# **Implementation of the US Environmental Protection Agency's Metal Finishing Facility Pollution Prevention Tool (MFFP2T)**

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To help metal finishing facilities meet the goal of profitable pollution prevention, the U.S. EPA is developing the Metal Finishing Facility Pollution Prevention Tool (MFFP2T), a computer program that estimates the rate of solid, liquid waste generation and air emissions. This program will allow users to insert computer models of standard metal finishing processes into the proposed manufacturing process, thereby estimating wastes generated by the metal finishing process lines. This paper will discuss the mathematical models used by MFFP2T to model the plating, cleaning, and rinsing processes. Additionally, the chemical equilibrium models utilized to estimate the sludge generation rate in various process tanks will be presented. The results of the individual models are combined to create a model of the overall waste generated by the process. The user will then be able to model the effects of changes to processing conditions on the quantity of wastes generated.

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# Introduction

The basic economic fact is that pollution prevention should not be an economic burden for any industry; instead, pollution prevention should provide the industry both environmental and economic benefits. A limiting factor in applying pollution prevention in most metal finishing plants is the paucity of process knowledge related to the pollution generating processes, and how production and waste minimization are correlated. The reality is that plants currently over-consume chemicals, energy and water; and that waste generation is always more than it should be. The key to waste reduction is the control of production quality. In order to implement a profitable pollution prevention program, the facility must understand the process principals that explain how parts are rinsed, cleaned and plated, and how the waste is generated in various operations. These principals are nothing more than mass balances, energy balances, thermodynamics and chemical kinetics.

Schwartz and McBride<sup>1</sup> conducted a survey of 458 metal plating shops located in Orange, Los Angeles, and Santa Clara counties in California to determine whether these shops were aware of waste reduction methods, whether the firm adopted or rejected the option, and what obstacles prevented firms from adopting additional waste reduction methods. The primary reasons for non-adoption of waste reductions techniques were economic, either high price or concern that non-complying shops would undercut prices, the technique would harm product quality or space limitations. Larger shops, those shops that spent more for waste disposal, were more likely to adopt hardware intensive waste reduction technologies. A significant number of shops indicated that organizational issues such as employees ignoring waste reduction techniques or employees who do not speak English well enough to communicate more than basic tasks, precluded adoption of waste reduction technologies.

Lo and Tsao<sup>2</sup> conducted an economic analysis of waste minimization by surveying 35 electroplating facilities in Taiwan and found that the majority of shops used source reduction techniques for waste minimization. Although process flow sheets varied, it was obvious that drag-out and rinse waters were the major sources of waste and that rinses accounted for the most water use and were the largest generation of wastewater. Of the 35 plants reviewed, 30 practiced rinse water reduction, and 21 utilized drag-out minimization. This investigation also included an economic analysis of three different pollution prevention schemes for a chromium and nickel plating facility. Of the three schemes evaluated, one scheme (still rinse after plating bath with rinse solution concentrated by reverse osmosis and returned to the plating bath) was profitable while two other schemes (electrolytic recovery with rinse water purified by ion exchange and reused; and still rinse followed by a two stage countercurrent rinse and electrolytic recovery of nickel from the rinsewater) were not.

These studies illustrate both the current obstacles and the potential benefits of implementing a pollution prevention program. A goal of the Metal Finishing Facility Pollution Prevention Tool (MFFP2T) is to provide a mathematical model of the processes in the facility that generate waste, and estimate the quantity of wastes that can be reduced through the implementation of various pollution prevention technologies. In this way, the obstacles faced by metal finishing facilities with respect to both identifying and evaluating pollution prevention technologies can be ameliorated.

# **Process Modeling**

In order to accomplish the goal of estimating waste generation, the tool must provide a model of the chemical processes involved in metal finishing. This requires the tool to implement a chemical process simulator. The key anticipated benefit of developing the simulator for use in metal finishing facilities would be the ability to readily utilize similar tools developed for use in the general chemical process industry. This is accomplished through the use of the CAPE-OPEN project's middleware standards.

