Evaporation recovery of chromium plating rinse water
by L. N. Elicker at R. W. Lacy

Presently, the commonly used procedure for treating metal finishing waste waters involves separation of oil and grease, oxidative destruction of cyanides, reduction of chromates, neutralisation, separation of the metal hydroxides and disposal of the sludge. However, the quality of the treated effluents is generally not suitable for recycling and the precipitated heavy metal sludges present a potential pollution problem when disposed of on land. As a result of these limitations and the US Government Federal legislative goal of no discharge of pollutants, there has been significant emphasis on developing, demonstrating and expanding the application of process technology for recovering metals from metal finishing waste waters, as well as sludges.

Recent years have seen a rapidly expanding collection of knowledge and experience in chemical recovery efforts within the metal finishing industry. This greatly involves technology, both in well-established processes and the development of new processes, now offers many options in equipment selection. As a result, metal finishers now need more information concerning the economic and performance of the variety of recovery systems available.

Among the more attractive approaches for recovery chemicals from metal finishing waste waters are evaporation, ion exchange, reverse osmosis, electrodialysis, and electrolytic techniques.

The study published here study focuses on providing more comprehensive performance and economic information on a new evaporative approach for recovering chemicals and purifying chromic acid rinse waters for reuse.

The study demonstrated the economic viability of an evaporative recovery system for waste waters and the project also showed that the effluent from plating rinse water can be virtually eliminated. It relates only to decorative chromium operations, though other electropolishing solutions are currently being recycled successfully.

The site selected for the project was Advance Plating Company, Cleveland, Ohio. The plating line involved was a Udylite Sidearm 350 two-lane machine with several cleaning stations, a copper strike tank, a copper plate tank, three nickel plating tanks, and a chrome plating tank, all with appropriate rinses. This report concerns only the chrome plating operation.

Evaporator

The evaporator employed was a Corning PCR-60 plating chemical recovery unit manufactured by Corning Glass Works. Dilute rinse entering the evaporator mixes with solution already in the unit. Water is boiled off by the steam-heated boiler with vertical tubes—a climbing film evaporator. The water vapour and concentrated solution enter the separator chamber where the concentrated acid rises into the recirculatory loop and the water vapour exits through the mist pad into the condenser. Condensed water is removed from the system by a liquid ring vacuum pump, and is returned to the third rinse tank in the counter-flow rinse system.

The recovery acid remains in the system while additional water is boiled off. An automatic controller senses when the recovered acid reaches a pre-set concentration and initiates a drain cycle. At Advance Plating, this concentration was 650 ppm. The evaporator then drains 20 gal of recovered concentrated acid into a product storage tank. This drain cycle takes four minutes and occurs usually once in 16 operating hours.

Installation

The layout of the chrome plating line and recovery loop evaluated in this project is shown schematically in Fig. 1. The system has four rinse tanks. The first three are in a counterflow configuration. The fourth is a still rinse.

Though most of the parts are of diecast zinc, with a small percentage of aluminium, some are brass and steel. The chrome acid used is a Udylite K-40 proprietary solution which contains Type 107 fluoride catalyst and MSP-2 wetting agent for mist control and dragout reduction. Barium carbonate is added as required to maintain the proper sulphate level. The company's chrome consumption for this line in 1975 ranged from 225kg to 420kg per month.

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are eschuteoris with pockets that create rhesc continuously sensed chrome density nonitored the total amount of dilute rinse transmitter was installed in parah with he evaporator's automatic controller.

The evaporator is boiling. The concentration between the highest liquid level (point plating tank. Other applications have used in order to obtain additional

Calculations using the data from the event recorder were performed in the following manner. (See fig. 2).

Rinse Feed Rate
The volume of water in the rinse feed tank is represented by the difference between the highest liquid level (point A, as feed to the measuring chamber is stopped) and the lowest liquid level (point B, as feed to the measuring chamber is started). This was measured to be 166.54lbs (44 gal). The time (from A to B) required to empty the chamber was determined by measuring the distance between A and B and calculating its time equivalent. The boil-off rate of the evaporator is then:

volume of chamber/time to empty

Steam Condensate Rate
The volume in the chamber of the steam condensate tank was measured to be

6.245ls (1.65gall). Multiplying the frequency of the pump actuations (C and D, for example) by the volume provides the steam condensate rate.

