

## Advice & Counsel

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## More on MP&M

At the request of the U.S. EPA, this author got a chance to review the data in the model metal finishing facility that was produced by EPA and used to develop pollutant equivalent benefits from MP&M. The model consists of 85 processes (unit operations) and associated rinses. For each process and rinse system, EPA averaged analytical data to produce representative concentrations in each process solution and rinse. While the 85 processes include such vague items as "laundering" and "Kerfing," they also included many of the processes used in the metal finishing industry. Due to time constraints, my review was limited to the processes discussed below. However, we intend to eventually review all of the data (1600 data points), and will provide additional guidance to EPA, if it is warranted.

The following are observations made after our initial review of most of the processes (shown here with EPA process numbers) common to metal finishers, and were added to our comments on the MP&M rule. For the latest version of my comments, log on to the AESF website. Industry comments produced by the Policy Group—and incorporating some of our findings—will be listed on our website as well.

## **Unit Operation Comment(s)**

**1** (Abrasive Blasting). The Total Kjeldahl nitrogen is 0.73, while the ammonia nitrogen is 9.84. This cannot be, as the total nitrogen includes the ammonia nitrogen. The TSS in the process is 153 ppm while the rinse is 324 ppm. This also cannot be.

**3** (Acid Treatment w/Cr). The rinse following this process must be flowing at an astonishing rate, as the

aluminum in the process is at 4,120 ppm while the rinse is at 2.24, a dilution ratio of almost 2,000. The dilution ratio is inconsistent, ranging on selected parameters from 111 to 1,872. The process is indicated to be acidic, but the data include alkalinity of 12 ppm for the rinse and 1 ppm for the process. At the same time, the rinse is indicated to contain acidity of 17.5 ppm and the process has an acidity of 4,120. These numbers conflict and/or don't make sense.

**4** (Acid Treatment w/o Cr). The rinse ratio for this process varies from 3.6 (oil & grease) to 495 (iron). The rinse ratio should be relatively constant in a real-world process.

**5** (Alkaline Cleaning-oil rem.). The pH of the process is at 12.9, yet an acidity of 35.5 ppm is indicated in the rinse (pH 10.13), and an acidity of 16,739 is indicated for the process. The process also has an indicated alkalinity of 15,022. This data appears to be useless and does not reflect reality.

**6** (Alkaline Treat w/CN). The rinse ratios vary from 38 (copper) to 355 (chloride). This is not representative of what is typically found.

**10** (Aqueous Degreasing). The degreasing solution is shown to contain 1.66 ppm gold. This is highly unlikely and indicates the ICP was not compensating for possible interferences on a concentrated solution (such as an aqueous degreasing bath).

The pH of the degreasing bath is 10.1. While there are specialized aqueous degreasing solutions designed for use in degreasing aluminum which have a pH of around 10, this is not typical of degreasing baths used to degrease ferrous and nickel based alloys, which have a pH of 13-14. The aluminum content of the degreasing bath is only 2.02 ppm, indicating this is not a degreasing bath used on aluminum. It is not reflective of most commonly used degreasing baths.

The TDS of the degreasing bath is only 12,329 or 1.2 percent, which translates to 12 g/L, which is a very weak formulation. Typical degreasing baths used in degreasing ferrous alloys are made up at 8 oz/gal which translates to 60 g/L or 60,000 ppm.

The rinse after degreasing contains 2.0 ppm aluminum indicating no dilution (no rinse flow), since the aluminum in the bath is also 2 ppm. This is not normal. Gold is at 0.086 ppm in the rinse, indicating a dilution ratio of 19:1. The TDS in the solution vs. the rinse is at a ratio of about 2:1. Molybdenum in the rinse is at 46.7 ppm, while in the degreasing bath it is at 10.48. This cannot be. The rinse is always lower in concentration in a rinse than in the bath itself.

A typical industry-used rinse ratio for a single running rinse is 100:1. Boron is 156 ppm in the bath and 0.9 ppm in the rinse, indicating a rinse ratio of 173:1. The inconsistent rinse ratio calculated from the data confirms a sampling or analytical problem. This also may be due to use of "averages of averages" when some outliers yield an extraordinary effect on the data. In either case, the model contains numerical data that cannot reflect reality.

