THE MASSACHUSETTS TOXICS USE REDUCTION INSTITUTE

Fact Sheet 4

Non-Cyanide Plating Processes

Today, many metal platers are seeking alternatives to traditional cyanide plating processes. Concerns over occupational health and safety, waste treatment costs, regulatory compliance ,requirements, and potential liability have encouraged process managers to investigate new, non-cyanide plating technologies.

Non-cyanide-based alternatives are available for cyanide-based copper, zinc, and cadmium plating processes. These substitute processes can reduce regulatory and reporting requirements, lower risks to workers, decrease environmental impact, and reduce corporate liability.

This fact sheet summarizes some viable alternatives to traditional cyanide plating methods. The alternatives presented are not all-inclusive, nor is one alternative recommended over another. The options listed are reasonably available and in most cases permit use of existing equipment with minor capital investment for modifications.

Cadmium Alternatives

Several non-cyanide plating finishes, including zinc, zinc alloy, and tin alloy, provide corrosion protection. These alternatives may be used in place of the toxic cadmium plating methods; the choice of alternatives depends on desired deposit characteristics.

General Considerations When Using Non-Cyanide Processes

- More than one non-cyanide process may be required to meet all the needs of a single facility.
- Process controls and cleaning practices must be maintained within tighter limits.
- Without the complexing ability of cyanide, periodic removal of iron and other potential contaminants may be required to assure deposit quality. Filtration is generally necessary when using non-cyanide-processes.
- The color shades obtained in chromating over non-cyanide deposits do not always match those obtained with the same colors of chromates over cyanide deposits. Customers should be notified when it is important to segregate products with color shade differences.
- Some non-cyanide processes do not satisfactorily adhere to all surfaces and tend to become brittle at high temperatures.
- Alkaline non-cyanide processes generally provide more ductile deposits for subsequent forming operations than do acid non-cyanide processes.

non-cyanide substitutes usually incorporate more organic brightening agents than alkaline non-cyanide substitutes. In both acid and alkaline non-cyanide processes, higher levels oforganic or non-organic brightening agents provide a more cosmetically appealing result. However, chromating may be more difficult with high levels of brighteners, particularly organic brighteners, as a deposit surface film.

- Acid substitution processes require an appropriate (e.g., plastic) liner.

Environmental, Health, and Safety Considerations

Examination of alternatives should include consideration of environmental and health and safety tradeoffs at all stages of production, including raw materials acquisition, processing; and recycling or disposal.

- Material safety data sheets must be reviewed and vendors should be questioned about the presence of ammonia, formaldehyde, or other agents in some substitute chemistries that may present worker or environmental concerns and which may require redirecting of waste streams for treatment compliance.

Alternatives Matrix

The matrix on the following pages provides comparative information on a wide range of different options. Information on product quality and process parameters is provided for a range of zinc, cadmium, and copper alternatives. These parameters include corrosion protection, finish appearance, color, ductility, plating uniformity, and other process considerations.

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Cyanide Process	Alternative	PRODUCT QUALITY			
		Corrosion Protection	Finish Appearance	Chromate Colors	Ductility
Zinc[1]	**Zinc Alkaline**	(+) Good, greater protection in difficult to rinse areas	(+) Good brightness	Full line available	(+) Good, may be reduced at higher thickness
	Zinc Acid Chloride	(+) Good, but less protection in difficult to rinse areas	(+) Excellent brightness and leveling	Full line available	(−) Higher brightener levels may reduce ductility (+) little hydrogen embrittlement
Cadmium[1]	**Cadmium Neutral or Acid Sulfate**	(+) Good	(+) Satisfactory	Full line available	(+) Good, little hydrogen embrittlement
	Cadmium Acid Fluoborate	(+) Good	(+) Satisfactory	Full line available	(+) Good, little hydrogen embrittlement
	Zinc Nickel Alkaline	(+) Excellent with chromate conversion coating	(+) Good	Specialized chromates: bronze, yellow, iridescent, black	(+) More ductile than acid zinc
	Zinc Nickel Acid	(+) Good	(+) Good brightness at higher efficiency	Specialized chromates: bronze, yellow, iridescent, black	(−) Less ductile due to higher brightener levels
	Zinc Cobalt Acid	(+) Good	(+) Excellent (+) Provides deep uniform black without use of silver	Specialized chromates: bronze, yellow, iridescent, black	(+) Fair, lower hydrogen embrittlement than alkaline
	Zinc Cobalt Alkaline	(+) Good	(+) Provides deep uniform black without use of silver	Specialized chromates: bronze, yellow, iridescent, black	(+) Better than acid bath
	Zinc Iron Acid or Alkaline	(+) Good, not recommended for high temp. applications	(+) Provides deep uniform black without use of silver	Black, others limited based on bath conditions	(+) Good
	Tin Nickel Acid or Near Neutral	(+) Good resistance to corrosion and tarnish	(+) Can be decorative in appearance	N/A	(+) Good
	Tin Zinc Acid, Alkaline or Neutral	(+) Good with chromate applied (+) Does not undergo bimetallic corrosion	(−) Fair	Limited to yellow	(+) Excellent (soft deposit)
Copper	**Copper Alkaline**	N/A	(+) Good appearance	N/A	(+) Good
	Copper Acid Sulfate or Fluoborate	N/A	(+) Good appearance (+) Excellent leveling	N/A	(+) Good to Excellent
	Copper Pyrophosphate	N/A	(+) Good, fine grained and semi-bright	N/A	(+) Good

