Best Practices

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Rinsewater Quality in Immersion Rinsing

Rinsing is, in concept, one of the simplest of all critical surface finishing practices. However, most operations fail to optimize fully their rinsing practices. Effective rinsing is critical to product quality and efficient rinsing is critical to overall operational efficiency. Surface finishing wastewater is typically greater than 90% rinsewater, with scrubber blowdown and concentrated bath dumps making up the balance of generated wastewater. Wastewater treatment costs are a function of hydraulic and mass loading, waste stream segregation and pretreatment (oxidation/reduction, oil separation, etc.) requirements. I will discuss mass loading, waste stream segregation and pretreatment in future columns. Hydraulic loading can be primarily controlled with good rinsing practices. Obviously, drag-out control is also critically important to cost-effective rinsing but that will also be discussed in detail in another column.

Rinsing serves the following functions:

1. Stops a chemical reaction between solution drag-out and the part substrate (etching, chromating, bright dipping, etc.) and,
2. Minimizes drag-in of incompatible chemistry from the previous process to the following process, if the rinse is an intermediate process step, or,
3. Minimizes drag-out residue left on the part after drying, if the rinse is a final process step.

Rinsewater quality

Logically derived rinsewater quality limits are essential to effective and efficient rinsing. If rinsewater flow rates are too low relative to drag-in, then product quality suffers. If rinsewater flow rates are too high, then water and wastewater treatment costs become exorbitant. In many operations, rinsewater quality limits are arbitrarily derived or nonexistent. Flow restrictors control concentration indirectly and cannot be considered a reliable rinsewater quality control, unless flow can be correlated to drag-in and production levels are steady. In my consulting practice, I often ask for rinsewater quality standards and get "all rinses have five gpm flow restrictors." That is not a rinsewater quality standard. Alternatively, "all rinses have conductivity controllers set to 500 μS/cm." That is an arbitrary rinsewater quality standard.

Conductivity or its corollary total dissolved solids (TDS) is the most common measure of rinsewater quality. A conductivity sensor measures how much electricity is being conducted through a centimeter of water. Specific conductivity of water and rinsewater is expressed in micromhos (microsiemens) (μS/cm).

Alternatively, conductivity can be correlated to specific rinse constituents, such as Ni, Cu, CN, Cr, Ag, Au, etc. The calibration is greatly simplified if the water feed is pure water.

To convert the electrical conductivity of a water sample (μS/cm) into the approximate concentration of total dissolved solids (ppm), the μS/cm is multiplied by a conversion factor. A value of 0.5 is commonly used as an approximation if the actual factor is not known:

$$\text{TDS (ppm)} = \text{Conductivity } (\mu\text{S/cm}) \times 0.5] \qquad (1)$$

One μS/cm is equivalent to approximately .5 ppm TDS.

Figure 1 provides an illustration of two sequential processes. Drag-out from the second and final rinse of "Process 1" is drag-in to "Process 2," and, if the chemistry in "Process 1" is incompatible with "Process 2," then contaminants are introduced through drag-in. In order to manage this contamination source, it is important to set a concentration limit on the second and final rinse of "Process 1."

Example I:

If "Process 1" is a hydrochloric acid pickle process and "Process 2" is a cadmium cyanide plating process, then it is important to avoid dragging acid into the cadmium plating solution. Chloride can also react at the steel anodes in the cadmium solution and generate chlorine gas. This will etch the steel, introducing iron into the solution. The concentration of the second and final rinse after hydrochloric acid pickling should be maintained at ≤ 50 ppm TDS in order to minimize drag-in of contaminants to cadmium cyanide plating. If parts leaving cadmium cyanide plating are handled by operators prior to hydrogen embrittlement relief baking then the second and final rinse after cadmium cyanide plating is important to control staining after drying AND it is important to control the exposure of operators to residual cyanide during part handling and the final rinse should be maintained at ≤ 10 ppm TDS.

