Chrome Electroplating Waste BAT

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During the past several years, waste produced by the electroplating industry has attracted attention due to the level of pollutants found in the waste stream, the difficulty associated with treatment, and the cost of waste disposal. EPA has enacted regulations to control the discharge from plating facilities and estimates that 140 million lb of metal pollutants will be prevented from being discharged to publicly owned treatment works.

The current pretreatment regulations are oriented toward meeting standards using Best Practical Technology (BPT). These requirements can be normally achieved using cyanide oxidation, chromium reduction, and acid alkali neutralization. By July 1984, however, the second generation National Pollutant Discharge Elimination System (NPDES) permits for point source dischargers must be capable of treating toxic pollutants using Best Available Technology (BAT), as required by the Clean Water Act. The pretreatment standards for industrial users will also reflect BAT.

The categorical standards for the electroplating industry were revised in August 1982 to include the metal finishing industry. The pretreatment standards for existing sources must be capable of meeting BAT standards by January 1984. The level of treatment to achieve BAT will probably include internal plant controls, flow reduction, resource recovery, and closed loop systems where economically achievable. Additionally, the Resource Conservation and Recovery Act (RCRA) regulates the disposal of sludges containing toxic materials. All sludges generated from the treatment of electroplating wastewater are listed hazardous wastes and must be hauled to a licensed landfill. Some industries have been successful with delisting electroplating sludge; however, this is not felt to be a long term solution to the problem.

The conventional treatment of electroplating wastes using BPT produces a large volume of sludge. For example, chrome reduction produces 1.98 lb of dry solids using NaOH and 2.24 lb of dry solids using Ca(OH)₂ for each pound of waste hexavalent chrome. In either case, the production of hazardous waste has been doubled through the treatment process. Furthermore, the average costs of plating and waste treatment chemicals have risen significantly over the past several years. Plating chemicals, for example, have risen 50 to 150 percent in the last decade. Chromic acid, which cost $0.37/lb in 1972, is currently costing electroplaters over a $1/lb.

The changes in metal prices, cost of treatment/disposal, and future environmental regulatory goals, dictate that the technology of water pollution control for the plating industry be reevaluated. Alternatives which take advantage of resource recovery, minimization of sludge production and are compatible with future standards based on BAT should be investigated.

This article discusses the economics of a closed loop system for the hard chrome plating lines installed at a Naval Aircraft Rework Facility. An automated high vacuum vapor recompression (VC) module has been developed to evaporate 20 gph of rinse water. The concentrate is discharged to a waste heat evaporator and evaporation is continued until the concentration is high enough for use in the plating bath makeup. The distillate from both units is sent to the final rinse tanks for reuse in the cleaning operation. The VC module has the energy efficiency equivalent to 12 effects over conventional atmospheric evaporators. The waste heat module is designed to make maximum use of waste heat available in the plating shop hot wells and there are no treatment/disposal costs for the hexavalent chrome.

Evaporators as a Waste Control Technique

Pollution control for the electroplating industry has been developed around two philosophies: (1) The stabilization of pollutants in the waste stream by some form of chemical treatment, or (2) the elimination of the pollutant from the effluent by a recovery process. Chemical treatment of the plating waste has two distinct disadvantages due to the inability to recover metals, and the additional cost associated with hazardous waste disposal. There are several processes which are available to the plating industry for the removal of metals.

Figure 1. High vacuum vapor compression unit.

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from the waste stream. However, conventional techniques as reverse osmosis or ion-exchange have had difficulty maintaining performance standards due to fouling or deterioration. RO units also have difficulty reaching the desired high concentrations required for plating bath makeup and do not reject all the plating bath impurities. The major drawback of the ion-exchange is the regeneration process which complicates operation and requires treatment of the backwash solution.

Evaporation was the first separation process used to recover plating chemicals lost in rinse water and has proven to be successful on most types of plating processes. The disadvantage of the conventional atmospheric or vacuum single effect evaporation is the cost of energy. A single effect evaporator requires approximately 1000 Btu's to evaporate one pound of water. The cost of evaporation has been reduced by installing a multi-effect system in series but requires the large capital investment of several evaporators and higher operating temperatures.

