Treatment of Electroplating Wastes

By H. S. S. Chiu, B.A., M.P.H. (Member), K. L. Tsang, B.Sc., M.Sc., D.I.C. (Member) and R. M. L. Lee, B.Sc., B.A.Sc (Member)

Senior Consultant, Consultant and Assistant Consultant, Environmental Management Div., Hong Kong Productivity Council, respectively

Introduction

With the increasing concern over the protection of the environment, the electroplating industry is likely to be one of the industries to be affected by the introduction of the water pollution control legislation in Hong Kong. The effect may be even more pronounced for the operators of small and medium-sized electroplating factories since they are unlikely to have any expertise in pollution control and will therefore require outside technical information and assistance.

During the past few years, the Hong King Productivity Council has acquired first hand data on the characteristics of effluent discharged from local electroplaters and has been involved in the design of wastewater treatment systems for a number of plating factories.

The purpose of the paper is to present a review of some findings of the Productivity Council on the treatment of electroplating wastes. In the paper, the typical electroplating processes appropriate to local factories as well as the general characteristics and volume of the plating wastewater are discussed. The various practical measures that can reduce pollutant discharge and some methods of treatment of electroplating wastes are also described.

The Electroplating Industry of Hong Kong

According to the Census and Statistics Department of the Hong Kong Government there were approximately 847 electroplating establishments in Hong Kong at the end of June 1984 (including buffing and polishing establishments) and about 98% of them were predominantly small and medium-scale operations employing less than 50 employees. These plating factories, like the other local manufacturing industries, are generally housed in multi-storey industrial buildings which are uncommon for other areas outside Hong Kong.

Typical Electroplating Processes

The types of plating processes practised in Hong Kong are plating of copper, nickel, chromium, zinc, gold, silver, tin, lead as well as aluminium anodizing. A great majority of the electroplating shops are engaged in the plating of copper, nickel and chromium for decorative metal surface finishing. It is also common that in a single factory several different types of plating are practised at the same time. The typical chemical compositions of the various types of plating baths used in Hong Kong are summarized in Table 1, which shows that the plating baths are generally highly acidic or alkaline and often contain toxic substances such as cyanide and heavy metals. Hence, their discharge and disposal should be carefully controlled and treated to minimize the impact on the receiving water-bodies.

Table 1. Typical Chemical Compositions of the Plating Baths Used in Hong Kong

Type of plating	Plating bath composition	
Copper	Copper cyanide	20–25 g/l
	Sodium cyanide	30–35 g/l
	Sodium carbonate	15–30 g/l
Nickel	Nickel sulphate	240–300 g/l
	Nickel chloride	45–60 g/l
	Boric acid	30–40 g/l
Chromium	Chromic acid anhydride	250–400 g/l
	Sulphuric acid	2·5–4·0 g/l
Zinc	Zinc metal	25–45 g/l
	Sodium cyanide	35–105 g/l
	Sodium hydroxide	35–115 g/l
Tin	Stannous sulphate	30–50 g/l
	Sulphuric acid	40–70 g/l
	Phenolsulphuric acid	30–60 g/l
Tin-Lead	Stannous sulphate	12–20 g/l
	Lead	8–14 g/l
	Fluoboric acid	350–500 g/l
Gold	Potassium gold cyanide	1–6 g/l
	Potassium cyanide	30 g/l
Silver	Silver cyanide	36–75 g/l
	Potassium cyanide	60–90 g/l
Aluminium anodizing	Sulphuric acid	15–25% (wt)