Example II:

If "Process 2" is a Watts nickel solution, then chemistries of "Process 1" and "Process 2" are compatible, and the concentration of the second rinse after hydrochloric acid pickling could be maintained at ≤ 500 ppm TDS without impacting nickel plating. The second rinse after nickel plating should be maintained between 10 and 50 ppm TDS, depending on the following process (hot water rinse, drying, chromium plating, etc.).

Example III:

If "Process 1" is a cadmium cyanide plating process and "Process 2" is a chromate solution, then it is important to avoid dragging cyanide into the chromate solution. The concentration of the second rinse after cadmium cyanide plating should be maintained at ≤ 25 ppm TDS, in order to minimize drag-in of contaminants to

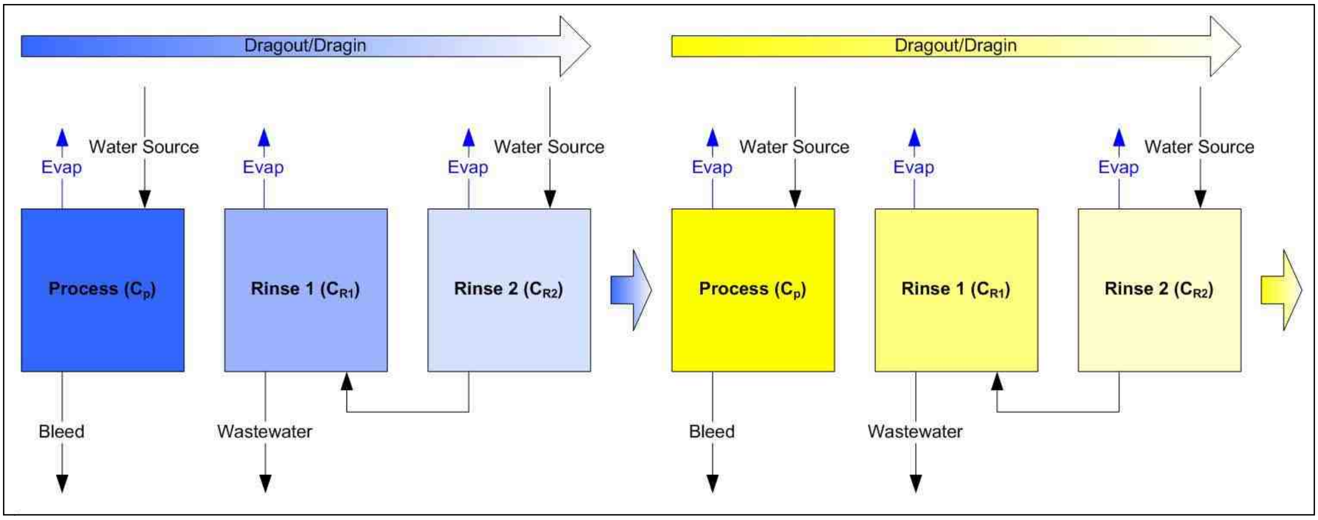

Figure 1—Rinsewater quality.

the chromate process. It is also important to maintain the concentration of the second rinse after chromating at ≤ 25 ppm TDS, in order to control staining after drying and assure part quality, AND it is also important to control the safety of operators handling parts with residual chromate. In this example, it is also important to control the concentration of the first rinse after chromating as well, because the chromate will continue to react with the substrate if the concentration is too strong.

These examples are not presented as a rinsewater quality prescription but rather to illustrate the logic of thinking through rinsewater quality standards.

Basic rinse expression

The basic expression which defines the calculation of single and countercurrent rinse parameters is shown in Equation 2. This is the classic steady state rinse equation. Steady state simplifies the mathematics and the results are accurate enough for our purposes. This is, however, an approximate expression. Equation 2 is further simplified by assuming that the rinses are perfectly mixed:

$$F_n = D\,(C_p/C_{rn})^{1/n} \qquad (2)$$

where F_n is the feed water flow rate to the nth rinse, C_p is the concentration of the process tank(s), C_{rn} is the rinse concentration in the nth rinse tank, and n is the number of rinse tanks. The rinse equation calculates the flow to the nth rinse tank. If the flow is known and the concentration in the nth rinse is unknown then Equation 2 can be rearranged as Equation 3 to calculate the concentration of the nth rinse:

$$C_{rn} = C_p/(F_n/D)^{1/n} \qquad (3)$$

C_p/C_{rn} is the dilution ratio and F_n/D, or F/D, is the rinse ratio. Effective rinsing requires control of the dilution ratio. In a single stage rinse, if drag-in = 1, then C_p/C_{rn} and F/D are equivalent.