There are currently four basic types of evaporators available to industry. Two of the evaporators, the spray and rising film, operate so that the heating surface is covered with only a film of wastewater. The submerged tube and atmospheric exhaust evaporators operate by transferring heat to a reservoir of wastewater. The surface film evaporators have a higher heat transfer coefficient and are therefore more efficient. The high cost of corrosive resistant materials has resulted in the selection of heat transfer mediums with the highest heat transfer coefficients. The size or surface area of the heat exchanger can be reduced considerably which results in capital cost savings. All the evaporators can return the made distillate to the rinse tanks except the atmospheric exhaust system which vents the distillate to the air.

Another technique called vapor compression evaporation is used to reduce the treatment process cost. This technique has the lowest energy consumption. A mechanical compressor is used to increase the pressure and temperature of the separated water vapor and is used to heat the plating solution. The distillate is sent to the final rinse tanks and the concentrate is used in the plating bath makeup.

Previous efforts to use vapor compression units have shown limitations due to the corrosive carryover of acid fumes and have, therefore, been used with only alkaline solutions. Conventional vapor compression techniques also do not evaporate the waste solution under vacuum and the high temperatures associated with this process cause degradation in the plating chemicals. The advantage over other evaporation techniques is the elimination of cooling towers and external steam requirements. The innovative technology developed through the Navy’s study is a new vapor separator column which allows the VC module to be used to recover chromic acid waste. The separator column eliminates previous problems with compressor corrosion. The VC module has also been developed to allow the plating solution to be evaporated under vacuum at low temperatures which results in the increased efficiency over previous models.

The capital investment of evaporators is based on the quantity of rinse water to be treated. The quantity of rinse water is a function of the maximum allowable dragout in the final rinse tank which will not interfere with the plating process. Flow rate controllers, spray washers, or counter-current rinse tanks are installed which concentrate the dragout to the maximum allowable limit and minimize the rinse water discharge. Spray washers are an acceptable rinse technique for flat surfaces; however, they cause considerable problems with contoured and inner surface cleaning. The flow rate controller can reduce the quantity of waste effluent but it is only a fraction of what can be accomplished by employing counter-current rinse tanks. For example, using the following:

\[ r = \left( \frac{C_p}{C_N} \right)^{1/N} \]

where

- \( r \) = ratio of rinse volume to dragout volume
- \( C_p \) = concentration in the process solution
- \( C_N \) = required concentration in the last rinse tank
- \( N \) = number of rinse tanks

If a chrome plating solution contains 250,000 ppm total dissolved solids and 20 ppm are the maximum allowable limits in the final rinse, then 12,500 gal of rinse water are required for each gallon of process dragout. Assuming the dragout for a chrome plating tank is 0.4 g/hr, the wastewater effluent is 5,000 g/hr. By installing two counter-current rinse tanks the flow rate is reduced to 44 g/hr, three counter current rinses to 9.3 g/hr, and four counter flow rinses to 4.23 g/hr.

### High Vacuum Vapor Compression Unit Thermodynamics

**Description of Recovery Process**

Referring to Figure 1, the chrome plating waste enters the recovery system at point G. The waste enters the reactor vessel at point A after picking up heat from the regenerative heat exchanger. The waste material is concentrated to the
desired strength and leaves the evaporator via A and is returned to the chrome plating bath. The compressed vapor enters the reactor vessel at point C and is condensed in the Bayonette tube heat exchanger. The condensate is removed at point D and is used to provide desuperheat, point B, or rinse water makeup, point I. A vacuum is maintained on the reactor by recirculating the condensate through an eductor.

The waste heat evaporator operates with the same principle as the VC unit except the energy to sustain boiling is obtained from waste heat. Therefore, an arbitrary value was assigned to the waste heat and a process thermodynamic evaluation was developed for only the VC module.

