Appendix H – Capsule Report: Innovative Rinsing

Introduction

This capsule report was prepared under EPA Grant 00E02050, funded through the EPA Source Reduction Assistance Grant Program.

Various tasks have been performed under EPA Grant 00E02050. The purpose of this particular project was to implement a methodology for evaluating and improving rinsing practices at electroplating facilities. The methodology was developed was under a separate task of the EPA pollution prevention project and is referred to as the *Rinsing Manual*. It is publicly available on Surface Technology Environmental Resource Center (STERC) at http://www.sterc.org/subs/rinseman.php.

Overall, the Rinsing Manual methodology consists of five steps:

- 1. Establish a baseline through data collection and by evaluating existing rinse systems.
- 2. Evaluate alternative methods of improving rinsing.
- 3. Implement changes.
- 4. Measure results, calculate savings.
- 5. Institute a program of continuous monitoring and recordkeeping.

To test the methodology, a project was performed at a Michigan electroplating shop. The facility agreed to allow a team to assess their operations and develop recommendations for improvement. The facility had the option of implementing any or all of the recommendations and they were responsible for any costs associated with the implementation.

An automated zinc/nickel (Zn/Ni) electroplating rack line was selected for evaluation. A baseline for the rinse systems was established using both historical data and new measurements. Alternative methods of improvement were evaluated and recommendations for improving rinsing were developed and communicated to shop management. Some of the recommendations were implemented by the facility. Following implementation, the plating line was re-evaluated and savings were estimated. The results are presented in this capsule report.

Facility Description

The *Rinsing Manual* protocols were tested at an electroplating facility in Michigan. This shop has various electroplating processes, including the automated Zn/Ni rack line that was evaluated during the project. The Zn/Ni line consists of 18 tanks including cleaners, electroplating, conversion coatings, sealer, rust inhibitor and rinse tanks. The line is normally operated 7 days a week, 24 hours per day. Various automotive parts are plated on the line, including tubular parts and various sized flat and angled parts. A photograph of the Zn/Ni line is shown in Figure H-1.



Figure H-1. Automated Zinc/Nickel Rack Plating Line

Baseline Evaluation

Using the methodology found in the *Rinsing Manual*, a baseline evaluation of the Zn/Ni line was performed. The information from that evaluation is presented in this section.

Tank layout. A diagram of the plating line is shown in Figure H-2. Unplated parts are racked at Station 101. There are two racks used per load. Different rack configurations are used, depending on the shape and size of the parts being plated. Once the racks are loaded, a hoist raises the two racks from the load station, moves them horizontally to the soak cleaner (Tank 101) and lowers them into that tank. The racks remain in the soak clean for approximately ten minutes. During this time period, the hoist is busy moving other sets of racks through the process. After ten minutes, the hoist returns to Tank 101 and transports the racks to the next tank in sequence (Tank 102: Electrocleaner). From start to finish, the process takes approximately 1.5 hours. Typically, there are eight sets of racks being processed through the line at any given time.

Each tank has one station (a station holds one set of two racks) with the exception of Tank 110, the Zn/Ni plate tank, which has four stations. A larger number of stations are needed in this tank because the racks are retained there for about 45 minutes to allow a sufficient thickness of Zn/Ni electrodeposit to occur.

Rinse systems. Rinsing is performed in two and three-stage counterflow immersion rinse systems. Two spray rinses are located above two of the immersion rinse tanks (111, 118).

The counter flow rinses are well designed. Incoming water lines are located in the second rinse of each system (3^{rd} rinse tank in the case of the 3-stage system). Flow restrictors are present on incoming water lines, limiting the flow to 3 gpm per rinse system. Incoming water is dispersed in the 2^{nd} rinse by air agitation and it overflows a weir to the first rinse. The first rinse is also mixed by air agitation. Water exits the first rinse via a weir and is conveyed by gravity flow to the wastewater treatment system.



Figure H-2. Zinc/Nickel Electroplating Line

Tank 111, the first rinse following Zn/Ni plating, had an auxiliary incoming water line that did not have a flow restrictor. The flow rate was variable during the study, but averaged 1.5 gpm. This additional water is used to keep the first rinse sufficiently low in conductivity.

Air Agitation. Air agitation is achieved using a blower. Air is conveyed into each rinse tank via PVC piping that is run down the side of each rinse tank and across the bottom of the tank. Small holes are drilled in the bottom PVC pipe that evenly distribute the escaping air and causes mixing as the bubbles float to the surface of the tank. Air flow to each rinse tank is controlled by a hand valve. Although air agitation is available for each rinse tank, it was observed to be inadequate in most tanks. Using an arbitrary 0-5 scale (5 being the best), only one tank received a score of 5 (Tank 118). Scores for the other tanks ranged from 0 to 3. Figure H-3 compares the air agitation of Tank 111 (score of 1) and Tank 112 (score of 4).



Figure H-3. Visual Comparison of Tanks with Poor (left) and Good (right) Air Agitation

In part, poor air agitation at this shop was a result of precipitated solids building up on the bottom of the rinse tanks. In some cases, a sludge blanket completely covered the air agitation piping on the bottom of the tank and prevented air from being released.

Dragout. The volume of dragout from the Zn/Ni tank (110) that enters the rinse system (Tanks 111/112) was measured using the procedure outlined in the *Rinsing Manual*. The measurements were conducted for this tank only, because, due to its high metal content, it contributes much more significantly to WWT sludge generation than the dragout from the other tanks on the plating line. Test results indicated that the dragout from Tank 110 is 1.02 gph. On the average, 4.9 rack sets (9.8 racks) are processed per hour. Therefore, the dragout rate per rack set is 0.21 gal.