The CAPE-OPEN project was initially conceived to develop, test, describe, and publish standards for the interfaces of various process simulation components.<sup>3</sup> Process simulation is becoming more vital for the synthesis, design, monitoring, and optimization of chemical and related processes. The main objective of the CAPE-OPEN project is to allow native components of a process simulator to be replaced with components from other simulators with minimal effort and as seamlessly as possible through the creation of standard interfaces for either Microsoft's Component Object Model (COM) or the Object Management Group's (OMG's) Common Object Request Broker Architecture (CORBA). The next step in the evolution of these technologies is web services. Web Services are essentially built around the COM and CORBA standards that enable objects on different computers to communicate, activate other objects, and share information using technologies such as the extensible markup language (XML) and simple object activation protocol (SOAP).

MFFP2T is being developed for the Microsoft Windows platform using Microsoft Visual Studio. The primary reasons for this are 1) the wide use of the Microsoft Windows Operating System, 2) the programming tools for COM development provided by Visual Studio, such as the Active Template Library, 3) the ability to utilize existing pollution prevention tools developed at the EPA such as the Waste Reduction (WAR) algorithm, and 4) the future ability to expand the program to include web-enabled technologies and real-time process monitoring that may be provided by third-party vendors. MFFP2T will consist of CAPE-OPEN compliant thermodynamics property package and material object, unit operation modules, and a simulation executive. Once these components have been developed, optimization routines can be created to evaluate processes. Because middleware standards were utilized in creating the components, standard function calls are available that allows add-on modules created by third parties to interact with the software.

# **Thermodynamic Models**

MFFP2T will utilize thermodynamic models to determine the oxidation/reduction (redox) state and pH of the solution, and whether a precipitate will be formed in any of the process tanks. Aqueous processes are governed by equations such as the solubility product of the salt, acid-base equilibrium, the Debye-Hückel equation, and the Nernst equation.

# Chemical Equilibrium

Chemical reactions do not always go to completion; rather they reach an equilibrium based on thermodynamic considerations. A general chemical reaction can be written in the following form:  $aA + bB \rightarrow cC + dD$ , where *a*, *b*, *c*, and *d* are stoichiometric coefficients for species A, B, C, and D. For a chemical or ionic equilibrium, such as the above reaction, the condition for chemical equilibrium is<sup>4</sup>:

$$a\mathbf{m}_{A} + b\mathbf{m}_{B} = c\mathbf{m}_{C} + d\mathbf{m}_{D}$$
 or  $\sum \mathbf{n}_{i}\mathbf{m}_{i} = 0$  (1)

where  $v_i$  is the stoichiometric coefficient of species i, and  $\mu_i$  is the chemical potential is defined as the partial molar Gibb's Free Energy of the species, or

$$\boldsymbol{m}_{i} = \left(\frac{\partial G}{\partial n_{i}}\right)_{T,P,n_{j\neq i}}$$
(2)

where  $n_i$  is the number of moles of species i.

In aqueous solutions, the chemical potential of a species is typically expressed in terms of its activity. The relationship between chemical potential and {A}, the activity of component A, is defined as follows:

$$\boldsymbol{m}_{A} = \boldsymbol{m}_{A}^{0} + RT \ln \{A\} \tag{3}$$

where  $\vec{m}_A$  is the reference state chemical potential of species A. Inserting Equation (3) into Equation (1) gives the following equation:

$$a\mathbf{m}_{A} + b\mathbf{m}_{B} - c\mathbf{m}_{C} - d\mathbf{m}_{B} = a\mathbf{m}_{A}^{0} + b\mathbf{m}_{B}^{0} - c\mathbf{m}_{C}^{0} - d\mathbf{m}_{B}^{0} + RT \ln\left(\frac{\{C\}^{c} \{D\}^{d}}{\{A\}^{a} \{B\}^{b}}\right) = 0$$
(4)

where R is the ideal gas law constant, T is the temperature, in Kelvin. The standard state chemical potential,  $\vec{m}$  is equal to the molar Gibbs Free Energy, or,

$$\mathbf{m}_{A}^{0} = \overline{G}_{A}^{0} \tag{5}$$

where  $\overline{G}_{A}^{0}$  is the Gibbs Free Energy per mole of the compound. Equation (4) can then be rewritten for a generalize reaction as:

$$\Delta \overline{G}_{rxn}^{0} = \sum_{i} \boldsymbol{n}_{i} \overline{G}_{i}^{0} = RT \ln \prod_{i} \{i\}^{\boldsymbol{n}_{i}}$$
(6)

where  $\Delta \overline{G}_{rxn}^0$  is the standard Gibbs Free Energy change of the reaction and {I} is the activity of species i. Based on this equation, an equilibrium constant (K) is defined as:

$$\ln K = -\frac{\Delta G_{rxn}^0}{RT} = \ln \prod_i \{i\}^{n_i}$$
(7)

