The Green Machine
Metal Finishing – Green Chemistry 2007

by Brian Wassell
Metal Finishing Association of Southern California
MFASC President 2005-2007

Plating is the general surface coating technique in which a metal is deposited onto a conductive surface. Plating is indispensable as a corrosion inhibitor for the manufacture of computers, mobile phones and electronic devices as well as other uses such as solderability, hardness, wear resistance, friction loss, paint adhesion, conductivity, shielding, etc. Moreover, it is a key technology for the development of new machines and technology. Typical metal finishes are brass/bronze, cadmium, copper, chromium, gold, nickel, silver, tin and zinc, among others.

The metal finishing process electrodeposits metallic coatings onto metal surfaces to impart a property to the exterior surface that is not a property of the base metal material.

The need for green

In a 2006 report issued by the University of California - Berkeley, entitled *Green Chemistry in California: A Framework for Leadership in Chemicals Policy and Innovation*, the research states that, "the U.S. produces or imports 42 billion pounds of chemicals **per day**, 90% of which are created using oil, a nonrenewable feedstock." The report predicts that every 25 years and by 2033 that, based on current trends, chemical production will double.

The USEPA published a 2006 report, entitled *U.S. Greenhouse Gas Inventory Report*.* Although the direct greenhouse gases CO_2 (carbon dioxide), CH_4 (methane) and N_2O (nitrous oxide) occur naturally in the atmosphere, human activities have changed their atmospheric concentrations. From the pre-industrial era (*i.e.*, ending about 1750) to 2004, concentrations of these greenhouse gases have increased globally by 35%, 143% and 18%, respectively. The primary greenhouse gas emitted by human activities in the United States was CO_2, representing approximately 85% of total greenhouse gas emissions. The largest source of CO_2, and of overall greenhouse gas emissions, was fossil fuel combustion.

The use of solvents and other chemical products can result in emissions of various ozone precursors (*i.e.*, indirect greenhouse gases). Non-methane volatile organic compounds (NMVOCs), commonly referred to as "hydrocarbons," are the primary gases emitted from most processes employing organic or petroleum based solvents. Surface coatings accounted for approximately 41% of NMVOC emissions from solvent use in 2004, while "non-industrial" uses accounted for about 38% and degreasing applications for 7%. Overall, solvent use accounted for approximately 25% of total U.S. emissions of NMVOCs in 2004.

The major categories of solvent uses include degreasing, graphic arts, surface coating, other industrial uses of solvents (i.e., electronics, etc.), dry cleaning and non-industrial uses (i.e., uses of paint thinner, etc.).

So how is metal finishing green chemistry?

Metal finishing chemistries are 99.9% inorganic salt compounds. Acids and alkalis are used for cleaning and activation while a salt bath provides a conductivity medium for electrodeposition of metals from an anode to the parts. The compounds are derived from sources that could be termed "infinitely renewable," based on sources such as seawater, naturally-occurring mineral deposits and metallic ore.

The metal finishing compounds are derived from sources that could be termed "infinitely renewable."

While 20 years ago, degreasing operations may have utilized organic solvents, California operations have converted to aqueous cleaning systems - by regulatory mandate.

In the report by UC-Berkeley, the current Toxic Substances Control Act (TOSCA) Inventory has 81,600 chemicals in the registry. Currently, only 1,134 of these chemical have been evaluated for human toxicity, ecotoxicity and bio-persistence. While information is well known on inorganic compounds and metals, the organic chemistry chain remains "the unknown."

The main counterparts or competitors to plating are paints and plastics. While certain binders, catalysts, pigments and reactive agents for paint manufacture are synthesized from renewable sources (*i.e.*, corn, soy plants and other biomass), the result is still an organic chemical where molecular chains have been modified and thus contribute to the current conundrum surrounding the TOSCA Inventory. By and large the paint industry still relies heavily on petroleum-based organics which ultimately are discharged to the air in the drying process.

* *USEPA, Inventory of U.S. Greenhouse Gas Emissions and Sinks (1990-2004), Document #430-R-06-002 (See also http://epa.gov/climatechange/emissions/usinventoryreport.html) (2006).*

Who is this metal finishing industry?

According to the U.S Census Bureau, in *2002 Economic Census Manufacturing California*, there are 570 establishments/employers** that conduct electroplating, plating, polishing, anodizing and coloring under North American Industry Classification System (NAICS) #332813. Gross sales for the category are $852 million, with $341 million in wages paid to 11,586 employees.