Efficient rinsing requires control of drag-in, and the rinse ratio and countercurrent rinsing is the classic technique used to manage the rinse ratio. Spray rinsing is another technique for increasing rinse efficiency. However, effective spray rinsing requires the part geometry to be relatively simple, as spray rinsing is essentially line-of-sight. Figure 2 illustrates a simple process with two countercurrent rinses and n = 2, while Fig. 3 illustrates the cascading impact of imperfect rinsing on rinsing effectiveness and efficiency.

Factors which impact immersion rinse efficiency are rinse dwell time, tank design, agitation, temperature and part complexity. Figure 4 illustrates the importance of rinse tank design on rinsing efficiency.

Water quality

The basic rinse equation assumes that water feeding the nth rinse in a series of one to n rinses is pure. Water contaminants in the feed water increase the actual feed water flow rate required to maintain the target nth rinse concentration limit. Water quality is normally measured in conductivity or resistivity units.

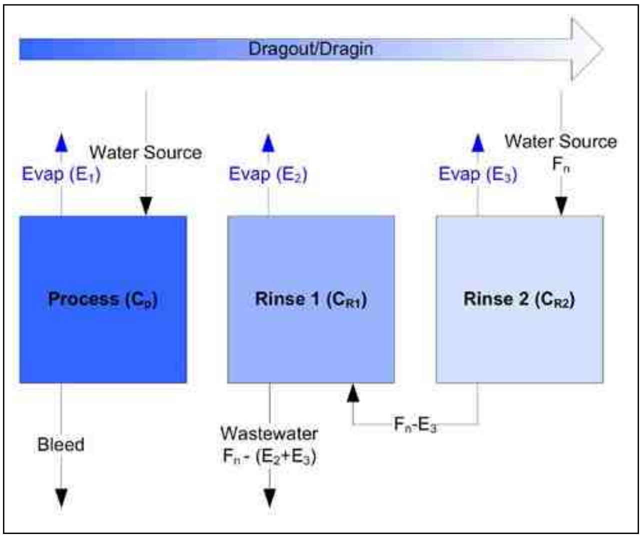

Figure 2—Countercurrent rinsing.