The activity of each species in the solution is determined from the concentration of the species using the equation:

$$\{i\} = \boldsymbol{g}_i[i] \tag{8}$$

where {i} is the activity of species i,  $\gamma_i$  is the activity coefficient of species i, and [i] is the molar concentration of species i. The activity coefficient,  $\gamma_i$ , can be determined using the Debye Hückel equation: <sup>5</sup>

$$-\log \mathbf{g}_{i} = \frac{A z_{i}^{2} \mathbf{m}^{2}}{1 + B a_{i} \mathbf{m}^{2}}$$
(9)

where: A is a solvent constant having a value of 0.509 in water at 298K,

B is a solvent constant having a value of 0.328x10<sup>-8</sup> in water at 298K,

 $a_i$  is a constant related to the hydrated radius of the solute ion, approximately  $3.5 \times 10^{-8}$ ,

 $z_i$  is the charge of species i,

 $\mu$  is the ionic strength of the solution, calculated using the equation:

$$\boldsymbol{m} = \frac{1}{2} \sum_{i} c_i z_i^2 \tag{10}$$

where :  $c_i$  is the concentration of species i.

#### Salt Solubility

Most salts are only slightly soluble in water. A specific example is the precipitation of Iron (II) (or ferrous) phosphate, which can be written as:

$$Fe_3(PO_4)_2 \leftrightarrow 3 \cdot Fe^{2+} + 2 \cdot PO_4^{-3}$$

which indicates that three ferrous (Fe<sup>2+</sup>) ions and two phosphate (PO<sub>4</sub><sup>3-</sup>) ions are released by the dissolution of one molecule of ferrous phosphate. A solubility product ( $K_{sp}$ ) is defined for this reaction from Equation (7), as follows:

$$K_{sp} = e^{\left(-\frac{\Delta \overline{G_{ran}^0}}{RT}\right)} = \{Fe^{2+}\}^3 \{PO_4^{3-}\}^2$$
(11)

where  $\{Fe^{2+}\}$  is the activity of the ferrous ion, and  $\{PO_4^{3-}\}$  is the activity of the phosphate ion.

#### Acid-Base Chemistry

Acid-base reactions involve the movement of a Hydrogen ion ( $H^+$ ) between an acid and its conjugate base. An example would be the ionization of hydrogen chloride into hydrogen and chloride ions. Hydrogen chloride is a considered a strong acid because the ionization reaction goes to completion. Weak acids are acids that the ionization reaction does not go to completion, such as acetic acid (CH<sub>3</sub>COOH), which is ionized to the acetate ion (CH<sub>3</sub>COO<sup>-</sup>). The chemical equation for the ionization of acetic acid is:

# $CH_3COOH \leftrightarrow CH_3COO^- + H^+$

The resulting equation for the fraction ionized is as follows:

$$K_{a,CH_{3}COOH} = e^{\left(-\frac{\Delta \overline{G}_{ran}^{0}}{RT}\right)} = \frac{\{CH_{3}COO^{-}\}\{H^{+}\}}{\{CH_{3}COOH\}}$$
(12)

Another issue that must be considered is the fact that some acids, such as phosphoric acid,  $H_3PO_4$ , and carboxyllic acid,  $H_2CO_3$ , have multiple hydrogen ions that can be removed. The acid-base equilibrium can affect the solubility of the salt, by changing the proportion of an ion present in solution as pH changes. For example, calcium carbonate, which is typically present in water supplies, is soluble at low pH, but becomes insoluble at higher pH values. The pH at which calcium carbonate becomes insoluble is called pH<sub>s</sub>, and can be determined using the equation:

$$pH_{s} = pK_{a HCO_{2}^{-}} + pK_{so} + p[Ca^{2+}] + p[HCO_{3}^{-}]$$
(13)