Test programme
The test programme for this project was divided into three areas of investigation:

1. Measurement of trace contaminants in the bath.
2. Measurement of rinse flow rates through the counterflow rinse system.
3. Analysis of chrome concentration in each rinse tank.
4. History of chromic acid additions to the plating bath.
5. History of the production rate (number of racks plated per month).

A discussion of these variables is given later in comparison to corresponding data obtained during the operation of the recovery system.

Active study programme
The scope of the active study programme involved determining the effect that varying rinse flow rates had on recovery economics and rinsing quality. These data were used to determine the relationship between the theoretical mathematical formulas used in sizing evaporator equipment and actual counterflow system performance.

The determination of operating costs and recovery efficiency of the evaporative recovery system relied on measurements made prior to operation (the data base) as well as actual operating data. For this purpose, additional information was recorded on variables such as cooling water flow rates, steam and electrical consumption, and rate of return of the product to the plating bath.

Chrome consumption
Key reasons for collecting data on chrome usage prior to the start-up of the recovery system were to determine the plating bath dragout rate and to establish a basis for comparison when looking at recovery economies.

Average dragout rate can be calculated by using the average operating time of 20 hours per day, the number of operating days during the period of time, the chrome consumption for that month. Using these figures, the calculation provides an average chrome usage of 2.731 (0.72 gall) of bath per hour. Previous experience has shown that approximately 10% of the chrome used is actually plated on the work while 90% is dragged out to the rinse waters.

Using that same ratio, a dragout rate of 2.461 (0.65 gal) of plating bath per hour can be expected. The average plating bath concentration at the time the data were collected was 300g/l (400oz/gall).

In order to verify the magnitude of the dragout rate, a second method of measurement was also used. For this measurement, the first rinse tank was filled with clear tap water. The chrome content in the first rinse water was measured hourly for four hours with the following results:

Sample taken gm/l CrO3
Start 0.0022
After 1 hour 0.52
After 2 hours 1.90
After 3 hours 2.77
After 4 hours 3.81

Average increase in concentration per hour was 0.95 g/l or 0.127 oz/gall. The volume of the rinse tank is 1014 hr (268 gall) making the amount of chrome carried into the first rinse tank 96.3g (34oz) per hour or 3.11 (0.81 g/l) per hour of dragout. Bath concentration was measured at 312g/l (420oz/gall).

The first calculated dragout rate of 2.461/hr (0.65 g/h) represents an average over an extended period of time. This number may be slightly inaccurate because of changing bath concentrations and the fact that during a working day not all racks of ware are chrome plated.

The second calculation of 3.101/hr would be nearer the maximum dragout rate encountered, since it assumes that all plated parts go through the chrome plating tank. The actual figure lies between these two numbers and the use of any dragout rate within these values is accurate for the
Table 1. Chrome concentrations in first, second and third counterflow rinse tanks