By contrast, the California manufacturing sector accounts for 48,478 establishments, generating $378.6 billion dollars in sales, with $66.4 billion in wages paid to 1.6 million employees. The metal finishing industry directly services the Fabricated Metal Products Sector (NAISC #332) as well as the Primary Metal Manufacturing Sector (NAISC #331) which when combined, accounts for 8,441 establishments/employers, generating $28.1 billion in sales and paying wages of $6.8 billion to 179,464 employees.

An interesting comparison between the volume of environmental regulation applicable to metal finishing operations vs. the fact that the metal finishing sector only accounts for 0.2% of revenue and 0.7% of those employed in the manufacturing sector, is when one examines Federal, State and Local regulations. It could easily be shown that well over 25% of the regulatory requirements directly apply to metal finishing operations as listed in Table 1 for the situation in Southern California at the end of this article.

Bad Press? Chromium VI? How can this industry possibly pronounce itself green?

The past 20 years have shown extremely high regulatory enforcement on plating facilities. Fears stemming from acids, metals, illegal disposal, fires, etc. have been routine clips in the media. Fears of chromium (VI) were brought to the public arena through the popular Erin Brockovich story and through many other sinister actions involving irresponsible evil-doers in our industry.

From 1998 to 2001, the USEPA Region IX and Los Angeles Regional Water Quality Control Board (LARWQB) jointly investigated wells in the San Fernando Valley. The “Well Investigation Program” (WIP), was in response to chromium (VI) levels detected in underground water wells located in the Burbank area. The problem was due to past practices of dumping “cooling tower water” that utilized chromium (VI) to control algae and mineral deposits. These spent waters were dumped directly into the San Fernando Aquifer “recharge basin.” These practices dated back to the 1930s and were not associated with metal finishing operations. In 2004-2005, LARWQB required some 53 out of a possible 200 facilities to conduct soil sampling for all “California Metals.” There were approximately eight metal finishing facilities at the time.

There were two plating facilities that had been operating pre-WW2 where operations were conducted on open exposed soil, and they are currently listed as hazardous waste sites. Of the remainder of the sample sites (to include non-metal finishing facilities), the extent of contamination of metals was from 1 to 5 feet below grade surface (bgs), at de-minimus concentration levels. Contaminated sites had historic use of solvents that provided a transport medium for the metals. Most all facilities were at the location for over 30 years and prior to RCRA standards.

While this program revealed less than flattering results, it also served to demonstrate the lack of migratory leaching properties of metal-bearing solutions through soil media. By comparison, organic solvents, such as perchloroethylene, 1-1-1 trichloroethylene, etc., cause huge underground “plumes” that migrate rapidly downward to groundwater. In fact, this area of Burbank/Glendale is a huge Superfund site as a result of “organics.”

Chromium (VI) discharged in air media has been the subject of great concern. In 1998, the South Coast Air Quality Management District (SCAQMD) started Part 2 of a study called MATES II to identify major sources of hazardous air pollutants (HAPS). Subsequent to the study, chromium emissions from metal finishing operations were discovered to be almost 100 times less than previously calculated. After two years of “round table negotiated rule-making”*** and additional advances in control technology, Rule 1469 was amended, thus establishing 99.998% control efficiency for chromium metal finishing operations in the South Coast Basin.

> *Chromium emissions from metal finishing operations were discovered to be almost 100 times less than previously calculated.*

In 2006, the California Air Resources Board adopted a similar “statewide program” that will go into effect, thus reducing the **“total statewide chromium emissions from metal finishing operations”** to 1.8 lb/yr. By contrast, the total statewide inventory of chromium emissions is calculated to be over 3,000 lbs.

Beginning in 1997 and finally in 2006, federal OSHA promulgated the federal “Prolonged Exposure Limits”(PELs) for Chromium (VI). The levels dropped from 52 $\mu g/m^3$ to 5 $\mu g/m^3$. MFASC conducted sampling on some 50 facilities and some 140 employees with only two sample aliquots showing detection for chromium well below the “action level” of 2.5 $\mu g/m^3$.

What happens to these chemicals when you are done with them?

The simplicity of inorganic chemistry allows simple treatment or neutralization. Typical wastes or “waste streams” at a plating facility are primarily rinse waters and acid/alkaline solutions. Most plating solutions consist of an acid or alkaline chemistry by which the metallic molecule is in an “ionic state.” By simply bringing the wastewater or plating solution to a neutral state, the metallic ion is oxidized, converted to a hydroxide salt and it precipitates or falls out of solution. Subsequently, the metal hydroxides are filtered and separated from the resulting wastewater. While laden wastewater can contain metal concentrations of up to 10,000 ppm (1%) of metals, the precipitation/neutralization/filtration process will typically remove metals down to less than 1 ppm of total metals. The wastewater discharge is regulated under the Federal Clean Water Act† and generally requires less than 5 ppm removal for each individual metal.†† Resulting wastewater containing inert salts and soaps is discharged to the sewer and they are removed at a sewage treatment facility or POTW.