where  $pK_{a,HCO_3^-} = 10.49$ , the negative log of the acid-base constant for bicarbonate to carbonate;  $pK_{SO} = 8.15$ , the solubility product of calcium carbonate (8.15);  $p[Ca^{2+}]$  is the negative log of the molar concentration of calcium ion; and  $p[HCO_3^-]$  is the negative log of the molar concentration of the bicarbonate ion. If the actual pH of the water (pH<sub>a</sub>) is greater than pH<sub>s</sub> then calcium carbonate will precipitate. The difference between pH<sub>a</sub> and pH<sub>s</sub> (pH<sub>a</sub> - pH<sub>s</sub>) is called the Langelier Index, and is typically kept slightly positive in city water supplies to reduce corrosion problems in the distribution system by creating a layer of calcium carbonate on pipes.<sup>5</sup>

#### *Coordination Chemistry*

Metal ions in solution often form complexes with ligands that may be present in the solution. Ligands are ions or molecules that form complexes with metals in solutions. For example, copper(II) forms a complex with ammonia (NH<sub>3</sub>) called amine copper complex,  $Cu(NH_3)^{2+}$ . The chemical reaction for the formation of this complex is:

$$\mathrm{Cu}^{2+} + \mathrm{NH}_3 \rightarrow \mathrm{Cu}(\mathrm{NH}_3)^2$$

Like solubility and acid-base reactions, this reaction is governed by an equilibrium constant called the formation or stability constant. The equation for the stability of this complex is:

$$K = e^{\left(-\frac{\Delta \overline{G}_{ran}^{0}}{RT}\right)} = \frac{\{Cu(NH_{3})^{2^{+}}\}}{\{Cu^{2^{+}}\}\{NH_{3}\}}$$
(14)

It should be noted that ammonia is a weak base, and its conjugate acid is the ammonium ion  $(NH_4^+)$ . For this reason, the amine copper complex would be present at higher solution pH where the ammonia is present as ammonia, not the ammonium ion.

# Oxidation/Reduction Chemistry

Oxidation/reduction, or redox reactions are the bread-and-butter of the electroplating processes. In a redox reactions, electrons are transferred from one species to another. The redox reaction is typically divided into two half cells, an oxidation half cell where a reactant is oxidized (loses electrons) and a reduction half cell where a reactant is reduced (gains electrons). Equilibrium in redox reactions is determined using the Nernst equation:

$$E = E^0 - \frac{RT}{nF}Q \tag{15}$$

where E is the cell's equilibrium electrical potential,  $E^0$  is the standard electrode potential of the cell, and Q is the reaction quotient. Cell potential and Gibb's Free Energy are related through the following equation:

$$\Delta \overline{G} = -nFE \tag{16}$$

#### *Equilibrium Calculations*

The above discussion shows that chemical equilibrium calculations can be made for solutions used in the electroplating process based upon thermodynamic considerations. Typically, solutions will have precipitation, acid-base, complexation, and redox reactions occurring simultaneously. In order to calculate the equilibrium concentration for each species present, a set of simultaneous equations can be created and solved. Once the resulting concentrations are determined, the quantity of solids generated in the material can be estimated using a material balance around the tank.

#### **Parts Plating**

Electroplating occurs by formation of a metal atom from a metal ion, causing the deposition of the atom onto the electrode. A typical reaction might be the deposition of copper from a copper(II) sulfate solution onto an electrode. The chemical equation for this reaction would be:

$$\operatorname{Cu}_{aq}^{2+} + \operatorname{SO}_{aq}^{2} + 2e^{-} \rightarrow \operatorname{Cu}_{(s)}^{0} + \operatorname{SO}_{4}^{2-}$$

In this reaction, the sulfate ion does not participate in the reaction, and is called a spectator ion. Further, for each copper atom reduced, two electrons are required. The reaction rate can be determined from the current

(charge, or number of electron, per time). As discussed above, there is an equilibrium potential between an electrode and a solution of the ions, which can be calculated using the Nernst equation. In an electroplating tank, electrical voltage is applied, resulting in a current flow and the deposition of metal onto the electrode. The difference between the applied voltage and the cell voltage is called the overpotential  $(\eta)$ .