14 (Conv. Coat, no Cr). The metals content of the drag-out rinse, which typically immediately follows the process bath, contains far lower concentrations of heavy metals than the rinse, which typically follows the drag-out rinse. Examples: Aluminum in rinse is 0.49 ppm, drag-out is 0.058 ppm, iron in rinse is 6.8 ppm, while the drag-out is at 0.03 ppm. Similar discrepancies for antimony, arsenic, boron, calcium, chromium, cobalt, copper, magnesium, manganese, molybdenum, nickel, sodium, titanium, zinc and others. This indicates that possibly the dragout rinse sample is actually the rinse sample and the rinse sample is actually the drag-out sample. Other possibilities are that the operators were only sporadically using the drag-out rinse. In all cases, these data make no sense and should not be used.

The rinse ratio (concentration in rinse vs. concentration in bath is highly inconsistent, ranging from 4 to 165 for selected metals. This ratio is typically a fixed value set by the concentration in the bath and the flow rate in the rinse. A typical value is 100:1.

15 (Chemical Milling). The ratio between the concentrations in the rinse and bath of certain parameters selected is highly variable, ranging from 4.5 (calcium) to 6,628 (ammonia as nitrogen). This does not reflect what is normally encountered. The inconsistency indicates an analytical, sampling or other unidentified problem. Also, chloride (21.77 ppm in the rinse vs. 1 ppm in the bath), oil & grease (2.21 in the rinse vs. 1.08 in the bath) and oil & grease as HEM (6.49 ppm in the rinse vs. 6.25 in the bath) make no sense at all. The pH of the rinse is at 6.25 while the bath is at 0.07. This would indicate a dilution ratio of 100,000 to 1, which also makes no sense.

16 (Chromate Conv. Coat). The rinse ratio for selected parameters ranges from 2.64 (COD) to 928 (barium) indicating that this data is inconsistent with what one would find in the metal finishing industry. Cyanide was detected at 0.05 ppm in both the bath and the rinse, which is not possible. Also, the pH of the bath is 6.3, while the acidity is 27,061 ppm. This is chemically and in practice impossible. A pH of 6.3 is essentially neutral while the process mechanism requires chemical attack of the metal by an acid. The oil and grease vs. oil & grease HEM in the bath is 13.7 vs. 185 ppm respectively. The total petroleum hydrocarbon is 7 ppm, indicating that the 185 ppm reading is wrong.

**17** (Corrosion Prevent. Coat). The oil and grease is indicated at 30,366 in the bath, while the oil and grease (HEM) is indicated to be 8.5. Since the HEM procedure is intended to replace the conventional analytical procedure, these numbers should be identical. Obviously, one is wrong. The TPH is indicated at 6.5, so the 30,366 reading

may be the wrong one. On the other hand, the rinse has an oil and grease of 6.2, indicating almost no rinse flow, which makes no sense. The bath has a pH of 6.66 while the rinse has a pH of 4.47, which makes no sense because the rinse is 100 times more acidic than the bath.

**18 (EDM)**. This process must not have been in use, as there are no metals that are present in the process bath. The highest is zinc at 10 ppm.

**19 (ECM)**. This process solution is incompletely characterized as the TDS is over 400,000 ppm, yet only sodium was identified (at 98,400 ppm). All the other parameters tested for are very low in concentration. The TDS in the rinse is only 1092, indicating a dilution ratio of about 400 to 1, while the test parameters are far off this ratio (*e.g.*, calcium in the rinse is only 10 times lower in the rinse than in the process solution). The data appear to be erroneous.

**20** (Electroless Plate). This process does not reflect what is most commonly used in the industry. It appears to be an electroless nickel plating process, but the nickel content is extremely low in concentration (2,463 ppm vs. a typical EN solution at 6,000 ppm. Further, the acidity datum (54,500 ppm) does not match up with the pH which is alkaline (8.91). This cannot be. The most popular EN plating processes are acidic at a pH value of 4-5.

Some parameters in the rinse are higher than the process (chloride at 953 ppm in the rinse vs. the process at 397 ppm, calcium at 10.4 ppm in the rinse vs. the process at 6.1 ppm), magnesium 3.45 ppm in the rinse and 1.76 ppm in the process. The rinse ratios vary to a great degree from a negative value (rinse higher than the process) to 400:1 (for ammonia nitrogen).

The data provided conflicts with reality to the point of making it use-less.

