions.	• Solutions are less stable, therefore require more monitoring and control.	More research is required for electronic application.
Cobalt hardened (no free cyanide) gold	• Works well on slide-wear applications.	• Deposits are brittle and thermal shock may cause cracking. • Limited information is available on solution.	More research is required for electronic application