Dwell time in rinse tank. The programming of the hoist allows for sufficient dwell time in the rinse tanks. A minimum of 3 minutes of dwell time was observed. In most cases, dwell time was longer than 4 minutes.

Rack withdrawal rate. The rack withdrawal rate was the same speed for all process and rinse tanks, 1 ft./sec.

Drain time. The plating hoist is programmed to drain racks over most of the process tanks for 2 seconds after being removed from the tank and before traveling to the next station, which takes an additional one second. The only exception is Tank 110 (Zn/Ni plate), where the drain time is set at 8 seconds (measured from when rack is out of the bath to moving). Travel time is 1-3 seconds for Tank 111, depending on the starting position.

Observations and testing made during the survey indicated that the drain time is too short. This is especially the case for the Zn/Ni tank. The Zn/Ni solution is very viscous, causing the solution to drain off slowly. The racks and parts are still significantly dripping when they are moved to the first rinse (111), as shown in Figure H-4.



Figure H-4. Dragout Still Draining Just Prior to Rinsing

Conductivity of rinse water. The conductivity of rinse water is measured regularly by the facility. Average conductivity values for a five month time period are shown in Table H-1. The measurements are presented in both microsiemens/centimeter (μ s/cm) and millisiemens/centimeter (ms/cm). Note that 1,000 μ s/cm equals 1 ms/cm.

Rinse efficiency. Rinse efficiency was measured using the method described in the *Rinsing Manual*. The manual defines rinse efficiency as C1/C2, where:

- C1 = the conductivity of the water remaining on the rack or parts after rinsing
- C2 = the conductivity of the rinse tank water

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	Average Conductivity	Average Conductivity
Rinse Tank	(five months)	(five months)
	(μs/cm)	(ms/cm)
104	1,390	1.390
105	280	0.280
107	9,320	9.320
108	410	0.410
111	3,620	3.620
112	360	0.360
116	850	0.850
117	300	0.300
118	260	0.260

Table H-1. Rinse Tank Conductivity Measurements

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Under ideal conditions, C1/C2 = 1. However, testing performed under this EPA P2 project showed that the ratio of C1/C2 is usually above 2.0, and can be much higher.

C1 was measured by capturing the drips of water coming off of the rack and parts after being removed from a rinse tank. This was accomplished using a four foot section of 3-inch PVC pipe that was cut lengthwise and capped on the ends. When the rack was lifted from the rinse tank, the pipe was held under the rack and it captured the dripping water (Figure H-5). The sample (C1) was then measured for conductivity. A sample of the rinse tank was also taken and measured for conductivity (C2).

Results of the rinse efficiency study are shown in Table H-2, for Tanks 104 and 111. In each case, the test was performed twice, with air agitation set at 0 and 4, using the arbitrary scale described above. In each case, rinse efficiency improved significantly with good air agitation. The range of improvement was 23.5-45.2%.



Figure H-5. Sampling Drainage After Rack Removed From Tank

Table H-2. Measurements of Rinse Efficiency

Rinse Tank	Air Agitation 0-5 scale	C1 ms/cm	C2 ms/cm	C1/C2	Improvement Due to Increased Air Agitation
104	0	2.42	0.78	3.1	-
104	4	1.33	0.77	1.7	45.2%
112	0	0.78	0.23	3.4	-
112	4	0.57	0.22	2.6	23.5%

Spray rinsing. Spray rinses are present on two rinse tanks (111 and 118). They were fabricated inhouse using 1-inch PVC pipe and spray nozzles. The spray bars, with seven nozzles per side, are mounted on the lip of the rinse tanks. They are automatically activated for six seconds by a momentary switch when the rack is lifted from the tank. Each nozzle deliveries 0.06 gal of fresh city water per cycle. Therefore, the set of 14 nozzles delivers 0.84 gal per cycle. The spray rinse system is shown in Figure H-6.

A semi-quantitative test was performed at Tank 111 to see if the spray rinses were effective. Immediately following a spray event, the drips from the rack/parts were collected and the conductivity was measured as was the conductivity of the rinse tank. The conductivity of the rinse tank was 0.57 ms/cm. However, the conductivity of the drips was 4.53 ms/cm, indicating that the sprays were very effective in removing dragout from the racks/parts that the immersion rinse left behind.



Figure H-6. Spray Rinse on Tank 111

Drip/drain boards. No drip boards were present on the plating line. This was especially apparent between Tank 110 (Zn/Ni plate) and Tank 111 (rinse tank), where a buildup of chemicals occurred on a PVC pipe covering tank busing and on the tank lip (Figure H-7). Some of the dragout falling in that zone flowed into the rinse tank, which increases the need for rinse water. As mentioned previously, a separate incoming water line was needed to maintain a sufficiently low conductivity in Tank 111.



Figure H-7. Buildup of Chemicals Occurs Between Tanks Due to Lack of Drip/Drain Board

Plating racks. The plating racks used at this facility are generally not conducive to good drainage. Most racks are designed such that parts are hung directly above other parts, thus increasing the path that dragout flows before returning to the process tank. As a result, dripping continues to occur for multiple seconds longer than necessary. Considering the short drain times used, a significant amount of dragout enters the subsequent rinse tank.

Poor rack maintenance is also contributing to increased dragout (Figure H-8). On many racks, the plastisol rack coating is damaged causing process chemicals to collect between the rack frame and coating. The trapped solution does not drain freely and is carried over to the next tank. This causes a need for higher rinse flow rates and contaminates subsequent process tanks.