Notes: 1. Alkaline and acid zinc may also be used as cadmium cyanide plating substitutes.
2. N/A = Not Applicable

Alternative	PROCESS		GENERAL COMMENTS
	Plating Uniformity	Process Considerations	
Zinc Alkaline	(+) Good, uniform in high and low density areas (+) Good throwing power	(-) Narrow optimum operating range of bathparameters	(-) Lower conductivity than acid zinc (+.) Better for some forming operations (-) Harder to plate on cast iron and carbonitrided steel
Zinc Acid -Chloride	(-) Variable with current density	(-) Liners necessary in steel or porous tanks (+) High cathode efficiency at high current densities (-) Agitation required	(+) Higher conductivity results in energy savings (-) Bleedout of entrapped plating solution may limit use for complex parts (+) Plates readily on cast iron and carbonitrided steel
Cadmium Neut/Acid Sulfate	(-) Poor throwing power	(-) Liners required for acid, preferred for neutral	(-) High toxicity, low discharge limits for cadmium; not preferred toxics use reduction (TUR) option
Cadmium Acid Fluoborate	(-) Poor throwing power	(+) High cathode efficiency at high current densities (+) Good stability	(+) Good data on use available - widely used in barrel plating (-) High toxicity, low discharge limits for cadmium; not preferred TUR option
Zinc Nickel Alkaline	(+) More uniform thick-ness and alloy distribution than acid Zn Ni (+) Good throwing power	(-) Chiller required to maintain optimum temperature (-) Slower plating speed than acid Zn Ni (+) Chemistry similar to alkaline Zn	(+) Good corrosion properties maintained after forming and heat treating (-) May contain chelators
Zinc Nickel Acid	(-) Poor thickness distribution, alloy variation from high to low current density	(-) Requires additional inert anodes and segregated rectification (+) Faster plating speed than alkaline Zn Ni	(+) Good corrosion properties maintained after forming and heat treating (-) May contain ammonia or chelators
Zinc Cobalt. Acid	(-) Poor throwing power (-) Variable with current density	(+) Good plating speed (+) High cathode efficiency	(+) No silver required for black chromating (-) May contain chelators
Zinc Cobalt ‘Alkaline	(+) More uniform than acid ZnCo	(-) Lower efficiency than acid ZnCo	(+) No silver required for black chromating (-) May contain chelators
Zinc Iron Acid or Alkaline	(+) Good throwing power	(-) Iron content must be controlled to prevent blistering	(+) No silver required for black chromating (-) May contain chelators
Tin Nickel Acid/Near Neutral	(+) Deep throwing power	(-) Chiller required (-) Lined tanks recommended	(+) Good hardness (between Ni and Cr) and wear resistance, low contact resistance (+) Ability to retain oil film for lubrication
Tin Zinc Acid, Alkaline or Neutral	(-) Poor throwing power (+) Excellent covering power	(-) Chiller required	(+) Excellent solderability properties
Copper Alkaline	(+) Better throwing power than cyanide	(+) Operating pH range 8.0 to 10.5	(+) Can be used as heat treat maskants (+) Less corrosive (+) May be used as strike bath
Copper Acid Sulfate or Fluoborate	(-) Less macrothrowing power than alkaline (+) more microthrowing power than alkaline	(-)Lined tanks and appropriate anode baskets required (+) Fluoborate allows use of higher current densities	(+) Good use data available (-) Corrosive on coatings and some substrates
Copper Pyro-phosphate	(+) Good throwing power	(+) Operating pH 8.0 to 8.8 (-) More sensitive to organic contaminants than acid Cu (-) May require longer plating time	(+) May be used as strike bath (-) May contain ammonia

References

Resources listed are available from the publishers and may be viewed at the Technology Transfer Center of the Massachusetts Toxics Use Reduction Institute.