The overpotential results in an electrical current flowing through the cell, plating metal onto the cathode. The electrical current is typically in terms of the area of the electrode, which is called the current density (i). By knowing the current density, the area of electrode, and the number of electrons required to convert the metal ion in solution to metal atoms on the electrode, the plating rate for the metal can be determined. The Tafel equation is commonly used to relate overpotential to the current density, using the following relationship:<sup>6</sup>

$$\boldsymbol{h} = a + b \log i \tag{17}$$

where a and b are empirical constants.

The overpotential is typically separated into four components: charge transfer ( $\eta_{ct}$ ), diffusion ( $\eta_{d}$ ), reaction ( $\eta_{r}$ ), and crystallization ( $\eta_{c}$ ) overpotentials, as shown in the following equation:

$$\boldsymbol{h} = \boldsymbol{h}_{ct} + \boldsymbol{h}_{d} + \boldsymbol{h}_{r} + \boldsymbol{h}_{c} \tag{18}$$

One of these overpotentials, typically the diffusion overpotential typically limits. In the case where diffusion limits the current density, the Cottrell equation is used to determine the current density, as follows:

$$i_{d} = nFA \frac{Dc}{\sqrt{\mathbf{p}t}}$$
(19)

where  $i_{t}$  is the diffusion limited current density, n is the number of electrons required, F is Faraday's constant, A is the surface area of the part, D is the diffusion coefficient of the metal ion in water, c is the concentration of the metal ion in the solution, and t is the time.

# **Parts Cleaning**

Cleaning operations are typically carried out using alkaline cleaners (e.g. surfactants, phosphates, sodium hydroxide) and/or solvents. Acid cleanings are used to remove metal oxides from the surface of the part, which provides a more active, rough surface, improving the adherence of the plated metal.

Solvents are compounds which are typically liquid at room temperature and atmospheric pressure that are able to dissolve other substances without chemically changing the dissolved substance. The dissolved substance is called the solute and the mixture of the solvent and solute is called a solution. Ideal solvents generally have the following properties:<sup>7</sup>

- 1. Clear and colorless
- 2. Volatile without leaving a residue
- 3. Good long-term chemical stability
- 4. Does not react
- 5. Slight or pleasant odor
- 6. Anhydrous
- 7. Constant physical properties meeting manufacturer's specifications
- 8. Low toxicity
- 9. Biodegradable
- 10. Low cost

Solvents are of concern in pollution prevention because they are generally regulated as hazardous wastes, having United States Environmental Protection Agency waste numbers F001, F002, F003, and F005 (40 CFR 261). These waste classifications consist of compounds such as: tetrachloroethene, trichloroethene, methylene chloride, 1,1,1-trichloroethane, fluorochlorocarbon, benzene, ethylbenzene, xylene, toluene, acetone, and ethyl acetate. These compounds can be divided into three general classes, (1) chlorinated solvents, (2) hydrocarbon solvents, including aromatic compounds, and (3) compounds containing oxygen, such as ketones, alcohols, esters, and ethers. Waste classification of spent (used) solvents are dependent on type of solvent and how the solvent was used. Disposal of spent solvents has become more expensive because of the land disposal restriction imposed by the Resource Conservation and Recovery Act (RCRA) in the 1970s.

Solvents have a variety of uses. Painting and coating are the largest use of solvents, accounting for nearly half of the solvents used in the United States. In solvent-based paints and coating, the solvent provides solubilization of some of the paint components, reduces the paint's viscosity, wets the surface to which the paint is being applied, promotes adhesion, and enhances gloss. The solvent functions as a carrier for the coating during application; and solvent is typically added to coating to meet the viscosity requirements of the application technique. Once the coating has been applied, the solvent that did not evaporate during application evaporates, causing a film to form on the surface. Finally, the presence of the solvent in the applied coating can soften the primer (underlying) coatings, increasing adhesion<sup>7</sup>. With the Clean Air Amendments of 1990, solvent use has been restricted, often requiring the use of low solvent coatings and/or emissions controls when coatings are applied. Solvents used in coating processes are typically discharged to air and are may result in air permitting requirements for facilities.