During the study, a drainage sample was collected after a rack with damaged rack coating was removed from Tank 111. The sample had a conductivity of approximately 10 times greater than samples collected from undamaged racks exiting the same rinse tank. Obviously, the Zn/Ni solution (Tank 110) had entered the space between the rack and rack coating and was not completely removed by rinsing.



Other data identified by the Rinsing Manual protocols are shown in Table H-3.

Figure 8. Rack Maintenance Issues

Table 3. Additional Shop Data	
Item	Cost or Quantity
Water/sewer cost (\$/1,000 gal)	\$10.42/Kgal
Water Use, Kgpy	6,080 Kgal/yr
Wastewater treatment cost, \$/Kgal	\$10.28
Sludge generation	18,600 lbs/yr
Sludge disposal cost, \$/lb	\$3.36/lb

Evaluation and Recommendations

The facility requested that the P2 project focus on two main objectives:

- Reducing water use.
- Reducing wastewater sludge generation.

With these objectives in mind, evaluations of current rinsing and dragout were performed with a focus on the Zn/Ni bath (Tank 110) and the subsequent rinse system (Tanks 111 and 112).

Rinsing. The current rinse system (Tanks 111 and 112) was compared to an ideal system using the <u>STERC Rinse Systems Calculator</u>. The STERC calculator uses widely accepted formulae for multiple tank rinse systems, but the results are based on idealized conditions. The performance of actual rinsing systems depends on the rinsing efficiency of the tanks, the variability of the introduction rate of drag-out and other factors. In short, few real-world rinsing systems will perform as indicated; most will require a significantly higher rinse water flow to maintain a given criterion.

Using the STERC Calculator, it was determined that the theoretical flow rate of water needed to maintain the current rinse cleanliness is only 0.74 gpm. This is a small fraction of the current water use, which is 4.5 gpm.

The large discrepancy between theoretical and actual water use is likely due to several factors:

- There are two water inlets to the Tank 111/112 rinse system, 3.0 gpm flowing into Tank 112 and 1.5 gpm flowing into Tank 111. The flow into Tank 111 is short-circuiting the counter flow system. For maximum effectiveness, all incoming water should be entering Tank 112.
- Rinse efficiency is hindered due to poor air agitation in Tank 111. This is mainly due to a buildup of solids in the bottom of the rinse tank.
- Damaged rack coatings retain concentrated solution even after rinsing in Tank 111. Therefore, the dragout from Tank 111 into Tank 112 is much higher than with well-maintained racks.
- Large tubes, which are frequently plated on this line, retain solution on the inside diameter which is not removed by the spray rinse.

Dragout. The drainage time and dragout rate following Zn/Ni plating were closely observed. Dragout was collected after the racks were lifted from the Zn/Ni bath, during the draining period (8 seconds) and travel period (1 to 3 seconds). The volume of solution collected during each interval was then measured. This information, together with a model of how the volume of solution dripping from the racks is expected to change with time, can be used to provide an estimate of the amount of dragout that could be avoided with a longer drip time.

A graph of drip volume versus time was published by the Beckman Instrument Company, and was reproduced in an EPA report (*Meeting Hazardous Waste Requirements for Metal Finishers*, EPA/625/4-87/018, September, 1987, p. 25)⁴. The graph appears here in Figure H-9. It shows three curves, one for vertical sheets, another for horizontal surfaces, and an intermediate case. The graph indicates the rate at which solution was observed to drip from each of the surfaces, so that the area

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⁴ Available on-line at <u>https://nepis.epa.gov/Exe/ZyPDF.cgi/300048GM.PDF?Dockey=300048GM.PDF</u>



Figure H-9. Drainage vs. Time Graph for Zn/NI (from Beckman Rinse Tank Control Handbook)

under each curve between two points in time represents the total volume which would be collected during that time interval. This makes it possible to adjust the curve to the measured volumes, and to read from the curve the volume of dragout that could be decreased by increasing the drip time over the bath.

In order to apply these curves to the data collected during operation of the facility's Zn/Ni line, it proved helpful to develop a mathematical model which reproduced the curves. The model is a formula that reproduces the shape of the curves, but include adjustable parameters that allow the curve to match the specific characteristics of the process being studied. Adjustments are necessary to account for the dependence of drip rates on solution viscosity, as well as on the particular shapes of the parts being plated. But using the model ensures that the qualitative behavior of the adjusted curves will match that of the Beckman graph.

Details of the model may be found in the Appendix. The results indicate that, in the case of the process measured here, a reduction of about 30-35% in avoidable dragout would be expected if the drip time over the plating tank were increased by 10 seconds.

Options for Improving Rinsing

Using the *Rinsing Manual* as a guide, various options for improving rinsing on the Zn/Ni line were evaluated. The most effective and viable options are discussed in this section.

1. Establish a schedule for cleaning out precipitated solids from rinse tanks. Solids collect at the bottom of rinse tanks and impede the flow of air from the PVC pipe running along the bottom of the tank, thereby reducing air flow and mixing. A schedule should be established for cleaning the rinse tanks. The most affected tanks, typically the first rinse tank in series (e.g., Tank 111), will likely require cleaning every 1-3 months. The second and third rinse of each counterflow system can be cleaned less frequently (6-12 months). Any parts that have fallen off the racks should be retrieved when rinse tank cleaning is performed.