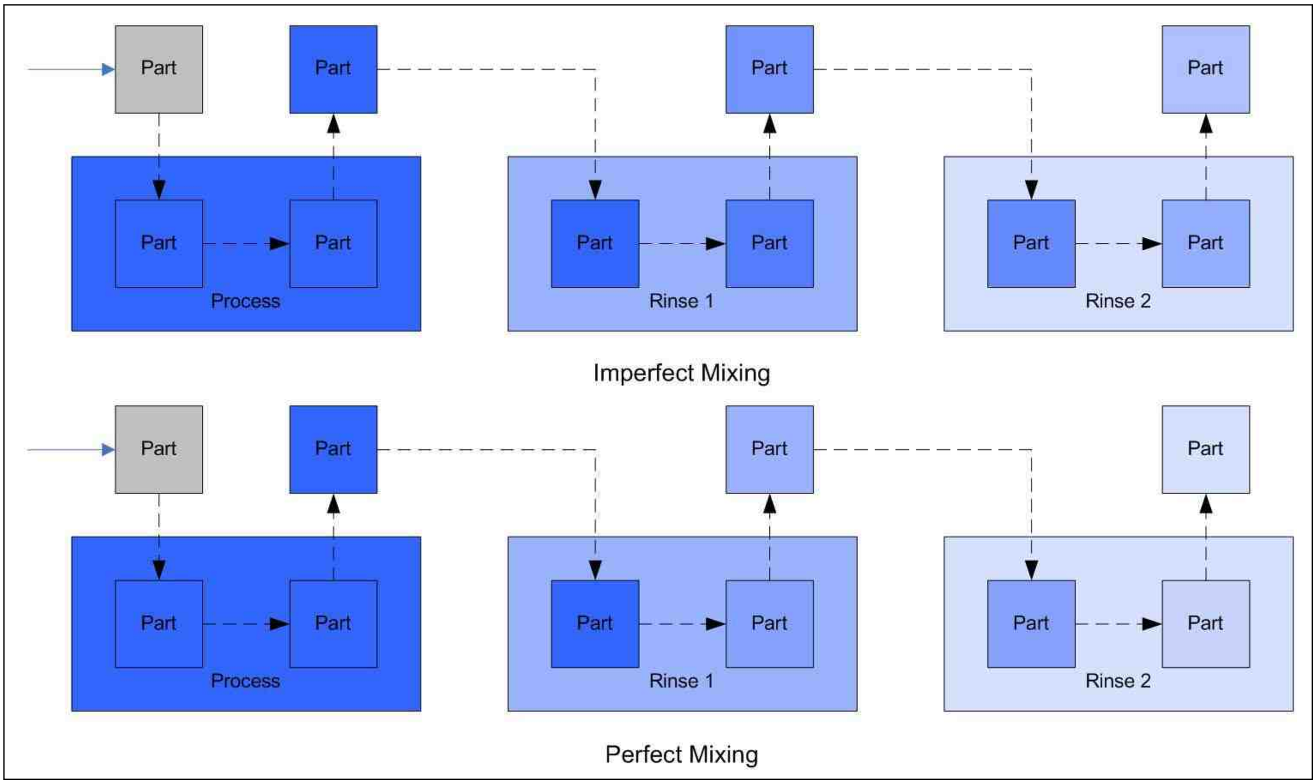

Figure 3—Illustration of the impact of mixing on rinsing.

Since conductivity varies with temperature, it is also necessary to correct the readings for changes in temperature. Most conductivity instruments contain circuits that automatically compensate for temperature and correct the readings to a standard 25°C. Figure 5 illustrates the relationship between water conductivity and resistivity.

I hope it is obvious that the quality or concentration of the water feed must be less than the target rinse quality. In order to calculate rinse flow with impure feed water, the water source TDS (TDS_w) is added to the rinse target TDS (TDS_p) where,

$$C_{rn} = \mathrm{TDS}_p + \mathrm{TDS}_w. \tag{4}$$

The results are reasonably close until the incoming water TDS begins to converge on the target rinse TDS. If the feed water quality is very low (high TDS) however, an iterative approach is required where the estimated flow is adjusted (increased) to converge on the target TDS_t where,

$$\mathrm{TDS}_t = \mathrm{TDS}_p + \mathrm{TDS}_w. \tag{5}$$

It is also important to understand that city and well water feeds contain contaminants (Cl, F, Ca, Mg, Fe, Cu, Zn, Si, etc.) that may impact processes, and high quality process water (≤ 1 μS/cm) is recommended for most rinsing applications.

Process Concentration and Drag-out

Drag-out is estimated from the production rate in ft^2/day or m^2/day and is adjusted by a factor for the wetted area of the production in Equation 6;

$$D = \text{[drag-out factor] [production factor] [wetted area factor]}, \tag{6}$$

where the drag-out factor is expressed in drag-out/1000 ft^2 or drag-out/100 m^2. The production factor is expressed as total ft^2 of production/hr. The wetted area factor is expressed as:

Wetted area factor =

$$\frac{\text{[production ft}^2\text{/hr + other wetted area ft}^2\text{/hr (for barrels, racks and fixtures)]}}{\text{(production ft}^2\text{/hr).}} \tag{7}$$