TABLE 2. CHARACTERISTICS OF PLATING WASTEWATER DISCHARGE FROM SIXTEEN LOCAL ELECTROPLATING SHOPS

Plating operation	Factory area (m^2)	Parameter							
		pH	Chromium (Cr) (mg/l)	Cyanide (CN) (mg/l)	Copper (Cu) (mg/l)	Nickel (Ni) (mg/l)	Zinc (Zn) (mg/l)	Aluminium (Al) (mg/l)	Silver (Ag) (mg/l)
Ni and brass	20	8·0	—	6	2	150	4	—	—
Ni and Zn	25	7·7	1	—	—	106	4	—	—
Cu, Ni and Zn	60	4·0	33	6	4	168	250	—	—
Cu, Ni and Cr	70	5·2	20	4	2	30	—	—	—
Cu, Ni and Au	80	7·8	1	2	1	5	—	—	—
Aluminium anodizing	100	6·2	3	—	—	—	—	10	—
Aluminium anodizing	100	2·7	—	—	—	—	—	230	—
Cr, Ni and Cr	120	2·5	31	4	2	13	—	—	—
Ni and Zn	150	8·2	1	—	—	95	10	—	—
Cu, Ni, Cr and Ag	150	1·7	9	1	—	8	—	—	2
Cu, Ni and Cr	200	4·5	25	6	3	230	—	—	—
Cu, Ni, Cr and brass	200	7·0	40	1	11	365	15	—	—
Cu, Ni, Ag and Cr	250	1·9	3	1	—	11	—	—	3
Ni, Cr and Au	300	5·6	38	—	—	3	—	—	—
Cu, Ni, Cr and brass	400	7·7	5	5	30	25	10	—	—
Cu, Ni and Cr	1000	5·5	20	3	1	15	—	—	—
Range	20–1000	1·7–8·2	1–40	1–6	1–30	3–365	4–250	10–230	2–3

CHARACTERISTICS OF WASTEWATER

More than 90% of the wastewater discharged from a plating shop comes from rinsing of workpieces with the occasional discharges of process solution, spillage or cleaning of process devices.

The characteristics of electroplating wastewater are a function of the types of plating processes, rinsing methods and plating practices. Table 2 presents the typical plating wastewater characteristics of sixteen electroplating factories surveyed in Hong Kong. The wastewater samples were collected from the main discharge pipes of the factories and therefore represented the combined characteristics of the various types of wastewater from various processes. According to the information obtained during the survey of the local electroplating factories, it was found that the characteristics of the plating wastewater varied from one factory to another even though both might be engaged in the same plating processes.

As observed during the survey, the combined plating wastewater was generally clear, colourless and with a pH ranging from acidic to slightly basic (pH 1·7–8·2).

Cyanide was detected in the combined wastewater discharged from copper and zinc plating factories with concentrations ranged from 1–6 mg/l. As the baths of these two plating processes contained cyanide, the sources of cyanide detected in the wastewater should be derived from the washing of the drag-out solution still attached on the surface of the plated items.

Similarly, chromium was detected in substantial amount (1–40 mg/l) in the wastewater discharged from factories engaged in chromium plating and zinc plating. The sources of the chromium were from the drag-out of the chromium plating bath and the passivating bath of the zinc plating operation. The chromium in the wastewater existed mostly in the hexavalent form.

Depending upon the type of plating processes, heavy metals such as copper, nickel, zinc, aluminium and silver were also detected in the wastewater and

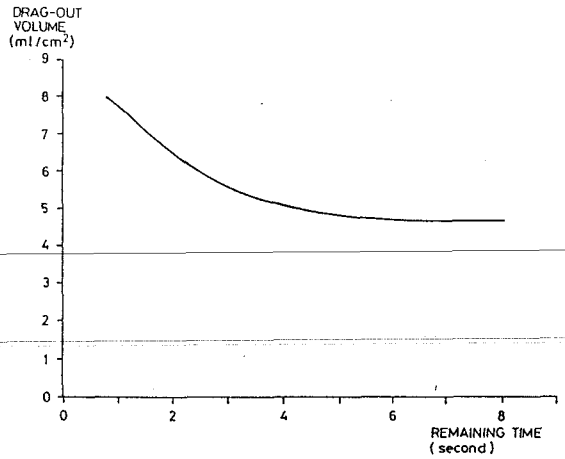

Fig. 1. Variation of drag-out volume with the remaining period of workpieces above a plating bath

the concentrations of which were generally less than 400 mg/l.

In summary, the combined plating wastewater generally contained cyanide, hexavalent chromium and heavy metals. As these chemicals possess a certain degree of toxicity to the human health and aquatic life, it is therefore necessary to provide treatment to reduce the level of these contaminants before the waste-water is allowed to discharge into receiving water-bodies.