- 2. Improve air agitation. Air agitation on the line was observed to be generally poor. Tests performed during the study showed that with improved air agitation, rinse water use could be substantially reduced. The existing air blower may be sufficient for increasing air agitation to Level 4 for all rinses. A higher air agitation rate (5) may be possible, but could result in parts being dislodged from the racks. Light, small parts are more likely to be dislodged than larger heavier parts, such as tubes.
- **3. Repair rack coatings**. Some of the racks being used have cracked or broken plastisol rack coatings. Bath chemistry enters these crevices, between the rack and the coating, and significantly increases dragout. Testing showed that the dragout is not well removed by rinsing and it is transferred down the line to subsequent tanks.

The facility owns roughly around 25 racks. Approximately 20% of these racks require repair. Affected racks could be rotated out of use several at a time and sent offsite for repair. This would prevent having a shortage of racks on-hand. Needed repairs consist mainly of removing the existing rack coating and reapplying a new plastisol coating. Some racks also require repair of contact tips.

4. Improving racking. Parts racked directly above one another increase the path that dragout must travel before dripping back into the process tank. When possible, the location of racked parts should be staggered to allow dragout to quickly return to the process tank. This may not be possible for high production parts that require the racks to be fully used.

When new racks are purchased in the future, the design should take into account the path of dragout to minimize carry over.

5. Add more spray rinses. The existing spray rinse on Tank 111 is well designed, it sprays an adequate volume of water at a sufficient velocity to remove dragout from the rack/parts. The spray rinse contributes only 100 gpd of wastewater, which is very small in comparison to the tank 111/112 immersion rinse system (4,320 gpd). The benefit of the spray rinse was measured by collecting rack/part drips after the rack was removed from the rinse tank. This was done with and without the spray rinse being activated. The immersion/spray rinse removed more than twice as much dragout than the immersion rinse alone. The water spray impinges the surface of the rack/parts and removes drag-out that otherwise would be carried over to the next tank.

Only two rinse tanks on the Zn/Ni line have sprays, Tanks 111 and 118. In both cases, the spray is activated automatically (momentary switch) when the rack is removed from the rinse tank. It is recommended that spray rinses be added to all other first rinse tanks on the line.

Adding spray rinses to Tanks 104, 107 and 116 will reduce the need for incoming water that enters the last rinse of each counterflow rinse system. Currently, all flow rates are set at 3 gpm.

6. Adjust drain time. The amount of drain time over the process tanks is too short and is causing excessive dragout to enter the subsequent rinse system. Overall, this increases rinse water use because it takes more fresh water to dilute the dragout. Also, it increases WWT sludge generation due to a higher mass of dissolved metal discharged to the WWT system. Following Zn/Ni plate, the rack is held in place for about 8 seconds before traveling to the rinse tank. For all other tanks, the drain time is 2 seconds.

The recommendation is to increase drain times to 20 seconds for Zn/Ni plate and 10 seconds for all other process tanks. More drain time is needed for the Zn/Ni bath due to its higher viscosity.

- 7. Double dip rinse. It is likely that the tubes are not being adequately rinsed by the first rinse following Zn/Ni plating (Tank 111). Although the spray rinse is very effective at removing dragout from outer surfaces, it has little effect on inside diameters. Reprogramming the hoist system to include a double dip into Tank 111 would help remove dragout from these inner surfaces.
- 8. Add a drip tray after Zn/Ni. A buildup of Zn/Ni plating solution sludge is present between the process tank and the rinse tank. Some of the chemicals end up seeping into the rinse tank. This can be minimized by locating a drip tray between the Process Tank (110) and Rinse Tank (111). The tray should be slanted in a manner that causes solution to flow back into the Zn/Ni Tank (110).

This option will provide a small P2 benefit (water use and sludge generation) by reducing the volume of dragout entering rinse Tank 111. However, it is also a small cost item and it will significantly improve the appearance of the plating line.

Summary of recommendations. Table H-4 lists the recommended improvements for the Zn/Ni plating line and associated costs. Table H-5 shows the potential savings/impacts.

In addition to these cost savings, the maintenance of rinse tanks, etc. will likely provide improved work quality, and fewer rejects. These savings could not be determined during the project.

Recommendation	Description	Cost to Implement
1. Clean out precipitated solids from rinse tanks based on established schedule	Develop schedule based on observations. Rinse following Zn/Ni plating will likely be 1-3 mths. Other rinses likely to be 6-12 mths. Cost is labor for one year.	\$2,000/yr
2. Improve air agitation	Increase air flow to rinse tanks. Use maximum air flow that does not dislodge parts from racks.	\$0
3. Repair rack coatings	Repair plastisol coatings on 12 racks.	\$6,000
4. Improve racking procedure	When possible, instruct staff to arrange parts on racks in a manner that improves dragout drainage.	\$0
5. Add more spray rinses	Add spray rinses to rinse tanks 104, 107 and 116.	\$2,700
6. Adjust drain time	Reprogram automated hoist system to increase drain time to 15 sec. for all process tanks, except Zn/Ni plate, which should be set at 20 sec.	\$10,000
7. Double dip in rinse tank 111.	Reprogram automated hoist system to double dip in rinse tank 111.	Cost included in item 6.
8. Add a drip tray after Zn/Ni	Fabricate and install a drip tray between tanks 110 and 111.	\$800