Rinse concentration

Equation 2 can be used to estimate the rinse flow based on the concentration in the process tank (C_p), the target concentration in the final rinse (C_{rn}) and the drag-out rate (D) (Eq. 6). The concentration of each rinse preceding the final (n^{th}) rinse can be calculated by rearranging Equation 2 as Equation 6, where C_p equals the process concentration of the drag-in to each tank in sequence as shown below. F_n and D and C_p are already defined. The 1/n exponential term disappears in each equation because we are calculating concentration with a single rinse (1/n = 1 and any number raised to the first power is that number).

$$F_n = D\,(C_p/C_{rn})1/1 = D\,(C_p/C_{rn}) \tag{8}$$

Equations 9, 10 and 11 are rearrangements of Equation 8 and show how the flow defined in Equation 2 is used to calculate the concentration in each rinse.

$$C_{r1} = C_p\,D/F_n \tag{9}$$

$$C_{r2} = C_{r1}\,D/F_n \tag{10}$$

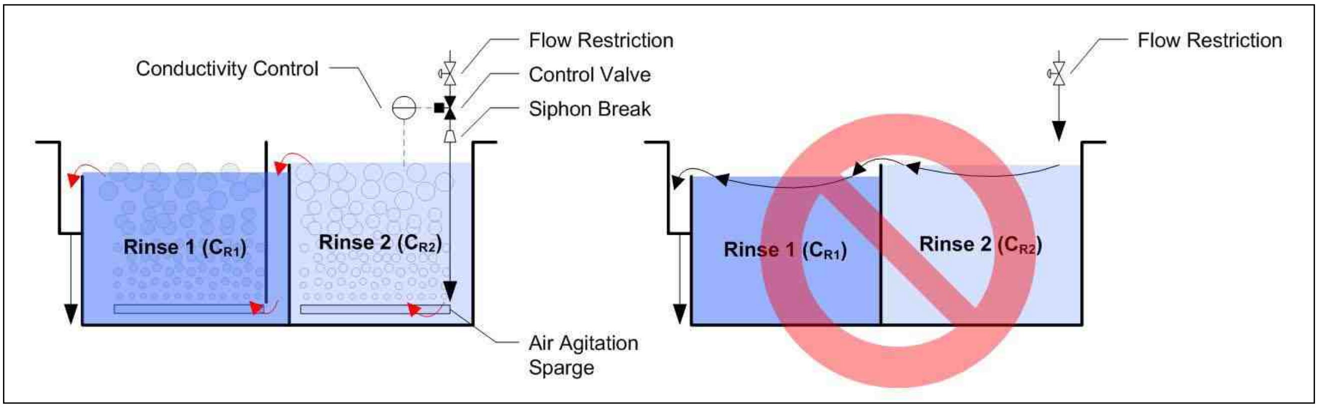

Figure 4—Rinse tank design.

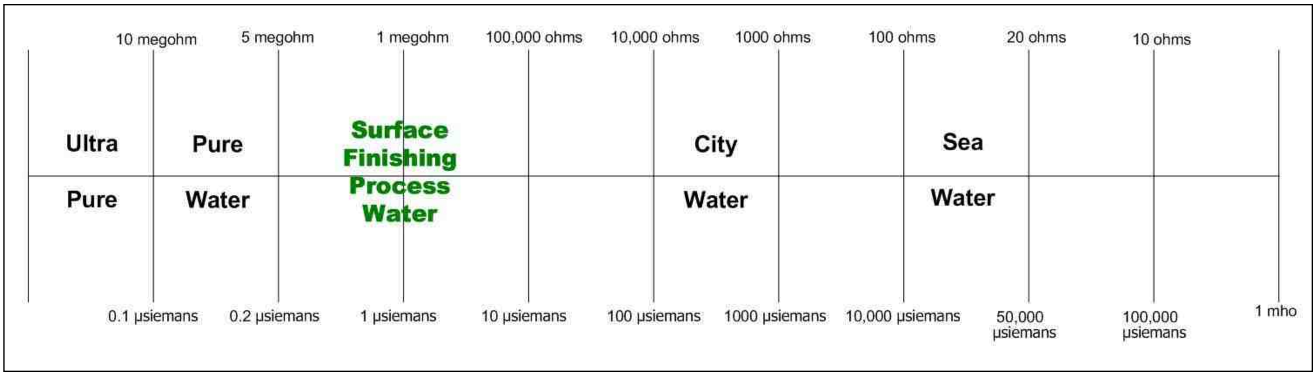

Figure 5—Conductivity vs. resistivity.