** *These employers would be “Job Shops” that do not own the parts for which they provide service and may or may not include “Captive Operations” that own and plate their own parts. Also excluded would be jewelry/precious metals factions.*

*** *Negotiated rulemaking involved metal finishers, SCAQMD Staff and environmental/community groups.*

† *40 CFR § 433 Metal Finishing Category and 40 CFR § 413 Existing Electroplating*

†† *413 maximum metals concentrations: Cd, 0.7 mg/L; Cr, 10 mg/L; Cu, 15 mg/L; Pb, 0.4 mg/L; Ni, 12 mg/L; Ag 5 mg/L; Zn 25 mg/L and 433 maximum metals concentrations; Cd, 0.7 mg/L; Cr, 1.7 mg/L; Cu, 2.0 mg/L; Pb, 0.43 mg/L; Ni, 2.3 mg/L; Ag, 0.2 mg/L; Zn 1.4 mg/L.*

By simply bringing the wastewater or plating solution to a neutral state, the metallic ion is oxidized and converts to a hydroxide salt and precipitates or falls out of solution.

The resulting metal hydroxide sludge or filter-cake is an EPA Listed waste code F006. The material is comprised of metals. Currently, the EPA is considering delisting the F006 waste because nearly all F006 waste is being recycled. In fact, it is considered a commodity because of the intrinsic metal content and the high current world metal prices. The fact is that, it only requires 5% of the total energy to recover metals from F006 waste compared to the mining, refining and smelting process of converting virgin ore. Efforts are currently underway to sell our U.S. F006 filter-cake to Germany for up to $100/ton. ("*Wait until China hears about this!*")

It only requires 5% of the total energy to recover metals from F006 waste compared to the mining, refining and smelting process of converting virgin ore.

What about cyanides and organometallic solutions?

Cyanides can be produced by certain bacteria, fungi and algae, and are found in a number of foods and plants. Cyanide is found, but in small amounts, in apple seeds and almonds. Cyanide has been used in metal finishing as well as mining, photography and metallurgy because of its affinity for metals.

Due to its historic uses, there are a number of myths and misconceptions relating to the toxicity of cyanide. It is important to realize that cyanide:

- Occurs naturally,
- Is not toxic in all forms or all concentrations,
- Does not persist in the environment,
- Is not cumulative,
- Is not a heavy metal,
- Is not radioactive,
- Can be manufactured, stored, transported used and disposed of in a safe manner.

About three million tons of hydrogen cyanide is produced annually worldwide, of which about 6% is converted into sodium cyanide and used in the metals industries (mining and metal plating). The remaining 94% of the hydrogen cyanide is used in the production of a wide range of industrial and consumer items.

The dangers associated with cyanide at a plating shop are due to the nearby presence of acid chemistry and the potential for hydrogen cyanide gas to be formed if they are accidentally mixed. Fortunately most cyanide-bearing waste streams at a plating facility are generated from rinsing and concentrations range from 500 to 2000 ppm. At these concentrations cyanide is easily destroyed using sodium hypochlorite (household bleach).

Organometallic complexes are extremely dangerous. One form is nickel carbonyl, which is an intermediate to pure nickel manufacture. While past plating processes may have used these substances, they would rarely be found at present because of their extremely hazardous properties. In 2000, Office of Health Hazard Assessment sought to regulate all nickel compounds based on health risks associated with nickel carbonyl and nickel subsulfide, which include flammability, carcinogenicity, acute toxicity (associated with the carbon monoxide gases) and their ability to explode. As we advance toward "green chemistry," it is important to evaluate the chemical species, not the metal.

So what happens to plated parts when they are disposed of?

Quite simply, plated parts outlast painted parts at least two to three times their life cycle. This means less energy used when a part lasts much longer. Concerns raised when a plated part is land-filled are speculative. According to a USGS survey conducted in the San Fernando Valley Basin, metals[†††] are naturally present in our soil, ranging from 5 to 50 parts per million (ppm). In a landfill there would have to be a phenomenon[‡] where the pH of leachate (water soaking through soil) would be at less than 3.0 for the metals to be released or etched from the articles, yet such metals would already be present in a pH 3.0 leachate due to naturally occurring metal levels.