Solvents used for cleaning are primarily halogenated solvents, including trichloroethene and tetrachloroethene. Tetrachloroethene, also known as perchloroethylene or "PERC," is common in dry cleaning, accounting for 80 percent of the dry cleaning solvents used, because it exhibits good solvency, easy recovery, and is not flammable. Additionally, tetrachloroethene is not very volatile and can be easily recovered from air emissions from the cleaning operation.<sup>8</sup>

Cleaning operations also include degreasing of parts. Again, chlorinated solvents are favored in this use because they are good solvents of grease and are not flammable. Most degreasing had historically been conducted with mineral spirits, but, due to flammability, the use of mineral spirits has been reduced. 1,1,1-Trichloroethane has historically been widely used in vacuum degreasing due to its low boiling point, however, it was regulated under the 1990 Clean Air Act as a ozone-depleting substance, prohibiting its production, so interest in trichloroethene for that use is increasing.<sup>8</sup> The hydrocarbon solvents, except toluene, are typically blends of a variety of compounds selected specifically for the proposed use. The specified parameters include boiling point range, solvency (aniline cloud point), specific gravity, and flash point. The composition of these solvents differ by manufacturer, therefore, even though two solvents can meet the same set of specifications, their chemical composition can vary greatly from manufacturer to manufacturer.<sup>8</sup> Halogenated and aromatic solvents have been identified as suspect human carcinogens, increasing the hazards associated with their use and disposal. These chemicals are widely used by small businesses, which are typically exempt from RCRA Hazardous Waste regulations as small quantity generators. This may result in environmental contamination from improper disposal, which is a rapidly-growing concern.

As with equilibrium considerations, above, the solubility of a solute in a solvent can be determined from thermodynamic considerations. For a solvent and solute to be miscible, the Gibb's free energy of mixing must be negative, or:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S < 0 \tag{20}$$

where  $AG_{mix}$  is the free energy of mixing,  $AH_{mix}$  is the enthalpy of mixing, T is temperature in degrees Kelvin and  $AS_{mix}$  is the entropy of mixing. The enthalpy of mixing is based upon regular solution theory, which states that the mixing enthalpy is calculated from the interaction of contacting atoms.<sup>9</sup> In the case where molecular interactions such as hydrogen bonding are present,  $AH_{mix}$  is proportional to the difference in the squares of the values of the Hildebrand solubility parameters for the solvent and solute,  $a_1$  and  $a_2$ , respectively. The value of the  $(a_1 - a_2)^2$  or  $a^2$  is the cohesive energy density (CED), which is the ratio of the molar energy of vaporization, AE, to the molar volume, V:

$$d^2 = \frac{\Delta E}{V} \tag{21}$$

The molar energy of vaporization is the energy that holds the molecules together, and is therefore a measure of the intermolecular energy. Because the  $(\ddot{a}_1 - \ddot{a}_2)$  term is squared, the difference between  $\ddot{a}_1$  and  $\ddot{a}_2$  always contributes significantly to a positive  $\ddot{A}H_{mix}$ , and must be balanced by a greater value in the entropy term.

Hansen (1967) recognized that the interactions of different types exist between the solute and solvent including dispersive (non-polar), polar, and hydrogen bonds. Hansen expressed the solubility parameter for the solvent and solute as:<sup>10</sup>

$$\boldsymbol{d}^2 = \boldsymbol{d}_d^2 + \boldsymbol{d}_p^2 + \boldsymbol{d}_h^2 \tag{22}$$

The values of  $\ddot{a}_d$ ,  $\ddot{a}_p$ , and  $\ddot{a}_h$ , are the cohesive energy density components due to dispersive, polar, and hydrogen bond interactions, respectively. These components of the cohesive energy density can be used to define an additional parameter,  $R_{AO}$ , the radius of the "solubility sphere" for the solute. Chemicals having cohesive energy densities that lie within the solubility sphere of the solute are solvents and outside the solubility sphere are not. In order to determine if a liquid is a solvent, the distance from the solvent's cohesive energy density to that of the solute,  $R_A$ , is calculated as follows:

$$R_A^2 = \left(2\boldsymbol{d}_{d.Solute} - 2\boldsymbol{d}_{d,solven}\right)^2 + \left(\boldsymbol{d}_{p.Solute} - \boldsymbol{d}_{p,solven}\right)^2 + \left(\boldsymbol{d}_{h.Solute} - \boldsymbol{d}_{h,solven}\right)^2$$
(23)

Solubility parameters for many solvents are listed in Table 1.