$$C_{rn-1} = C_{rn-2}\, D/F_n \qquad (11)$$

where C_{r1}, C_{r2} and C_{rn} are the concentration in the first, second and n^th^ rinses. Notice that C_{r1} replaces C_p in Equation 10. In Equation 11, the concentration in rinse n-1 is calculated using the concentration in rinse n-2. The concentration in the n^th^ rinse is calculated first (Equation 3) and there is no practical limit to the number of rinses possible.

The impact of other rinse parameters on calculations

The basic rinse relationship (Eq. 2) must be modified to account for other conditions that affect rinsing. These conditions include the influence of rinse evaporation on rinse flow and concentration and the influence of mixed chemistry processes (*i.e.*, multiple process tanks of different chemistry and/or concentration sharing the same rinses).

Multiple process tanks

It is common practice in surface finishing facilities that related process tanks often share the same rinse tanks. The following two scenarios are common:

1. Multiple process tanks of same or different size but of identical chemistry and concentration. The production rate (and drag-out) can be different in each tank.

2. Multiple process tanks of same or different size with different chemistries and/or concentrations can share these rinses.

Multiple process tanks affect the rinses based on their relative concentration and the production rate (and the drag-out created). Identical processes are the simplest to model because they behave essentially identical to a single process tank. Multiple process tanks of different chemistry and/or concentration (mixed processes) are more complex, and the chemistry is normalized as TDS for all rinse calculations. If a process is composed of n different process tanks, then the weighted average of the total process TDS is used to calculate an average process TDS for rinse calculations. The weighting fraction is derived from the relative production rate for each process.

For example, consider three process tanks sharing the same rinses with the following process concentrations (C) and production rates (X)

- Process 1 (P1): TDS 100 g/L, production 500 ft^2/day
- Process 2 (P2):TDS 250 g/L, production 100 ft^2/day
- Process 3 (P3):TDS 50 g/L, production 400 ft^2/day.

Then:

$$C_p = C_{avg} = C_1\,(X_{P1}/X_{total}) + C_2\,(X_{P2}/X_{total}) + C_3\,(X_{P3}/X_{total}) \qquad (12)$$

$= 100\text{ g/L }(500\text{ ft}^2/1000\text{ft}^2) + 250\text{ g/L }(100\text{ft}^2/1000\text{ft}^2) + 50\text{ g/L }(400\text{ ft}^2/1000\text{ ft}^2)$
$= 100\text{ g/L }(0.5) + 150\text{ g/L }(0.1) + 50\text{ g/L }(0.4)$
$= 85\text{ g/L}.$

The actual rinse calculations are otherwise identical.

Rinse evaporation

The actual or effective rinse flow rate is also affected by evaporation in the rinse tanks. Rinse evaporation can be significant in some environments, and the impact can also be significant if the rinsewater flow is small relative to the evaporation rate. If evaporation is > 5% of rinsewater flow, then it should be considered in rinse calculations. If evaporation is not compensated for, then the effective flow will be less than the required flow. If evaporation is compensated for, then the total flow will be increased by total rinse evaporation. Equation 13 shows that the total flow (F) to the nth rinse is the sum of the required rinse flow and the flow to make up for evaporation loss.

$$F_{TOTAL} = F_n + F_{E1} + F_{E2} + \ldots + F_{En} \tag{13}$$

where, E = evaporation and F_{En} = evaporation makeup for the nth rinse.

The actual concentration of each rinse tank is also impacted by evaporation.