Methods to Reduce Pollution Discharge

In order to minimize the cost of treatment of electroplating wastes, it is necessary for electroplaters to adopt measures to reduce pollutant discharge and volume of effluent. Some examples of these measures are described below.

Methods of Reducing Pollutant Discharge

(1) *Use of properly designed racks.* Workpieces to be plated are hung on racks which are generally coated with a thin layer of plastic material for insulation purposes. The total surface area of the racks usually amounts to 10–30% of that of the workpieces. In order to minimize the extra drag-out volume due to the racks, they should be properly designed to improve drainage such as evenly coating the racks with plastic materials and even to the point of placing drainage holes in appropriate places on the racks. However, this design aspect is often overlooked by local electroplaters.

(2) *Speed control of removal of workpieces from plating bath.* The speed of removal of workpieces from a plating bath is an important factor affecting the volume of drag-out. From Fig. 1, it can be seen that the longer the period that workpieces remain above the plating bath after emerging from the plating bath the lesser the volume of drag-out that will result. If the remaining period above the plating bath is 3 second or more, the drag-out volume reduces to about 60% of that at 1 second. In actual plating processes the remaining period should therefore be controlled at 4–6 seconds.

Methods to Minimize Waste Rinse Water

As observed during the factory visits, local electroplating factories often use an excessive volume of water to clean the surfaces of the plated workpieces without due regard to the washing efficiency. This unnecessarily large volume of rinsing water discharged will result in the increase of the capital cost of the treatment system. Hence, in order to reduce the cost of treatment of wastewater, measures have to be adopted to reduce the volume of rinsing water used. Some of the practical measures to reduce the consumption of rinsing water are:

(i) *Addition of air-mixing in rinse tanks.* Air mixing facilities, when added to rinse tanks, can increase the efficiency of rinsing by adequately providing turbulence between the workpieces and the rinse water and thus effectively remove the drag-out solution from crevices of the workpieces. However, it should be noted that the air pressure applied should not be excessive in order to avoid workpieces loosening from the hanging racks. It has been found that in a rinse tank of 460 mm water depth a 0·5 kg/cm² air pressure is sufficient to provide good mixing. Air supply can be accomplished by a perforated tube which is typically 20–25 mm diameter.

(ii) *Improving rinsing practices.* Improvement in rinsing practices can result in the reduction of waste rinse water volume and, more importantly, in ensuring the quality of workpieces.

In Hong Kong, some electroplaters still use a single rinse tank system, the disadvantage of such a practice being that it requires a large amount of water

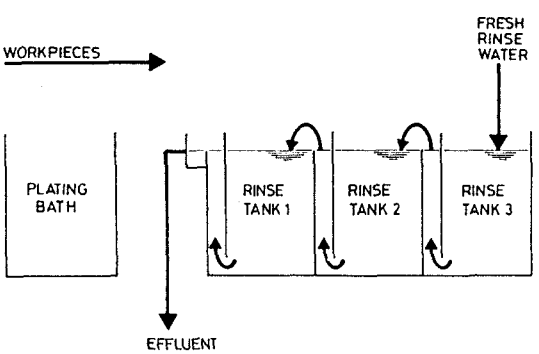

Fig. 2. Use of a countercurrent rinsing tank

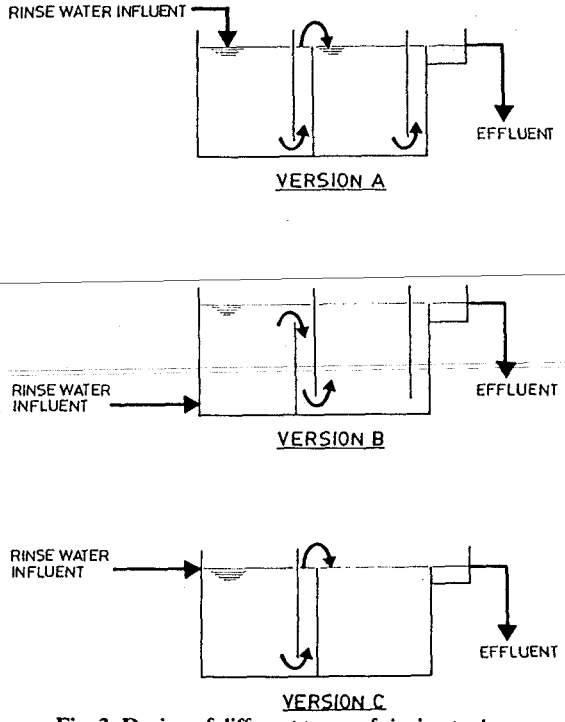

Fig. 3. Design of different types of rinsing tanks

to achieve the desired standard of cleanliness for the workpieces which is unfavourable in terms of wastewater treatment.