# **Parts Rinsing**

Rinsing is conducted after each step of the plating process prior to the next operation. A thorough rinse is required to prevent dragged out chemicals from one step from contaminating the chemical baths used in the subsequent processes. Contamination of a plating bath may render it unable to carry out its process and would result in it requiring replacement.

Gong *et al*<sup>11</sup> developed general models for cleaning/rinsing systems for barrel plating processes. Cleaning/rinsing steps are used to remove different kinds of dirt and chemical residues from the object to be plated. The operational efficiency of the cleaning step largely determines plating quality. Further, rinse efficiency can not only cut operating costs for plating operations, but can also reduce the costs for chemicals used in waste treatment.<sup>12</sup> In practice, rinse times are set conservatively to ensure proper rinsing because process dynamic behavior is not well known.<sup>11</sup> The process uncertainties not only limit the ability to increase process efficiency, but result in greater chemical and water usage through overcleaning and extended rinsing. Chemical concentration greater than optimal may lead to increased operational costs resulting from greater sludge and wastewater generation. Most plating plants generate more sludge than necessary (avoidable sludge) as a result of improper use of chemicals, high flow rate of rinse water, excessive drag-out into rinsing tanks, and unnecessary dumping .<sup>12</sup> The total amount of sludge generated in a cleaning process per day  $(S_T)$  is the sum of the amount of dirt removed from the part  $(S_d)$ , and chemicals used to remove the dirt  $(S_c)$ . In the rinse tank, the amount of sludge generated should consider both sludge resulting from impurities in the rinse waster  $(S_w)$ , and the sludge resulting from drag-out from the cleaning tank  $(S_g)$ . These individual sludge generation rates are calculated as follows:<sup>12</sup>

$$S_{d} = \sum_{i=1}^{N_{b}} \left( A_{i} \sum_{j=l}^{N_{d}} W_{c_{i,j}} \right)$$
(24)

$$S_{c} = \sum_{i=1}^{N_{b}} \left( A_{i} \sum_{j=l}^{N_{d}} \frac{W_{c_{i}} k_{c_{j}}}{m_{j}} \right)$$
(25)

$$S_g = \sum_{i=1}^{N_b} \left( A_i D_g \right) \tag{26}$$

$$S_w = k_w k_{pw} F_w \tag{27}$$

where:  $A_i$  = total surface area of the  $i^{th}$  barrel of parts,  $cm^2$ 

 $k_c$  = the precipitation constant for the j<sup>th</sup> cleaner, g-sludge/L-cleaner

 $N_b$  = the number of barrels processed per day, barrels per day

 $N_d$  = the number of types of dirt on the surface of the parts

 $W_{c_{i,j}}$  = the amount of the j<sup>th</sup> kind of dirt removed from the surface of the parts in the i<sup>th</sup> barrel, gdirt/cm<sup>2</sup>

 $\mu_i$  = the dirt removal capacity of the j<sup>th</sup> cleaner, g-dirt/L-cleaner

 $D_{g}$  = the drag-out rate of cleaning chemicals from cleaning tanks to rinse tanks

 $k_{pw}$  = the precipitation constant for the rinsewater, g-sludge/g-contaminant

 $k_w$  = hardness of the rinsewater, g-contaminant/cm<sup>3</sup>

 $F_w$  = volumetric flow rate of make-up and fresh water into rinsing system, cm<sup>3</sup>/day

The cleaning process occurs by the removal of particles or oils from the surface of the object to be plated. Cleaning is accomplished by applying mechanical, chemical, thermal, electrical, and/or radiation energy to the object to be cleaned to remove the dirt. The cleaning process occurring in a cleaning bath can be described by the following equation:<sup>11</sup>

$$A_{i} \frac{d W_{c_{i}}(t)}{dt} = -g_{c}(t) C_{a}(t) W_{c_{i}}(t)$$
(28)