Equations 9 thru 11 are rearranged as Equations 14 thru 17 to show the effect of increasing flow to compensate for rinse evaporation.

$$C_{r1} = C_p\, D/F_n \tag{14}$$

$$C_{r2} = C_{r1}\, D/(F_n + F_{E1} \tag{15}$$

$$C_{rn-1} = C_{rn-2}\, D/(F_{TOTAL} - F_{En}) \tag{16}$$

$$C_{rn} = C_{rn-1}\, D/F_{TOTAL} \tag{17}$$

Equations 18 thru 21 show the effect of rinse evaporation on rinse concentration without increasing rinsewater flow to compensate for evaporation losses.

$$C_{r1} = C_p\, D/[F_n - (F_{E1} + F_{E2} + \ldots + F_{En})] \tag{18}$$

$$C_{r2} = C_{r1}\, D/[F_n - (F_{E2} + \ldots + F_{En})] \tag{19}$$

$$C_{rn-1} = C_{rn-2}\, D/[F_n - (F_{En-1} + F_{En})] \tag{20}$$

$$C_{rn} = C_{rn-1}\, D/(F_n - F_{En}) \tag{21}$$

Ten rules for effective and efficient rinsing

The following ten rules for effective and efficient rinsing are offered in summary:

1. Rinse mixing efficiency should approach 100%. Mixing efficiency is dependent on dwell time, tank design, agitation, temperature and part complexity.
2. Countercurrent rinsing should be utilized whenever possible for immersion rinsing.
3. Rinse effectiveness is a function of the dilution ratio C_p:C_{rn}, and rinse efficiency is a function of drag-in, mixing and the rinse ratio F:D. Rinse efficiency can be improved by reducing drag-in or the rinse ratio, or by improving mixing.
4. Establish logically derived water quality standards. Water quality standards should consider specific constituents as well as TDS, hardness and pH.
5. Establish logically derived rinsewater quality standards. Rinsewater quality standards should consider specific constituents such as cyanide, chromate, chloride, etc., as well as TDS and pH.
6. Water quality affects rinse effectiveness and/or efficiency.
7. Rinse evaporation affects each rinse effectiveness and/or efficiency.
8. Assure chemistry is compatible in shared rinsing.
9. Size rinse tanks no bigger than necessary to accommodate the largest load.
10. Design rinse tanks to avoid short circuits in flow. ***P&SF***

Washington Update

Continued from page 6.

Following DoD Policy Memo, Meeting in Denver to Discuss Sustainable Surface Engineering for Aerospace and Defense

Attendees at the NASF Washington Forum heard the latest update from the Pentagon's on the April 8, 2009 memo issued by the Under Secretary of Defense for Acquisition, Technology and Logistics, "Minimizing the Use of Hexavalent Chromium." The memo, under development for nearly two years, would require DoD to reduce usage of Cr^{+6} processes and materials, while ensuring performance and cost-effectiveness continue to be met. To assist DoD organizations and the supply chain with meeting these requirements, the memo points to ASETSDefense as a resource for knowledge on research, development, test and evaluation (RDT&E) efforts and experience with alternatives.

ASETSDefense – Advanced Surface Engineering Technologies for a Sustainable Defense – is a SERDP and ESTCP initiative that aims to facilitate the implementation of new, environmentally friendly technologies for surface engineering by providing ready access to information and data from RDT&E efforts supported by DoD organizations and the private sector. A central repository of data and information is now available through ASETSDefense for those responsible for qualifying and approving the use of new surface engineering technologies on weapons systems.

An informational workshop "ASETSDefense '09: Sustainable Surface Engineering for Aerospace and Defense" is planned for September 1-3, 2009, in Denver, Colorado. ASETSDefense '09 will cover all environment, safety and occupational health (ESOH) coating issues in new and legacy aircraft, vehicles and ships although special emphasis will be given to hexavalent chromium in response to the recent memo.

To access the surface engineering database and obtain more information on the ASETSDefense '09 Workshop, visit www.asetsdefense.org.

For more information, please reach Christian Richter (crichter@thepolicygroup.com) or Jeff Hannapel (jhannapel@thepolicygroup.com). ***P&SF***