Table H-4. Costs to Implement Recommendations

Recommendation	Water	/Sewer	Sludge Trar Disp	ludge Transportation/ Disposal		Zn/Ni Process Solution	
	Kgal/yr	\$/yr	Lbs/yr	\$/yr	Gal/yr	\$/yr	\$/yr
1. Clean out precipitated solids from rinse tanks based on established schedule	608	\$12,586	0	\$0	0	\$0	\$12,586
2. Improve air agitation	1,216	\$25,171	0	\$0	0	\$0	\$25,171
3. Repair rack coatings	912	\$18,878	1,395	\$4,687	1,395	\$4,185	\$27,751
4. Improve racking procedure	304	\$6,293	465	\$1,562	465	\$1,395	\$9,250
5. Add more spray rinses (tanks 104, 107 and 116)	454	\$9,390	0	\$0	0	\$0	\$9,390
6. Adjust drain time	680	\$14,084	2,790	\$9,374	2,790	\$8,370	\$31,828
7. Double dip in rinse tank 111.	227	\$4,695	930	\$3,125	930	\$2,790	\$10,610
8. Add a drip tray after Zn/Ni	227	\$4,695	930	\$3,125	930	\$2,790	\$10,610

Table n-J. Estimated Fotential Savings From Recommended Changes	Table H-5.	Estimated Potential	Savings From	Recommended	Changes
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Table 5 notes: Savings for above recommendations were based on testing performed during the project as well as observations. These savings are not cumulative; implementing multiple recommendations will reduce the savings for individual options. The estimated independent savings for each of the above recommendations are based on: 1. Estimated water use reduction of 10% for Zn/Ni line. 2. Estimated 20% reduction of water use for Zn/Ni line 3. Estimated 15% water use, dragout and WWT sludge generation for Zn/Ni line. 4. Estimated 5% reduction of water use, dragout and WWT sludge generation for Zn/Ni line. 5. Estimated 10% water use reduction for rinse systems 104/105, 107/108 and 116/117/118. 6. Based on Appendix model, estimated 30% water use, dragout and WWT sludge generation for tanks 110/111/112. 7. Estimated 10% water use, dragout and WWT sludge generation for tanks 110/111/112. 8. Estimated 10% water use, dragout and WWT sludge generation for tanks 110/111/112.

Implementation of changes. The facility had the option of implementing any or all recommendations proposed by the project team. All costs associated with implementation were borne by the facility.

The facility decided to implement some of the recommendations immediately and some decisions were deferred. The recommendations that were implemented included:

- Established a cleanout schedule for rinse tanks
- Replaced broken rack coatings (Figure H-10)
- Added spray rinsing to Tanks 104, 107, and 116
- Installed a drip tray after Zn/Ni plating tank (Figure H-11)



Figure H-10. Racks with New Plastisol Coatings



Figure H-11. Pictures of Zn/Ni Tank Before and After Installation of Drip Board

Recommended changes that were not implemented during the project included:

- Adding an additional blower to improve air agitation
- Adjusting drain times (reprogramming)
- Adding a double dip (reprogramming

Measurement of Improvements

Following the implementation of the selected changes, the conductivity of the rinse tanks were tested and compared to previous conditions. These data are shown in Table H-6. The results show that adding spray rinses to Tanks 104, 107, and 116 improved rinse efficiency. In each case, the conductivity of the first rinse increased due to the effectiveness of the spray, i.e., more dragout is removed from the racks/parts before they are moved to the second rinse. Since less dragout is now

Rinse Tank	Average Conductivity	Conductivity After	Change
	Before Improvements, ms/cm	Improvements, ms/cm	After Improvements
104	1.39	1.62	+16.5%
105*	0.28	0.21	-25.0%
107	9.32	15.9	+70.6%
108*	0.41	0.35	-14.6%
111	3.62	1.23	-66.0%
112*	0.36	0.30	-16.7%
116	0.85	0.80	+5.8
117*	0.30	0.23	-23.3%
118	0.26	0.26	0%

Table H-6. Conductivity of Rinse Tanks Before and After Changes Implemented

Note: city water feeding rinse system has a conductivity of 0.17 ms/cm

going into the second rinse, the second rinse (105, 108, and 117) has less conductivity, with an average improvement of 21%.

Tank 111 was equipped with a spray rinse prior to the study, and therefore was not be expected to show an increase in conductivity. On the contrary, there was a major decrease in conductivity (66%). This change was most likely caused by the repair of rack coatings, the addition of a drip tray between Tanks 110 and 111 and improved air agitation.

Obviously the facility has made substantial progress toward rinsing improvement. Hopefully, the facility will be inspired by these results to implement the remaining recommendations.

Conclusions

The *Rinsing Manual*, developed under this P2 Grant, is an effective tool for evaluating and improving rinse systems. Its systematic approach includes data collection, evaluation of alternatives, implementation of improvements, and measurements of change. The data collection methods outlined in the *Rinsing Manual* include some unique methods including measurements of dragout, rinse efficiency (C1/C2) and adequacy of drain time. The resultant data allow for quantitative evaluation of options.

The *Rinsing Manual* is available free of charge on the Surface Technology Environmental Resource Center (STERC) website <u>http://www.sterc.org/subs/rinseman.php</u>.

Appendix

This section describes how to use measurements of the volume of solution draining from a rack of parts, sampled over successive time intervals, to estimate how much additional solution would have drained if drip time were extended. The drip rate decreases continuously over time, so some knowledge of the shape of the curve of drip rate vs. time is essential in order to calculate from the measured volumes what drip volume would be expected over some future time interval. A set of

curves reproduced in an EPA report⁵ provides a set of drip rate vs. time curves for a typical plating solution (unspecified in the report). In the following section, a formula is developed which matches the shapes of the typical curves, and provides the basis for the estimate.