A superior rinsing practice is countercurrent rinse (Fig. 2) whereby the amount of rinse water required can be much reduced. In fact, the total rinse water flow needed to achieve the same degree of cleanliness decreased by about 90% for each additional rinse tank in the countercurrent sequence as compared to using only one tank. For example a rinsing system may require 100 l/min. of water for single rinsing, with two rinse tanks connected in series for countercurrent rinsing the flow can be reduced to 10 l/min., and for three rinse tanks only 1 l/min. is required. At such slow water flow rates air mixing should be used to provide adequate turbulence. The disadvantage is that the work requires more processing steps and more equipment and space are mandatory. Hence, in practise the use of countercurrent rinsing is limited to two rinsing stages.

(iii) *Improved rinse tank design.* It has been observed in local electroplating factories that the importance of the design of the rinse tank has often been overlooked. In a poorly designed rinse tank, short-circuiting between influent and effluent rinse water is common, which results in poor rinsing efficiency.

In order to improve rinsing efficiency and thus achieve a reduction of the volume of rinse water required, the inlet and outlet of the rinse water to and from a rinse tank have to be properly designed. Fig. 3 shows three versions of rinse tank design, the best rinsing efficiency achievable by version A followed by B and lastly C.

In essence, a properly designed rinse tank should be able to prevent short-circuiting and allow rinse water to mix adequately, resulting in uniform concentration in the tank and also provide cleaner fresh water at the tank's surface so that when the workpieces emerge from the tank they are rinsed by the cleaner rinse water.

Treatment of Electroplating Wastes

In general, the contaminants contained in the electroplating wastewater that are toxic in nature and require treatment are cyanide, hexavalent chromium and heavy metals.

Several types of treatment methods have been developed for each specific contaminant. Each treatment method has its particular application and constraints. Table 3 summarizes the more common methods of treatment of the three types of contaminants.

Treatment of Cyanide

(1) *Chlorination.* The use of sodium hypochlorite to oxidize the cyanide to less toxic products is the most widely practised treatment method and is considered to be most suitable to small electroplaters of Hong Kong.

Table 3. Methods of Treatment of Electroplating Wastes

Parameter	Type of treatment method
Treatment of cyanide	Chlorination Ozonation Electrolysis Ion exchange
Treatment of hexavalent chromium	Reduction to trivalent chromium and precipitation Cementation Precipitation as barium salt Ion exchange
Treatment of metals	Neutralization and precipitation as hydroxides (for non-complexed metal) Precipitation as metal sulphide (for both complexed and non-complexed metal) Destruction of complexes and precipitation (for complexed metal) Ion exchange

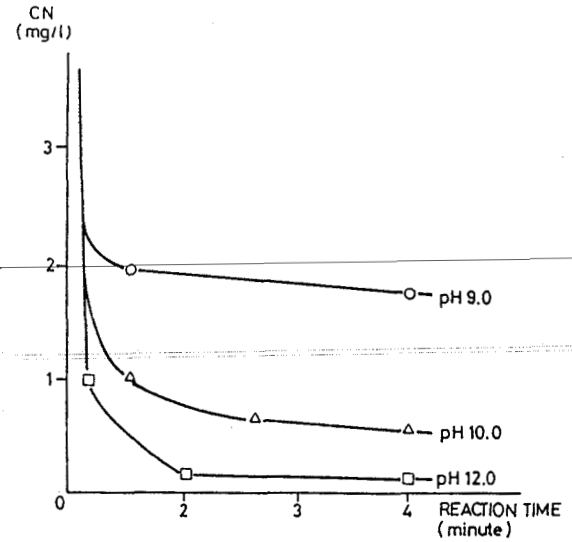

Fig. 4. Effect of pH on the destruction of cyanide by chlorination

The destruction of cyanide by sodium hypochlorite is accomplished in the following stages:

1st stage:

(a) $NaCN+NaOCl+H_2O \rightarrow CNCl+2NaOH$

(b) $CNCl+2NaOH \rightarrow NaCNO+NaCl+H_2O$

2nd stage:

$2NaCNO+2NaOH+3NaOCl \rightarrow 2Na_2CO_3+3NaCl+N_2+H_2O$

Overall:

$2NaCN+5NaOCl+2NaOH \rightarrow 2Na_2CO_3+5NaCl+N_2+H_2O$

The rate of destruction of cyanide is pH dependent and may be affected by the presence of metals. Figs. 4 and 5 show the effect of pH and different metal concentrations on the rate of reaction.

(2) *Ozonation.* Similar to chlorination, the destruction of cyanide by ozone occurs in two stages, with cyanate formed as an intermediate:

$NaCN+O_3 \rightarrow NaCNO+O_2$

$2NaCNO+3O_3+H_2O \rightarrow NaOH+2CO_2+N_2+3O_2$

Overall:

$2NaCN+5O_3+H_2O \rightarrow 2NaOH+2CO_2+N_2+5O_2$

In contrast to chlorination, strict pH control is unnecessary and consumption of chemicals can be reduced when the wastewater contains a substantial amount of ammonia. However, the initial capital costs and operating costs of this method are higher than those of chlorination.

(3) *Electrolytic oxidation.* Oxidation by anodic oxidation is particularly suitable for high concentrations. Removal rate can be as high as 260–380 mgCN/Ah for cyanide concentrations between 1000–3000 mg/l, but rapidly decreases at lower concentrations (Fig. 6). Electrolytic oxidation is mainly used to pre-treat highly concentrated cyanide waste from an electroplating shop, where there is direct current power supply, to a lower concentration after which conventional chlorination oxidation is used for complete treatment. The operating cost for the destruction of cyanide by electrolysis at high concentration is only about 40–60% of the cost of chemical treatment of chlorination.

(4) *Ion exchange.* Cyanide in wastewater may be removed by adsorption on anionic exchange resins. The adsorbed cyanide may later be eluted off by passing regenerants, such as sodium hydroxide or sodium chloride, through the resins. The regenerated cyanide may be reused as process chemicals or treated before discharge.

Treatment of Chromium

(1) *Reduction of hexavalent chromium and precipitation.* The most widely used method of treating hexavalent chromium is to reduce it chemically to a trivalent state and subsequently precipitate it out of solution as hydroxides. The common chemical reductants used by small electroplaters are sodium sulphite (Na_2SO_3), sodium bisulphite ($NaHSO_3$), sodium metabisulphite ($Na_2S_2O_5$) and ferrous sulphate ($FeSO_4.7H_2O$).

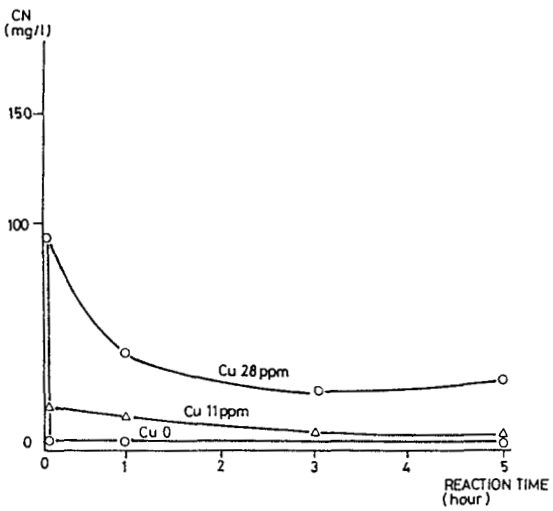

Fig. 5. Effect of metal concentration on the rate of destruction of cyanide by chlorination