Altmayer, Frank. "A Comparison of Several Ideas for Substitutes As Methods of Pollution Prevention." Unpublished paper. Chicago, IL: Scientific Control Labs, Inc., 1992.

Altmayer, Frank. "Comparing Substitutes for Cr and CU, to Prevent Pollution." *Plating and surface Finishing,* February 1993. pp. 40-43.

Altmayer, Frank. "Comparing Substitutes for Cr and CU. to Prevent Pollution, Part Two." *Plating and Surface Finishing,* March 1993, pp. 32-37.

Altmayer, Frank. "Contamination Prevention: Both Sides." *Plating and Surface Finishing,* August.1992, pp. 23-25.

Bleeks, Thomas W., and Tamara S. Davidson. "An Alternative to Cyanide Copper." *Proceedings, 13th AESF/EPA Conference on Environmental Controlfor the Surface Finishing* Industry, January 27-29, 1992.

Brooman, Eric W. "Alternatives to Cadmium Coatings for Electrical/ Electronic Applications." *Plating and* Surface *Finishing,* February 1993, pp. 29-35.

Graves, Beverly A. "Process of Most Resistance." *Products Finishing,* July 1992, pp. 46-51.

Krishnan, R.M.; S.R. Natarajan, VS. Muralidharan, and Gurdeep Singh. "Characteristics of a Non-Cyanide Alkaline Zinc Plating Bath." *Plating and Surface Finishing,* December 1992, pp. 67-70.

Metal Finishing Guidebook and Directory Issue, '93, Vol. 91, No. lA, January 1993.

Metals Handbook, Ninth Ed., Vol. 5, Surface Cleaning, Finishing, and Coating. Metals Park, OH: American Society for Metals, 1982.

Minnesota Office of Waste Management. "Alternatives to the Use of Cyanide Solutions in Electroplating," 1992.

Natorski, Theodore J. "Zinc and Zinc Alloy Plating in the '90s." *Metal Finishing,* March 1992, pp. 15-17.

Piekunka,Vincent G., and Edward P. Zimmerman. "Making It Work: Non-Cyanide Plating Alternatives."Bedford, MA: Mabbett & Associates, 1993.

Ramachandran, A., and S.M. Mayanna. "New Brighteners for Non-Cyanide Alkaline Zinc Plating Bath." Metal *Finishing,* February 1992, pp. 61-67.

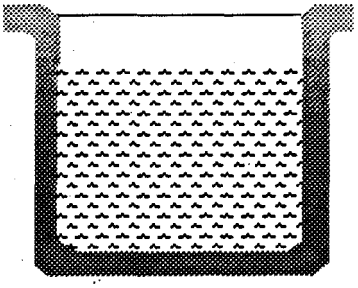
Smith, Blair A., W. Steve Rapacki, and Tamara S. Davidson. "Heat TreatmentMaskantMaterials-EvaluationofNon-Cyanide-Containing Electrolytes." *Plating and Surface Finishing,* August 1992, pp. 11-14.

Sriveeraraghaven, R.M. Krishnan, and S.R. Natarajan. "Corrosion Behavior of Zinc and Cadmium Deposits Obtained from Different Baths." *Metal Finishing,* August 1991, pp. 51-53.

U.S. EPA. *Guide to Cleaner Technology: Alternative Metal Finishes* (Draft, May 1993). Cincinatti, OH: U.S. EPA, Office of Research and Development, Risk Reduction Engineering Laboratory.

U.S. EPA. Guides *to Pollution Prevention: The Metal Finishing Industry.* October 1992. EPA/625/R-92/011. Cincinnati, OH: EPA, CERI Publications Unit

Zaki, Nabil, and Edward Budman. 'Zinc Alloy Plating Today."-Products *Finishing,* October 1991, pp. 46-51.



This fact sheet was compiled using the most current information available at the time of preparation. Users are advised to check with suppliers regarding specific criteria, applications, and environmental, health, and safety concerns.

Technical guidance for this fact sheet was provided by Vincent G. Piekunka. Information was also drawn from "Making It, Work: Non-Cyanide Plating Alternatives," prepared for the Massachusetts Toxics Use Reduction Institute by Mabbett & Associates, Inc.

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The Toxics Use Reduction Institute is amulti-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce.

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