**Process Dynamics**

The principle behind the high vacuum vapor compressor distiller concentrator is similar to the refrigeration cycle using water as the refrigerant. As the pressure is reduced, so is the boiling point of the solution. Therefore, rapid evaporation takes place at a lower temperature. The heat in the vapor is used to sustain the boiling operation. This now involves the Clausius statement of the second law of thermodynamics. Clausius states that it is impossible to construct a device which operates in a cycle and produces no effect other than the transfer of heat from a cooler to a higher temperature body. The implication of this statement is that a system that does produce the transfer of heat from a cooler to a hotter body requires the input of some additional work.

The system shown in Figure 2 is a simple heat pump to satisfy Clausius' statement. The absolute temperature of the source is $T_L$ degrees and the heat transferred from the source is the refrigeration effect, $Q_L$. The energy rejects into the heat sink at temperature $T_H$ degrees and this amount of heat delivery is $Q_H$. Both effects are accomplished by the input of work, $W$. For continuous operation, application of the first law of thermodynamics to the system shows that over a particular period of time, $Q_H = Q_L + W$. The high vacuum vapor compression unit is a practical application of the heat pump.

The same relationship of the ideal heat pump is maintained when we recycle the heat of the vapor to the plating solution to sustain boiling. In other words, the heat in the vapor, $Q_L$ plus the work input, $W$, must equal $Q_H$. It becomes apparent when working with the system that due to the mechanical inefficiencies of the compressor, $Q_L + W$ provides more heat output than is necessary to sustain boiling as shown by the data presented in Table 1.

In order to prevent the boiling point from continuously rising due to higher heat input than necessary, a second heat sink had to be found. If the system were operating at or above atmospheric pressure, a portion of the steam vapor could be wasted or sent to a separate condenser, but because the discharge pressure is at 5.75 in. Hg absolute, the injection of desuperheating cooling water evolved. It was also determined that injection of the desuperheating cooling water in front of the compressor improved the operation by providing sealing of the compressor lobes which increased the volumetric efficiency and decreased the work input requirement.

**Energy Efficiency**

The term thermal efficiency is not easily applied to a refrigeration machine or a heat pump. For a power cycle the thermal efficiency is the power output divided by the energy input. The ratio must always be less than unit. For the system shown in Figure 2, the heat delivered to the heat sink must be greater than the work energy supplied in accordance with the first law of thermodynamics (i.e. $Q_H = Q_L + W$). In place of the term thermal efficiency the term coefficient of performance (COP) can be used. This might be defined as "What you want to achieve divided by what you have to pay to achieve it." The personal pronoun "you" is used on purpose since, for a given situation, the numerical value of the COP will depend on the subjective judgement of what was desired such as the cooling effect or the heating effect. A heat balance on the system as shown in Figure 1 yields the following:

**Heat Balance on Evaporator Vessel**

1. Heat Out = 200 lb (1115.3 Btu) + 25 lb (97.86 Btu)
   \[
   = \frac{223,060 \text{ Btu}}{\text{hr}} + \frac{2446 \text{ Btu}}{\text{hr}} \]
   \[
   = \frac{225,506 \text{ Btu}}{\text{hr}} \]

2. Heat In = Heat Out = 225,506 Btu/hr

3. 225,506 Btu = 225 lb (h_3 \cdot h_4 \text{ Btu}) + 450 lb (h_3 \cdot h_4 \text{ Btu})
   \[
   = \frac{225 \text{ lb}}{(74.65 \cdot 53 \text{ Btu})} + \frac{450 \text{ lb}}{(74.65 \cdot 102.35 \text{ Btu})} \]
   \[
   = \frac{487 \text{ Btu/hr}}{\text{hr}} + \frac{450 \text{ lb} \cdot h_3 \cdot 46057 \text{ Btu}}{\text{hr}} \]
   \[
   h_3 = 602 \text{ Btu/lb} \]
This would correspond to a quality of 50 percent vapor in the compressor discharge.