Shape of the Curve

Plots of dragout volume (volume of solution still clinging to rack) vs. time are provided for three different surface orientations (horizontal, vertical, and an intermediate case). The curves begin with a rapid decrease in dragout volume, with the rate of decrease becoming smaller until the curve flattens out. This is qualitatively the kind of behavior that would be expected if the drip rate were proportional to the amount of solution still on the rack. The curve would then have the form of an exponential decay,

dragout = $V * e^{-k * t} + V_{end}$

where V, k, and V_{end} are constants. Specifically,

- V_{start} is the dragout volume on the rack at time t = 0
- k is the rate constant, which determines how rapidly the curve flattens out with time
- V_{end} is the solution that remains on the rack after arbitrarily long times.

The exponential decay curve applies in a wide variety of situations, but the case of dragout volume is apparently not so simple. An exponential curve fitted to the first few seconds of the curve will not match the rest of the curve, and vice versa. However, a very close match can be obtained by adding two exponentials, with individual initial volumes and rate constants:

dragout =
$$V_{start1} * e^{-k_1} * t + V_{start2} * e^{-k_2} * t + V_{end}$$

These curves were plotted on a spreadsheet, with the size of the grid adjusted to match the curves in the EPA report. The spreadsheet curves are shown below, superposed on a screenshot of the EPA report curves:



⁵ Meeting Hazardous Waste Requirements for Metal Finishers, EPA/625/4-87/018, September 1987, p. 25, available online at <u>https://nepis.epa.gov/Exe/ZyPDF.cgi/300048GM.PDF?Dockey=300048GM.PDF</u>

parameter horizontal bent sheet vertical units 5 5 5.2 ml/ft² V_{start1} = 0.15 0.22 k1 = 0.22 1/sec V_{start2} = 5 5.5 4.3 ml/ft² 0.055 k₂ = 0.055 0.055 1/sec 3.0 ml/ft² V_{end} = 4.7 1.4

The values of the parameters that provide this fit are:

The volumes are expressed in milliliters per square foot of surface area, to match the units used for the EPA report curves. The rate constants can be expressed simply as "percent per second", since for any single exponential decay curve, where the amount lost is proportional to the amount remaining, a constant percentage of the remaining weight will be lost every second. In this case, where two exponentials are being added, the percent in each case refers to the initial volume for that exponential.

For example, for the case of the vertical sheet, the total dragout volume left on the rack after the first second will be

 $e^{-0.22} * 5.2 = 4.17 \text{ ml/ft}^2$ from the first term, plus $e^{-0.055} * 4.3 = 4.07 \text{ ml/ft}^2$ from the second term.

After the next second, the remaining dragout volume will be

 $e^{-0.22} * 4.17 = 3.35 \text{ ml/ft}^2$ from the first term, plus $e^{-0.055} * 4.07 = 3.85 \text{ ml/ft}^2$ from the second term,

and so on for each subsequent second. (Note where the boldface terms in the first pair of equations show up in the second pair.)

In other words, the model behaves as if there are two separate exponential decays occurring, each starting with its own initial volume of solution. For one of the components, the remaining volume at any point in time will be $e^{-0.22} = 80.3\%$ of what it was one second before, or equivalently, it loses 19.7% of its volume every second. For the other component, the corresponding percentage will be $e^{-0.055} = 94.6\%$, or a loss of only 5.4% of its volume per second. The total dragout volume seems to consist of one portion that drips off relatively quickly, and a second portion that drips more slowly. After a long time, both of those exponentials will have decayed to nearly zero, leaving a third portion still on the rack that remains constant. (The other surface orientations have different parameter values, but the behavior is similar.)

This is consistent with the interpretation that some portion of the initial dragout volume is subject to bulk flow (V_{start1}), another portion is strongly influenced by surface forces (V_{start2}), and a third portion will remain clinging to the surfaces and never drip off (V_{end}). In practice, there wouldn't be sharp boundaries between layers, but the close agreement between the model and the measured curves suggests that a three-layer model is sufficient to produce a good estimate.

Data Collected at Michigan Electroplating Facility

Dragout samples were collected from an automated Zn/Ni plating line without interrupting normal operation. On this line, two racks travel side-by-side through a sequence of tanks. Racks remain in the plating tank longer than in other dip and rinse tanks, so the plating tank has the capacity to hold four rack sets (each set consisting of a pair of racks). When a rack set is to be moved into the first rinse tank, a lift raises the rack set completely out of the tank, and suspends it for eight seconds. The lift then moves the rack to a position over the rinse tank, holds for two seconds, and then lowers the rack set into the rinse. Depending on their position in the tank, racks will have spent 9, 10, 11, or 12 seconds with drip falling back into the plating tank. Solution dripping after that time will fall into the rinse tank, and will therefore be counted as dragout.

For these measurements, two identical sampling tubes were prepared. Each tube consisted of a twofoot section of PVC pipe, with a slot cut along the tube, extending nearly the entire length of the tube. The tube was capped on the ends. The tubes were positioned under a rack, and the solution draining from a representative length of the rack was collected. After collecting the sample, one end cap was then removed, and the collected solution was drained into a graduated cylinder and measured.

Each rack is about four feet wide, so the sampling tube collected about a quarter of the total drip from each rack set. On some racks, particularly those where the rack coating was peeling, more drip could be observed toward the corners of the racks than along mid-section of the bottom. Each tube collected the drip from a corner plus about half of the bottom edge of one rack; scaling up by a factor of about 4 was thus considered to provide a good indication of the total drip from the rack set.