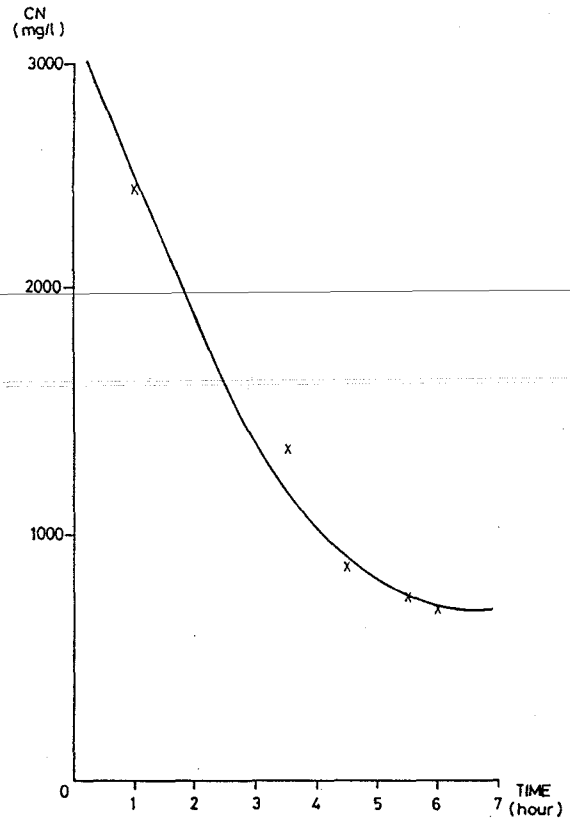

Fig. 6. Destruction of cyanide by electrolysis

The reduction reactions are:

With sodium sulphite:

$$2H_2CrO_4+3Na_2SO_3+3H_2SO_4 \rightarrow Cr_2(SO_4)_3+3Na_2SO_4+5H_2O$$

With sodium bisulphite:

$$4H_2CrO_4+6NaHSO_3+3H_2SO_4 \rightarrow 2Cr_2(SO_4)_3+3Na_2SO_4+10H_2O$$

With sodium metabisulphite:

$$4H_2CrO_4+3Na_2S_2O_5+3H_2SO_4 \rightarrow 2Cr_2(SO_4)_3+3Na_2SO_4+7H_2O$$

With ferrous sulphate:

$$2H_2CrO_4+6FeSO_4+6H_2SO_4 \rightarrow Cr_2(SO_4)_3+3Fe_2(SO_4)_3+8H_2O$$

All the above reactions have to take place at pH 2·5–3. The effect of pH on reaction rate of reduction of hexavalent chromium by sodium metabisulphite is illustrated in Fig. 7. The trivalent state chromium can then be precipitated as chromium hydroxides by pH adjustment.

(2) *Cementation.* Cementation is the use of scrap metal to electrochemically reduce the hexavalent chromium. By allowing the electroplating waste containing hexavalent chromium to come into contact with scraps of reactive metals (such as iron, zinc or aluminium), the hexavalent chromium is reduced. Although the cementation reactions with zinc and iron have to be carried out under acidic condition, the cementation reaction with aluminium scraps under alkaline condition has been tried with some degree of success. In this way, the reduction of hexavalent chromium to trivalent state and the precipitation of trivalent chromium can be accomplished in one step. Thus, this treatment process requires less operator attention and reduces the need for sophisticated control equipment. Fig. 8 shows some of the experimental results of alkaline cementation reaction with aluminium scraps.

In summary, the use of metal scraps for chromium treatment can lower the chemical costs and simplify the treatment operation by eliminating the need for careful dosage of treatment chemicals.

(3) *Precipitation as insoluble barium salt.* It is possible to precipitate chromium in the hexavalent state by forming the insoluble barium chromate.

$$CrO_4^{2-}+Ba^{2+} \rightarrow BaCrO_4$$

The reaction can be carried out at pH 8–9 and is only used as an emergency remedy because barium salt is expensive. Lack of treatment is apparent by the presence of a yellow colour which indicates the presence of unreduced chromate ions.