(4) COP = \frac{\text{Heat Out}}{\text{W}} = \frac{225,506 \text{ Btu/hr}}{6.66 \text{ KW/hr} \times 85\% \times 3142 \text{ Btu/KW}} = 11.67

A COP of 11 means that for every unit of heat input there are 11 units of heat output. To evaporate 1 lb of water using conventional technology 1000 Btu of heat input are required. The high vacuum vapor compressor only requires 90 Btu's of heat input to evaporate the same quantity of water.

**Methods and Materials**

Operation of the vapor compression evaporator under vacuum was acquired by employing the use of a favorite tool of the chemist—a water powered eductor. This simple device not only removes the noncondensible gases (air), it also removes the made distillate plus desuperheat water for recycling.

Operating under vacuum increases air infiltration with its detrimental effects on heat transfer in condensing steam. The extra 'water loading' or wet steam exiting from the compressor due to the water injection for desuperheating and water sealing also tends to reduce heat transfer rates. In a banked tube bundle the condensate loads up the tube surfaces and blanks the heat transfer surfaces. A novel adaptation of a bayonet tube heat exchanger was used to circumvent these effects.

The vapor flows through the annulus formed by a thin wall titanium sheath in contact with the boiling chromic acid. The condensing vapor sweeps the noncondensibles to the back end of the sheath where the small diameter bayonet tube or air lance continuously siphons off the noncondensible gases. This individual sweeping and purging prevents any pocketing of air and the creation of partial pressures and reduction in apparent heat transfer rates. The bayonet tube bundle is slightly pitched downward toward the steam and air plenums at the inlet end so that the condensate is individually drained from each tube rather than being allowed to drop down and build up on the lower tube banks forming films of condensate and blanketing the tubes.

The vacuum operation and corresponding low temperatures of the cycle permits the use of standard CPVC or fiberglass reinforced PVC construction for the enclosures and piping. Together with the use of the titanium sheathed heat exchanger, these materials of construction are impervious to the corrosive attack of the many different plating solutions.

A three stage separator assures high quality distillate and prevents carryover to the compressor. The compressor lobes and casing are electrolless nickel coated to resist corrosive attack from the recycled distillate which is used to seal the lobes and improve volumetric efficiency and prevent superheat which could rise as high as 350°F without this water injection. Mechanical seals are used to prevent oil leakage from the time gear casing to the vapor casing.

A 10 horsepower variable speed drive is used to vary the compressor speed and provide capacities ranging from 15 to 25 gph depending on the work load which can be sporadic in a military plating operation. Peak capacity is attained at a compressor speed of 3600 rpm. Three counterflow rinse tanks are used which will handle a dragout rate of 1 gph with a capacity of 25 gph from the distiller concentrator.

Since boiling point elevation (BPE) has a major effect on the energy required for the compressor, a special Cottrell apparatus was required to determine the effect of vacuum. At atmospheric pressure the BPE for chromic acid was 0.71°C at 60,000 mg/l, 2.68°C at 225,000 mg/l and 3.55°C at 300,000 mg/l. At 100 mm Hg (125°F) the BPE's were 0.52, 1.94 and 2.58°C, respectively. There is a decided energy advantage therefore in operating a vapor recompression evaporator at reduced pressures when concentrating plating wastes.

**Economic Analysis**

Table 2 shows a comparison of the estimated annual operating costs for the treatment of chrome waste using BPT; a conventional single effect evaporator; and, a high vacuum vapor compression and waste heat module. The data was based on a dragout rate of 0.6 gph of chromic acid at 240 g/l (32 oz/gal) operating 6600 hr/yr. During a five year period, the high vacuum vapor compression and waste heat module would save $107,877 over BPT treatment and $55,472 over conventional evaporation. The analysis did not include actual labor and maintenance cost due to the unavailability of the information at the present time. It is anticipated, however, that the high vacuum vapor compression and waste heat module will be considerably less labor intensive than BPT treatment.

**Conclusion**

Data collected on the operating performance of the high vacuum vapor recompression and waste heat module indicate that the system is a viable alternative to BPT for the electroplating industry. Rising treatment and disposal costs have made closed loop evaporation for chrome plating rinse water an economically achievable treatment process. The advanced technology developed through this study is compatible with future EPA regulatory requirements and will meet BAT standards.

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