As soon as a rack had been lifted from the plating tank, a sampling tube was placed under the rack, and moved under the rack until it had reached the edge of the plating tank. The tube was then removed and a second tube positioned under the rack until it began descending into the rinse tank. The volumes of solution collected over the plating and rinse tanks for three different rack sets, and the time intervals at the end of each sample collection, are tabulated below. (Start time for the plating sample was t = 0, so t_1 also equals the time interval in seconds over which V_P was collected. The corresponding interval for V_r was $t_2 - t_1$, or two seconds in all cases.)

MI plating facility data	Rack #			unite
	1	2	З	units
Volume collected over plating tank (V _P)	21	47	35	ml
Volume collected over rinse tank (V _R)	3	9	4	ml
Time at end of plating tank sample collection (t_1)	9	10	11	sec
Time at end of rinse tank sample collection (t_2)	11	12	13	sec

Estimate of Potential Dragout Reduction

These data can be used along with the drip curve model described above to estimate how much dragout could be reduced with a longer drain time over the plating tank. In this section, the method used to generate the estimate is summarized, and the results are presented. The full details of the calculations involved are provided in the concluding section.

The drip curve example available from the EPA report can help establish the validity of the model, but the specific numerical values found above for the rate constants k_1 and k_2 , and the initial volumes

 V_{start1} and V_{start2} and V_{end} that match the curve, cannot be carried over directly to solutions other than the particular solution used for the given curve, tested under the conditions used for that measurement. (This information is not provided in the EPA report.) Solutions with a different viscosity from the solution tested for the EPA report will have different values for all of these parameters. The same applies to any factors, such as solution temperature, which affect the viscosity.

For this estimation method, we assume that the qualitative behavior of the model, with two independent exponential decays, remains valid over the range of typical plating solutions, as long as the values of the parameters are chosen to reflect the particular solution and conditions being tested. We use the data gathered at the Michigan plating facility to determine the parameters. We can then use the model to determine how much solution will remain on the rack at any specified time, and thus how much dragout can be reduced by lengthening the drip time over the plating tank for any specified number of seconds.

The model requires five parameters. One of them, V_{end} , does not enter into the calculation – as far as the drip is concerned, it behaves as if it were part of the rack. That leaves two rate constants, and two initial volumes.

Ideally, rather than two samples for each rack set tested, it would be useful to have samples over four or more different time intervals. If more than four measurements are available to determine four unknowns, the system is overdetermined, and the extra measurements can serve as a further test of the validity of the model. Under the circumstances, more frequent measurements, or measurements over additional time intervals, would not have been possible without interrupting the process. With two measurements and four unknowns, the system is underdetermined, and two additional assumptions are necessary. The two assumptions used in this case are that the ratio of V_{start1} to V_{start2} is the approximately the same for typical plating solutions, and that this is also true for the ratio of rate constants. The ratios for the example curves are then used to provide two additional equations to the two generated from the facility data. With four equations and four unknowns, the values of all four parameters can be calculated.

Note that each of the three rack sets must be treated as separate cases, with different values for the parameters. Although the composition of the solution, the temperature, and most other factors were similar for each of the measurements, the parts being plated were different, with different surface areas and orientations, and the racks were not all in uniformly good condition. The values of the parameters calculated for each of the rack sets are tabulated below:

Model parameters		unite		
woder parameters	1	2	3	units
V _{start1}	111.9	1949.5	173	ml
K1	0.1000	0.0086	0.0900	1/sec
V _{start2}	122.0	2038.0	197.4	ml
К2	0.025	0.002	0.023	1/sec

When these values are put into the model equation, the dragout remaining on the rack can be calculated as a function of time. The results are listed below:

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	"Avoidable" dragout			
Time	(ml)			
(sec)		Rack #		
	1	2	3	
0	234	3988	370	
1	220	3966	351	
2	208	3946	333	
3	196	3925	317	
4	185	3904	301	
5	176	3884	287	
6	166	3863	273	
7	158	3843	261	
8	150	3823	249	
9	143	3803	238	
10	136	3784	228	
11	130	3764	218	
12	124	3744	209	
13	119	3725	201	
14	114	3706	193	
15	109	3687	186	
16	104	3668	179	
17	100	3649	172	
18	96	3631	166	
19	93	3612	160	
20	89	3594	154	
21	86	3575	149	
22	83	3557	144	
23	80	3539	139	
24	77	3521	135	
25	74	3504	131	

The total dragout from a rack will include the tabulated values above, plus V_{end} . An average value for V_{end} can be estimated from the total measured dragout (given above as 0.21 gallons per rack set). However, this will differ significantly among racks, carrying differently shaped and oriented parts. Additional drip time will not affect this value. The values in the table refer only to the portion of the dragout that can be avoided by extending the time the rack remains over the plating tank.

It will be noted that Rack #2 seems anomalous, in that it exhibits a significantly larger initial volume of dragout, and significantly slower drip time, than the other two racks. It is probable that the drip curve model is not applicable in this case. Liquid trapped in tubes, draining more slowly than solution dripping from open surfaces, could account for this behavior, delivering an overall greater volume that decreases more slowly with time. The values obtained for Racks #1 and #3 have rate constants slower than the curves from the EPA report, but not drastically so, as would be expected from the relatively high viscosity of the Zn/Ni bath.