(4) *Ion exchange.* Ion exchange is one of the more widely employed chromium and chromic acid recovery processes. Although cation exchange may be used to recover trivalent chromium it is seldom practised due to complexity of operation. On the other

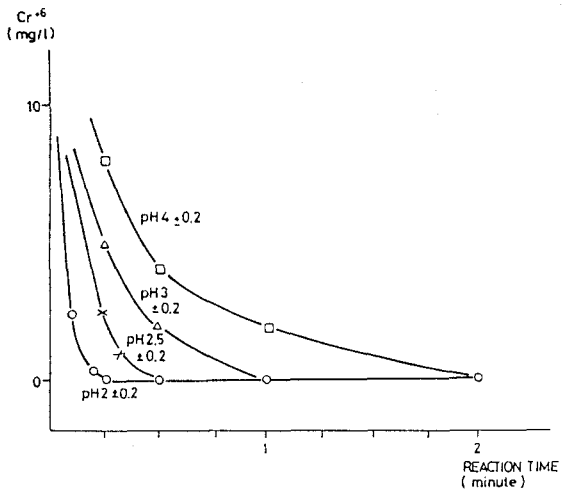

Fig. 7. Effect of pH on reduction of hexavalent chromium by sodium meta-bisulphite

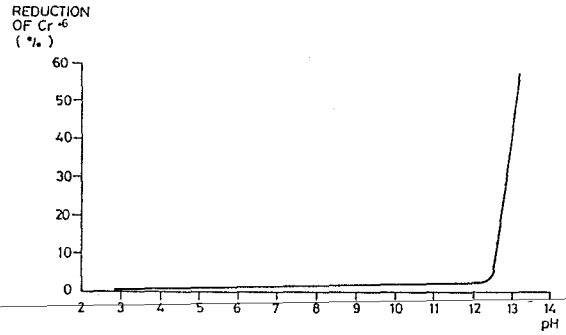

Fig. 8. Reduction of hexavalent chromium with aluminium at various pH values

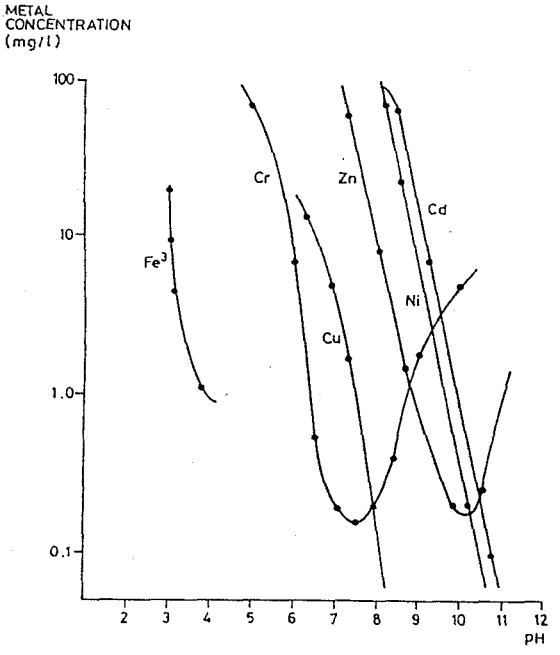

Fig. 9. Precipitation of metal salts at various pH values

hand, anion exchange is used for hexavalent chromium. With anion exchange, concentrated regenerated solution of up to 6% chromium acid may be obtained for re-use.

Treatment of Metal

(1) *Removal as hydroxides.* Precipitation of metals contained in the electroplating waste is the most widely adopted treatment method for removal of metals. Each metal species has a particular optimum pH range for its maximum removal. Fig. 9 shows the recommended pH range for the removal of some common metals as metal hydroxides[1-3].

The more commonly used chemicals for pH adjustment are caustic soda and lime, caustic soda being the more expensive. However, it will contribute to a much smaller amount of sludge generated when compared to the use of lime. Lime is cheaper to purchase but its reaction rate is slower and a considerable excess will be required if encapsulation occurs. Sedimentation of the resulting hydroxide sludge tends to be more rapid and may not require the use of a flocculant.

(2) *Removal as sulphide.* Owing to the inherent solubility of metal hydroxides, it may not be possible to reduce the metal contents to a very low concentration such as 0·1 mg/l by precipitation as metal hydroxides. In this case, it may be necessary to precipitate the metals as insoluble sulphides. The principle of sulphide precipitation is that the solubilities of metal sulphides are generally much lower than the hydroxides. The theoretical solubilities of metal hydroxides and sulphides are shown in Table 4[4]. Hence, by forming metal sulphides, the metal concentrations in a wastewater can substantially be reduced to very low levels.