If a pH 3.0 condition is indeed occurring, we should regulate the contributors to the condition, because the metals are already there.

Conclusion

Modern landfills are lined and leachate is collected at the base. While metals, nickel, cadmium and lead, are present from the disposal of batteries, cosmetics, colored glass and ceramics, there is no evidence that plated parts contribute to the concentrations. Furthermore, organics such as toluene/xylene (glues and paints), phenols/cresols (paints) and benzene (solvents and chemicals), have far greater impact on human health and the environment if there is threat of groundwater contamination.

For the past 20 years, based on the size and contribution of this faction, the metal finishing industry has been one of the most heavily regulated industries found in the pages of Federal, State and Local regulations. For the past 20 years, tens of millions of dollars have been spent learning, researching and evaluating the effects of this industry on human health and the environment.

The emergence of technologies from this research has resulted in safe chemical substitutions, and recovery technologies to reuse or return chemistries to the original bath. Technologies have been developed to remove 99.998% of contaminants from the air. Treatment technologies remove 99.99% of constituents from water. The accomplishments of "Green Existence" for this industry occur daily.

Referencing the USC Berkley Report, they state;

"*Global chemical production is expected to double every 25 years for the foreseeable future. Between now and 2033, the U.S. EPA expects 600 new hazardous waste sites to appear each month in the U.S. and require cleanup, adding to 77,000 current sites. Efforts at site mitigation are expected to cost about $250 billion. Given the scale, pace and burden of chemical production, the toxicity and ecotoxicity of chemicals are of great public importance.*"

In the context of organics, the size, expense, nature and extent of cleaning up the sites due to the ecotoxicity and environmental persistence of organics is of grave concern compared to the migratory patterns of metals observed at a plating facility.

[†††] *Metals = copper, chromium, nickel and/or zinc.*

[‡] *As oxygen sources are depleted, the waste becomes anaerobic, which supports fermentation reactions. This process results in an accumulation of carboxylic acids and the pH decreases, as low as pH 4.5, before the methane gas phase begins to consume the acids.*

Table 1—Metal finishing regulations

FEDERAL

EPA

RCRA (Resource Conservation and Recovery Act)
- Generator Standards
- Hazardous Waste Determination/Classification
- Underground Storage of Hazardous Substances
- Land Disposal Certification/Restrictions
- Hazardous Waste Generation Reporting

CWA (Clean Water Act)
- Stormwater Pollution Prevention Program
- Sewer Discharge Program/Limitations

SARA (Superfund Amendments and Reauthorization Act - Community Right to Know / Emergency Planning)
- Chemical Inventory Reporting
- Chemical Spill Reporting

CERCLA (Comprehensive Environmental Response, Compensation and Liability Act)

Comments: As established by RCRA, generators of hazardous waste have "cradle to grave" responsibility for the waste. This establishes total financial responsibility for past as well as current waste management practices at off-site TSD.

OSHA Standards (see CALIFORNIA)
- Hazard Communication / Worker Right to Know
- MSDS System
- RCRA Required Emergency Contingency Plans and Emergency Action Plans
- Hazardous Waste Operations and Training
- Confined Space Entry Determination
- OSHA Reporting / Log 300

DOT - Department of Transportation
- RCRA Hazardous Waste Shipping and Manifesting Program
- DOT Proper Shipping Names, Containers, Labels, Warnings and Placards
- Hazardous Materials Registration Program

CALIFORNIA

DTSC (Department of Toxic Substances Control) Hazardous Waste Control Law
- Generator Standards
- Hazardous Waste Determination/Classification
- Underground Storage of Hazardous Substances
- Land Disposal Certification/Restrictions
- Hazardous Waste Generation Reporting
- Permit by Rule and Fees
- California Land Disposal Restriction
- Waste Minimization - Source Reduction Evaluation Plans "SB 14"
- Hazardous Waste Manifest and Fees

SWRCB (State Water Resources Control Board)
- Stormwater Pollution Prevention Permit - Monitoring and Analysis Reporting
- Well Investigation Program - Soil Gas Survey
- Underground Storage Tanks

ARB (Air Resources Control Board)
- Toxic Hot Spots Program (report annual emissions)
- New Statewide Chromium Standard

California OSHA
- Injury and Illness Prevention Program
- Emergency Plans
- Fire Prevention Plans
- Hazard Communication Standards MSDS, Training, Labels etc.
- Ventilation Program (record testing)
- Respiratory Protection Program (respirators)
- Chemical Storage Requirements
- Confined Spaces Program/Determination
- Baseline Exposure Monitoring
- Personal Protective Equipment Program
- Forklift Program
- Exits/Means of Egress/Evacuation Plans
- Machinery and Hand Tools - Guarding
- Welding Equipment
- Compressor Permits
- Electrical Safety Programs
- Fire Extinguishers
- Emergency Eyewash /Showers Inspections and Locations