In this equation, the amount of dirt removed from the i<sup>th</sup> barrel of parts ( $W_{c_i}(t)$ ) is related to the looseness of the dirt on the part ( $\gamma_c$ ) and the concentration of the chemicals in the cleaning solution ( $C_a$ ). The looseness of the dirt ( $\gamma_c$ ) is a function of a kinetic constant, ( $\gamma_0$ ) and the time that the barrel is in the solution, as follows:

$$\boldsymbol{g}_{c}(t) = \boldsymbol{g}_{0}\left(1 - e^{-\boldsymbol{a}(t-t_{0})}\right)$$
(29)

The amount of chemical in the tank changes as the chemical is dragged out, or make-up chemical is added, as follows:

$$V_{c} \frac{dC_{a}}{dt} = k_{d} A_{i} (C_{0}(t) - C_{a}(t)) - \frac{A_{i} W_{ci}(t)}{m} + w_{c}$$
(30)

where  $V_c$  is the volume of the cleaning tank. Water consumption in a rinse tank depends on the amount of cleaning chemicals and associated dirt remaining on the part following removal from the cleaning tank, and can be calculated as follows:

$$A\frac{dW_{r_i}(t)}{dt} = -r_{r_i}(t) \tag{31}$$

$$V_r \frac{dx_r(t)}{dt} = r_r(t) + F_w(z_r(t) - x_r(t))$$
(32)

$$r_{r_{i}}(t) = k_{r} g_{c} \left( q \left( W_{r_{i}}(t) - W_{c_{i}}(t_{e}) \right) \right) - x_{r}(t)$$
(33)

where:  $k_r = mass transfer coefficient$ ,

 $r_{r}(t) = \text{dirt removal rate in rinse tank at time t, g/min}$ 

V<sub>r</sub> =volume of the rinse tank, liters

 $W_{\rm r}(t)$  = the amount of dirt on the surface of the parts in the rinse tank at time t, g-dirt/cm<sup>2</sup>

 $W_{c_i}(t_e)$  = the amount of dirt removed on the parts leaving the cleaning tank when leaving the rinse tank at time t<sub>e</sub>, g-dirt/cm<sup>2</sup>

 $x_r$  = pollutant concentration in rinsewater, g/cm<sup>3</sup>

 $z_r(t)$  = pollutant concentration in the make-up rinsewater, g/cm<sup>3</sup>

 $\theta$  = conversion factor, cm<sup>2</sup>/cm<sup>3</sup>-water

# **Discussion and Conclusions**

This paper presents the mathematical models for the electroplating process that will be incorporated by the USEPA into MFFP2T. These models evaluate the thermodynamics of aqueous equilibrium, the rate of metal deposition onto the electrode in plating tanks, and the interaction between solvents and dirts on parts in parts cleaning operations.

Once the process model has been completed and verified, further algorithms to minimize the quantity of wastes generated will be prepared. Currently, the EPA has developed tools that evaluate process waste to determine waste toxicity (the WAR algorithm) and suggest alternate solvents (PARIS II). These programs can potentially be modified for use in MFFP2T through the establishment and use of middleware standards for environmental simulation packages.

SOLVENTS	COHESIVE ENERGY DENSITIES (ä) (MPa <sup>1/2</sup> )		
	ä <sub>d</sub>	äp	ä <sub>h</sub>
Acetic acid	14.5	8.0	13.5
Benzene	18.4	0.0	2.0
Toluene	18.0	1.4	2.0
Ethylbenzene	17.8	0.6	1.4
o-xylene	17.8	1.0	3.1
2,2,4 trimethyl pentane (iso-octane)	14.3	0.0	0.0
Naphthalene	19.2	2.0	5.9
n-Butane	14.1	0.0	0.0
n-Pentane	14.5	0.0	0.0
Isopentane	13.7	0.0	0.0
n-Hexane	14.9	0.0	0.0
n-Octane	15.5	0.0	0.0
n-Nonane	15.8	0.0	0.0
n-Decane	15.8	0.0	0.0
n-Dodecane	16.0	0.0	0.0
n-Hexadecane	16.4	0.0	0.0
Cyclohexane	16.8	0.0	0.2
Methylcyclohexane	16.0	0.0	1.0
Trichloroethene (TCE)	18.0	3.1	5.3
Tetrachloroethene (PERC)	19.0	6.5	2.9
Water	15.6	16.0	42.3
Motor oil-SAE 20W	14.7	0.4	0.4

Table 1. Solubility Parameter for Liquids at 25C.<sup>13</sup>

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