From the table, we can calculate how much of the "avoidable" dragout can be avoided. For example, after nine seconds over the plating tank, Rack #1 is carrying 143 ml that could potential be removed with a longer drain time. Had it remained over the plating tank an additional 10 seconds, that portion of the dragout would have decreased to 93 ml, a 35% reduction. For Rack #3, the corresponding

reduction in avoidable dragout would be 32%. (For Rack #2, the decrease would only be 5%, since the initially larger dragout volume decreases more slowly with drip time. The apparent problem with this case would have to be addressed by some means other than extending the drip time.)

Calculation Details

Starting with the model equation,

dragout = $V_{start1} * e^{-k_1} * t + V_{start2} * e^{-k_2} * t + V_{end}$

with five unknown parameters, the goal is to determine what values of the parameters best match the measured values of the volume of solution dripping from a rack set. Since we are only interested in the difference in dragout volume for two different values of t, the V_{end} term will cancel out of the difference, and will not be considered further.

dragout difference = $V_{\text{start1}} * (e^{-k_1} * t_1 - e^{-k_1} * t_2) + V_{\text{start2}} * (e^{-k_2} * t_1 - e^{-k_2} * t_2)$

For each of the three racks measured, we have two measurements of the total drip volume collected from a 24" length of a rack set with a total bottom edge length of 104". The measured volumes were scaled up by a factor of 104/24 = 4.3.

Two measurements were obtained for each rack set: the volume collected over the plating tank, scaled up over the entire length of the rack (V_P), and the corresponding scaled-up volume collected over the rinse tank (V_R). This provides two equations, with four unknown parameters. Two additional equations are necessary to derive a unique solution.

The values of the parameters derived above for the curves in the EPA report will change if the model is applied to a solution with a different viscosity. For small changes in viscosity, it is reasonable to assume that the changes in the parameters will be linear functions of the viscosity change. Each parameter will have a different proportionality constant (change in value vs. change in viscosity). But the ratio of two parameters will stay approximately the same over a range of viscosities, since the viscosity change cancels out of the ratio. To the extent this approximation is valid, we can use the ratios measured in the EPA report curves to represent the ratios characterizing the parameter values for the facility data. The following equations use the ratios for the intermediate ("bent sheet") curve in the EPA report:

$$V_{start2} / V_{start1} = 5.5 / 5.0 = 1.1$$

 $k_2 / k_1 = 0.055 / 0.22 = 0.25$

The other two equations can now be written in terms of only two parameters. The values for times t_1 and t_2 are known for each measurement. We can simplify the equations further by noting that t_1 for the plating tank measurements is 0, that t_2 for a plating time measurement equals t_1 for a rinse tank measurement, and that $(t_2 - t_1)$ for the rinse tank measurements is always 2 seconds. Thus only one value of time is needed in each equation (with a value of 9, 10, or 11 seconds for Racks #1, 2, and 3 respectively. With these simplifications, the system to be solved is (dropping subscripts on k and t):

$$V_{P} = V_{start1} * (1 - e^{-k * t}) + V_{start2} * (e^{-0.25 * k * t} - e^{-0.25 * k * (t+2)})$$
$$V_{R} = V_{start1} * (e^{-k * t} - e^{-k * (t+2)}) + V_{start2} * (e^{-0.25 * k * t} - e^{-0.25 * k * (t+2)})$$

Although the system has been considerably simplified, with only three unknowns (V_{start1} , V_{start2} , and k), the presence of several different exponentials precludes an analytic solution by elementary means. The system can be solved numerically, but dealing with two coupled equations still presents computational complications.

However, it is possible to decouple the equations by solving for the unknowns, expressing each in terms of known quantities. The schematic form of the equation set is:

$$V_P = V_{start1} * A + V_{start2} * B$$

 $V_R = V_{start1} * C + V_{start2} * D$

where

$$A = 1 - e^{-k * t}$$

$$B = e^{-0.25 * k * t} - e^{-0.25 * k * (t+2)}$$

$$C = e^{-k * t} - e^{-k * (t+2)}$$

$$D = e^{-0.25 * k * t} - e^{-0.25 * k * (t+2)}$$

The system can then be solved for V_{start1} and V_{start2} as functions of known quantities and k:

$$V_{start1} = det * (D * V_P - B * V_R)$$
$$V_{start2} = det * (C * V_P - A * V_R)$$

where det is the determinant, (A*D - B*C). It is then convenient to form the ratio of V_{start2} to V_{start1} . The determinants cancel, and the quantity V_{start2}/V_{start1} can be calculated as a function of k. Now the problem can be solved numerically, by finding the value of k that makes the ratio equal to the value from the EPA report curve. The values found for each of the three rack sets are those tabulated in the "Model parameters" table above.

It only remains to determine either one of V_{start1} or V_{start2} , since the ratio between the two is assumed known. Adjusting either of the starting volumes up or down simply scales each of the terms proportionally. It is convenient to create a spreadsheet table with time in seconds starting from t=0 and continuing at least as far as the time intervals during which samples were collected. Values for all parameters are entered in reference cells, with V_{start1} undetermined. In an adjacent column, the formula is entered to compute the dragout from the adjacent time value and the information in the reference cells. Some starting value is entered into the cell for V_{start1} . The formulas column will then indicate the total amount of dragout calculated to be left on the rack for each second that has elapsed. The difference between any two dragout values represents the amount of dragout that would be collected in that time interval. That can be compared with the amount actually collected (scaled up to account for the entire rack set). The value of V_{start1} can then be adjusted until the quantities match. As a cross check, it will be noted that the same value of V_{start1} that satisfies the value for V_P also matches the amount collected for V_R . This is guaranteed by the way the value of k was calculated, as long as the assumptions behind the model are valid.