LOCAL

SCAQMD (South Coast Air Quality Management District)
- Permits for Potential Sources
- Toxic Hot Spots Report
- Annual Emissions Report
- Air Toxic Emission Inventory Plans - Annual Toxic Emission Report as per the "ATIP"

LA City Fire / County Health HazMat
- Annual Permit by Rule Notification/Submittal
- UST (Underground Storage Tanks) Permits and Registration
- UST Monitoring and Inspections
- AST (Above Ground Storage Tanks) Registration/Permit to Construct
- Business Plans and Chemical Inventories
- Community Right to Know/Disclosure of Hazardous Substances Program
- Fire/Lifeline Safety (exits, extinguishers flammable storage, etc.)
- Hazardous Materials and Waste Storage Requirements
- Personnel Training Records
- Proposition 65 Postings

LA City Bureau of Sanitation

Discharges to Sewer under the Federal Clean Water Act
- Permits
- Bi-Monthly Monitoring and Analysis Program
- Inspections
- Detailed Facility Diagrams, Schematics, Water Balance/Usage Records
- Emergency and Notification Plans
- Plumbing, Containment, Incompatibles, Berming, Diking Standards
- Unannounced "user" surveillance
- Continuous pH Monitoring Program
- On-site Hazardous Waste Treatment equipment, process and inspection

LA County Health Department
- Annual Backflow Prevention Device Testing

The simple "GREEN FACTS" about metal finishing are:

1. The process does not use hydrocarbons, as with the painting/plastic coating industry.

2. Raw chemistry is derived from infinitely renewable sources as opposed to nonrenewable petrochemicals.

3. Information on the effects of metals and associated inorganic chemicals on human health and the environment is well known, while 93% of organic chemistries remain unevaluated.

4. The core processes of metal finishing do not contribute to global warming by emitting CO_2, methane or nitrous oxide. However, our use/need for energy is an indirect contributor for which we as an industry have no control.

5. The metal finishing industry is a small yet absolutely vital process in the metal products manufacturing sector and in the overall technology sector of our economy.

6. The metal finishing industry has been heavily regulated for 20 years, yet now, it may be the one industry that is so well understood and easily controlled in harmony with society's demands.

7. Data is available on environmental impacts associated with past activities.

8. Metal finishing facilities can be operated at 99.99% plus control efficiencies with virtually inconsequential release to environmental media and impact on human health and the environment.

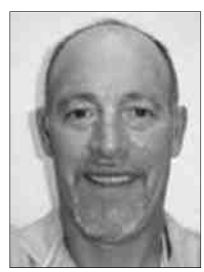
9. Byproducts from metal finishing operations are 100% recyclable, requiring only 5% of the original energy, 5% of the original greenhouse gases and 5% of the original consumption of nonrenewable fossil fuels to recover the metals.

10. The safety of workers being exposed is far less than previously thought and that simple work practices as well environmental controls for air emissions, are effective in reducing worker exposures to even less than minimal risk.
11. While certain hazards are associated with plating chemistry, an abundance of controls are in place to minimize risk and virtually eliminate potential for off-site consequence.
12. There are some metal chemistries that are "extremely hazardous"…but we don't use them anymore.

As President of The Metal Finishing Association of Southern California, I have never had such a positive outlook for our industry. I see how the historic regulatory "hammering" that we endured will now bear fruit as we emerge into a new "Green Chemistry" era. The history of "bad players" that have left an irrevocable mark on our industry have now been put out of business, and we have educated those who are responsible.

Our processes are energy intensive and we need energy. I put forth a request to our legislators, California agencies and policy makers and I believe I speak on behalf of the manufacturing sector when I say,

> *"Please develop and invest in new, clean and renewable source energy systems for our state as we move into this new era of Green Manufacturing."*



About the Author

Brian Wassell is currently serving as President of MFASC. After graduating from courses at UCLA in Environmental Regulatory Law and Sciences, he was accepted on the MFASC Board in April 1993. At the time, he had a vision to bring all metal finishers into a status of "compliance" through education. As a result, there has been excellent outreach in Southern California. His vision today is to demonstrate the past 20 years of environmental accomplishment in pronouncing metal finishing as the safest, most environmentally-friendly process, to add value and coat metal parts.