CHAPTER II

LITERATURE REVIEW ON ELECTROPLATING WASTEWATERS

2.F General Background

The general aims of electroplating process are to change the surface property of a product in order to improve corrosion resistance, to make the appearance more pleasing, to improve hardness, to increase wear resistance, to change surface conductiwity and/or to finish to suit specific engineering applications. The process may be directed toward:

-cleaning, which is the removal of surface oils, greases, buffing compounds and the like,

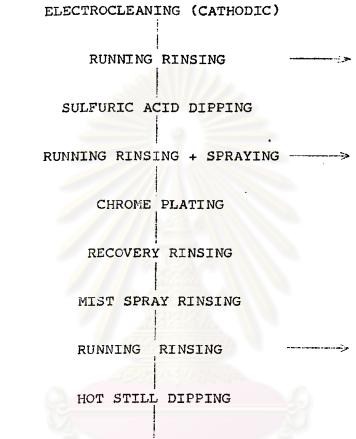
-removal of oxides, rust, scale, and other materials, -electrochemical or chemical processing to provide the basis metal with a surface coating consisting of a plated metal or a chemically deposited, so-called conversion coating such as phosphate and oxide film as in blackening.

It is evident that the cleaning and oxide removal steps are mainly preparatory steps for good adhesion and receptivity for the subsequent finishes to be employed. They are a major part of the activity in an electroplating plant, while they are steps of relatively minor importance for the manufacturer. An electroplating plant may also be engaged in mechanical finishing activities, such as polishing and buffing, sandblasting, or wire brushing. It may have cleaning or painting process employing solvents, mainly various chemical solutions using water as a solvent for the chemicals and as a rinsing medium between the various process solutions through which the work progresses. Most of finishing steps employ wet process and require rinsing steps and it can be seen that water pollution is caused by the deliberate or accidental discharge of the processing solutions and the contaminated rinse water.^(1,2)

2.2 Chromium Plating Process

There are two types of chromium plating: bright or orna mental plating and hard or industrial plating. The ornamental deposits are very thin, usually less than 0.00075 mm. (0.0003 in.) thick and are applied over a protective coating of nickel on steel, brass, or zinc. The industrial chromium coating are generally more than 0.025 mm. (0.001 in.) thick and are applied to steel and seldom to other basis metals. The hard chromium plating was used for applications where good lubrication was essential, e.g., air craft and Diesel engine cylinders and piston rings. These deposits consisted of chromium coatings that had been etched so as to produce or accentuate cracks or pores, in which lubricating oil could be retained.⁽³⁾ Compositions of chromium baths and flow diagram for some common chromium plating process are shown in Table 1 and Figure 1, respectively.

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RUNNING RINSING

HOT RINSING (SLOW OVERFLOW)

DRY OVEN

Note: Wastes overflowing to final effluent are indicated by an arrow

Figure 1 Flow Diagram for Some Common Chrome Plating Process⁽⁴⁾

Table 1 Composition of Chromium Baths (5)

Composition	1	2	3
Chromic acid, CrO ₃ oz./gal.	33,0	53.0	45.0
Sulfuric acid, H ₂ SO ₄ oz./gal.	0.33	0.53	0.29
Bath ratio, Cr03/H2S04	10031	100:1	155:1

2.3 Quantities and Composition of Electroplating Wastes

There are wide variations in both the volume and composition of electroplating wastewater from plant to plant. This is because the waste streams from these plants are the product of local plant conditions and practices such as dragout, rinsing techniques, recovery methods employed, and the admixture of other waste streams, such as those from machine shops. There is little or no information on the volume and composition of wastes that might be encountered in the smaller shops that do general plating. It must be assumed, however, that the rinse waters from the smaller establishments are extremely variable from shop to shop, and perhaps from day to day or hour to hour within a specific shop.⁽⁶⁾ Some quantities and characteristics of chromium bearing wastes are shown in Table 2.

2.4 Sources of Electroplating Wastewater

Waterborne wastes generated in the electroplating and metal finishing industry include the following.

1. Rinse water from plating, cleaning and other surface

Table 2 Volume of Chromium-Bearing Wastes from Typical Plating Operations in the Electroplating Industry (6)

	Chromi um - Bearing Waste			
Type of Work Plated	Volume, gal.	Analyses, ppm Cr Ni Cu		
Office furniture	24,000/day		-	
Typewriters and office machines	50,000/day	16	39	-
Home appliances	43,200/day	-	-	
Silverware	40,000/day	5	33	135
Instrument motors and electric clocks	112,000/day	-	-	-
Automobile manufacture	620,000/day	30	80	70

Note : - No report

finishing operations (shown by arrows in Figure 1.)

2. Concentrated plating and finishing baths that are intentionally or accidentally discharges.

3. Wastes from plant or equipment cleanup

4. Sludges, filter cakes, etc., produced by naturally occuring deposition in operating baths, chemical rinsing circuits, etc., when flushed down sewers.

5. Vent scrubber waters. (6)

The most important of these wastes is the rinse water. For chromium plating, rinse water is continuously discarded as wastewater contains 50 - 600 mg./cu.dm. Cr VI which is concentrated enough to be toxic.⁽⁵⁾

2.5 Treatment Methods Commonly Used for Rinse Water of Chromium Plating

2.5.1 Conventional Methods

- Reduction of hexavalent chromium by sulfur dioxide, sulfites and ferrous sulfate. Chromium plating rinse water are often disposed of by process involving the reduction of chromium to the trivalent form and subsequent precipitation of the reduced chromium with alkali. The reactions occur as the following

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
, $2CrO_3 + 3H_2SO_3 \longrightarrow Cr_2(SO_4)_3 + 3H_2O$ (1)

$$2Cro_{3} + 6FeSO_{4} + 6H_{2}SO_{4} \longrightarrow 3Fe_{2}(SO_{4})_{3} + Cr_{2}(SO_{4})_{3} + 6H_{2}O$$
(3)

$$Cr_2(SO_4)_3 + 6NaOH \longrightarrow 2Cr(OH)_3 + 3Na_2SO_4$$
 (4)

The precipitates from the neutralization step are composed of the hydroxides of the metals (chromium, nickel, copper, iron, etc.) - Precipitation of hexavalent chromium by barium compounds. This method of treatment usually involves the use of barium salts for precipitation of insoluble barium chromate. With barium chloride, for example, the following reaction takes place

$$BaCl_{2} + Na_{2}CrO_{4} \longrightarrow BaCrO_{4} + 2NaCl$$
(5)

The major disadvantages of this method is that the additions of barium chloride must be strictly controlled, as this chemical is highly toxic. The sludges produced also are toxic and may result in an additional disposal problem. Relatively few plants employ this process.⁽⁶⁾

2.5.2 Physical Methods

There are two physical methods that have been commonly used in the treatment of rinse waters. These are ion exchange process and evaporation.⁽⁶⁾

Techniques of ion exchange in chromium plating are

1 - The purification of contaminated plating baths by using cationic exchangers to remove iron, trivalent chromium, etc.

2 - The recovery of chromic acid from reclaimed rinsing system by the use of cationic exchangers for the removal of impurities followed by the concentration of the purified rinse solution by evaporative prodecures. 3 - The detoxification of rinse water containing chromium by using both cationic and anionic exchangers to affect the removal of both trivalent and hexavalent chromium as well as other impurities.⁽⁶⁾

On the other hand, evaporation is used to reconcentrate rinse water for the recovery of plating chemicals. It can be done by either vacuum evaporation or atmospheric evaporation. Vacuum evaporation seems to have more advantages that the water removed by this method can be recondensed and reused for rinsing.⁽¹⁾

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