**21** (Electrolytic Cleaning). The process is shown to contain 269 ppm ammonia nitrogen, but only 44 ppm total Kjeldahl nitrogen—an impossibility. The process is shown to have an acidity of 122 ppm yet the pH is 13.1, another impossibility. The oil and grease reading using the two procedures vary by about 100 percent, yet are designed to yield similar results. The rinse ratio between the process and rinse on selected parameters ranges from a little over 3 (acidity) to 752 (ammonia nitrogen), when

in reality, the rinse ratio should be similar for all parameters in a real-life process.

22 (Electroplating w/Cr). The data correspond to a chromium plating process that is based upon hexavalent chromium, in that the chromium concentration is about 125 g/L, which is typical for such a process. However, this process will not function in any usable way if it contains 130,833 ppm of chloride. This process can only tolerate, at most, about 90 ppm chloride without seriously affecting the quality of the deposit. It appears to me that a trivalent (chloride-based) process was averaged with a hexavalent process to yield a process that can never be used for chromium plating. The sulfate is also way too high in concentration. A typical hexavalent process has a sulfate content of about 2.5 g/L (2,500 ppm), while this process has almost 80,000 ppm. Since there is a trivalent process that is based upon sulfate, it is possible that three different kinds of chromium plating solutions were averaged together to yield this data. This is about as far from reality as one can get. The data also appears to be erroneous, in that the sulfate plus chloride plus chromium (as chromium trioxide) add up to 460,000 ppm, while the TDS is only 300,000 ppm.

The rinse ratio on selected parameters varies from 11 (copper) to 72 (iron) indicating sampling, data manipulation or analytical error(s).

One or more (chloride and sulfate) separate process entries for trivalent chromium plating should be made.

**23** (Electroplating w/CN). This process is shown to have an acidity of 33,400. This is impossible in a cyanide-based process, which is always alkaline. It is also shown to have an alkalinity of 69,896. Both cannot be right.

This appears to be an attempt to mix different cyanide plating processes, because the cadmium is at 7,585 ppm and the copper is at 69,896 ppm. However, cyanide is also used in silver, brass, bronze, zinc and tin-zinc plating which are not represented in this mix or separately. Each solution has different cyanide and metal concentrations. Either these processes need to be averaged in or (more correctly) each process be represented separately.

The rinse from this process is shown to contain 0.34 ppm cyanide "amenable" and a total cyanide of 5,041. This is clearly impossible as it indicates that the process contains no cyanide that can be treated by alkaline chlorination.

The drag-out rinse following the plating process contains concentrations that are far lower than the rinse. For example, the cadmium in the dragout is at 0.1 ppm while the rinse is at 1.0, the copper in the drag-out is 165 ppm while the rinse is at 3,093, and the cyanide in the drag-out is at 82 ppm while the rinse following the drag-out is at 5,041. This data is clearly erroneous.

The concentrations reported for the drag-out appear to actually be those that you would expect to find in the rinse. The cadmium readings, how-ever, make no sense across the board, as there is a high cadmium content in the process (7,585 ppm), but none in the drag-out (0.1 ppm) and only 1 ppm in the rinse. This appears to be an analytical error.

24 (Electroplating w/o Cr or CN). This process is supposed to be free of cyanide yet the rinse from this process (24R) is shown to contain 50 ppm of amenable cyanide, which is 100 times more than the above process which is supposed to contain cyanide. The cyanide reported to be present in the process is 0.09 ppm, yet the rinse contains 17 ppm and the drag-out rinse contains 4.3. This data is clearly impossible!

The data on the drag-out rinse is highly inconsistent, in that the dragout rinse contains less cyanide, lead, and tin, than the running rinse that follows it. This is not possible.

The rinse ratio between the drag-out rinse and the running rinse varies from negative to over 8,000!

The pH of this process is indicated to be 7.28 (neutral) yet the acidity of the process is reported at 100,644 ppm. The rinse has an acidity of 6,162 ppm with a pH value of 7.97 (alkaline), while the drag-out rinse has an acidity of only 100 ppm with a pH of 7.2. None of this is possible...or realistic.

**25 (Electropolishing)**. This process contains far lower concentrations of chromium, nickel, and iron that are normally found in electropolishing solutions by at least one order of magnitude. The solution is highly acidic (no pH reported), yet the rinse is shown to only have 150 ppm acidity. *PessF*