<table>
<thead>
<tr>
<th>Date</th>
<th>First Rinse</th>
<th>Second Rinse</th>
<th>Third Rinse</th>
<th>Rinse Rate</th>
<th>Rinse Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/l (oz/gal)</td>
<td>ppm</td>
<td>ppm</td>
<td>1/hr (gph)</td>
<td>R</td>
</tr>
<tr>
<td>3 Oct 75</td>
<td>1.08 (0.126)</td>
<td>15.0</td>
<td>4.5</td>
<td>1272 (336)</td>
<td>420</td>
</tr>
<tr>
<td>10 Oct 75</td>
<td>0.75 (0.100)</td>
<td>37.5</td>
<td>—</td>
<td>1090 (288)</td>
<td>360</td>
</tr>
<tr>
<td>15 Oct 75</td>
<td>1.13 (0.150)</td>
<td>—</td>
<td>—</td>
<td>636 (168)</td>
<td>210</td>
</tr>
<tr>
<td>17 Oct 75</td>
<td>1.13 (0.150)</td>
<td>—</td>
<td>—</td>
<td>659 (174)</td>
<td>217</td>
</tr>
<tr>
<td>22 Oct 75</td>
<td>0.56 (0.076)</td>
<td>—</td>
<td>—</td>
<td>659 (174)</td>
<td>217</td>
</tr>
<tr>
<td>24 Oct 75</td>
<td>0.75 (0.100)</td>
<td>—</td>
<td>—</td>
<td>704 (166)</td>
<td>232</td>
</tr>
<tr>
<td>14 Jan 76</td>
<td>3.00 (0.400)</td>
<td>125.0</td>
<td>15.0</td>
<td>136 (38)</td>
<td>45</td>
</tr>
<tr>
<td>16 Jan 76</td>
<td>3.00 (0.400)</td>
<td>119.0</td>
<td>16.0</td>
<td>151 (40)</td>
<td>50</td>
</tr>
<tr>
<td>4 Feb 76</td>
<td>4.50 (0.600)</td>
<td>104.0</td>
<td>14.0</td>
<td>148 (39)</td>
<td>49</td>
</tr>
<tr>
<td>2 March 76</td>
<td>6.00 (0.800)</td>
<td>110.0</td>
<td>23.0</td>
<td>151 (40)</td>
<td>50</td>
</tr>
<tr>
<td>10 March 76</td>
<td>3.80 (0.500)</td>
<td>132.0</td>
<td>78.0</td>
<td>167 (144)</td>
<td>55</td>
</tr>
<tr>
<td>15 July 76</td>
<td>20.00 (2.660)</td>
<td>640.0</td>
<td>67.0</td>
<td>45 (12)</td>
<td>12</td>
</tr>
<tr>
<td>16 July 76</td>
<td>27.50 (3.660)</td>
<td>1280.0</td>
<td>184.0</td>
<td>31 (8)</td>
<td>10</td>
</tr>
<tr>
<td>20 July 76</td>
<td>31.70 (4.220)</td>
<td>2000.0</td>
<td>240.0</td>
<td>34 (9)</td>
<td>11</td>
</tr>
</tbody>
</table>

Rinse tank performance

The theoretical rinsing equations discussed by Pinkerton and Graham have been shown by Abeeg to be in the general form:

\[ C_i = R \frac{(n+1)}{R (n+1)} \]

which, for large values of R, reduces to:

\[ C_i = R \]

where \( C_i \) = concentration in the plating bath, \( C_{i-1} \) = concentration in the \( i \)th rinse tank in the series (\( i = 0, 1, 2, \ldots n \)), \( n \) = number of rinse stages in the countercurrent series, and \( R \) = rinse ratio defined as rinse flow rate/dragout rate.

With this equation, the concentration in any countercurrent rinse position can be calculated. This, of course, assumes perfect rinsing. Pinkerton and Graham state: 

Good practice will approach this ideal as closely as possible by incorporating the following features:

1. Vigorous agitation of the rinse water with air.
2. Introduction of fresh water at the bottom of the tank.
3. Placing the overflow weir at the opposite end of the tank from the point at which water is introduced.

Advance Plating incorporates a rinsing system that is probably more typical than perfect. The first recommendation is incorporated in the first two tanks; the second is found in all three tanks, while the third is not used at all. Samples of the rinse tank waters from each of the three countercurrent rinse tanks were taken at regular intervals and analysed for chrome content (Table 1). The Rinse flow rate from the plating bath was calculated and the rinse flow rate was known, the rinse ratio can be calculated. Comparison of the data collected and theoretical curves indicate close agreement between the actual and theoretical performances for the first rinse tank (Fig. 3). The curve represents theoretical concentrations based on the actual dragout rate at Advance Plating. The points (from the data in Table 1) are actual concentrations at given rinse times. Data on rinse flow rates taken before the start-up of the recovery system illustrate the typical use of higher rinsing rates. (The data points at high rinse ratios are shown near the horizontal slope of the curve). The data plotted below rinse ratio 100 was taken during the active test programme and reflect operation at very low rinse rates.

Figs. 3 and 4. Chrome concentration in first rinse tank (below left) and in third rinse tank (below right).