The sulphide reagent may be added in form of soluble sodium sulphide or insoluble ferrous sulphide. This removal method, however, suffers from some operational difficulties such as less settleable sludge and the need for control of addition of reaction chemicals.

(3) *Destruction of complexes and precipitation.* Some of the metal finishing operations may involve the use of complexing agents. The wastewater discharged from these operations may therefore contain complexed metal species which are often found to be unamenable to conventional treatment methods such as hydroxide precipitation. To effect metal removal the complexes would have to be broken but a ready treatment method to destroy the complexes does not exist. Depending upon the type of complex ions concerned the measures that may be applicable for metal complex destruction are dilution, oxidation, etc.

An example of dilution to result in destruction of metal complexes is in the treatment of ammonium

TABLE 4. THEORETICAL SOLUBILITIES OF HYDROXIDES AND SULPHIDES OF HEAVY METALS IN PURE WATER

Metal	Solubility of metal ion *(mg/l)*	
	As hydroxide	As sulphide
Cadmium (Cd^{++})	$2{\cdot}3\times10^{-5}$	$6{\cdot}7\times10^{-10}$
Chromium (Cr^{+++})	$8{\cdot}4\times10^{-4}$	No precipitate
Cobalt (Co^{++})	$2{\cdot}2\times10^{-1}$	$1{\cdot}0\times10^{-8}$
Copper Cu^{++})	$2{\cdot}2\times10^{-2}$	$5{\cdot}8\times10^{-18}$
Iron (Fe^{++})	$8{\cdot}9\times10^{-1}$	$3{\cdot}4\times10^{-5}$
Lead (Pb^{++})	2·1	$3{\cdot}8\times10^{-9}$
Manganese (Mn^{++})	1·2	$2{\cdot}1\times10^{-3}$
Mercury (Hg^{++})	$3{\cdot}9\times10^{-4}$	$9{\cdot}0\times10^{-20}$
Nickel (Ni^{++})	$6{\cdot}9\times10^{-3}$	$6{\cdot}9\times10^{-8}$
Silver (Ag^{+})	13·3	$7{\cdot}4\times10^{-12}$
Tin (Sn^{++})	$1{\cdot}1\times10^{-4}$	$3{\cdot}8\times10^{-8}$
Zinc (Zn^{++})	1·1	$2{\cdot}3\times10^{-7}$

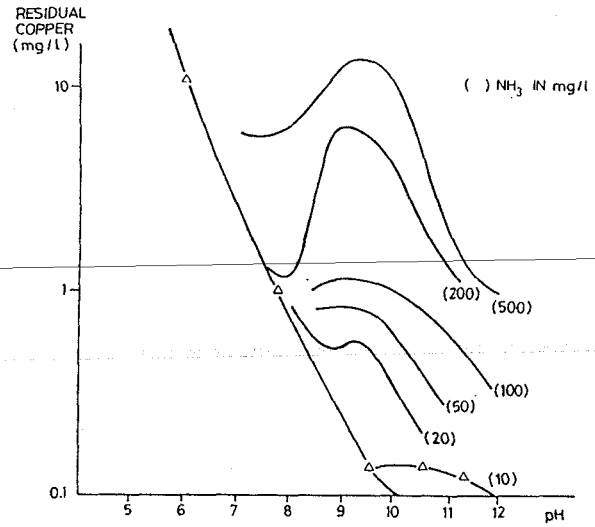

Fig. 10. Effect of residual ammonia concentration on copper removal

persulphate solution which is generated during the surface treatment of printed circuit boards. In this solution up to 5% copper is dissolved in the ammoniacal complexed form. By using hydroxide precipitation method little removal of copper can be achieved, even by adjusting the pH to 13. Instead, copper removal can be effected simply by providing dilution to reduce the ammonium concentration in the solution. Fig. 10 illustrates the effect of dilution on copper removal from spent ammonium persulphate solution.

Conclusions

(1) The electroplating wastewater generally contains chemicals that are toxic in nature and adequate treatment has to be provided to safeguard the receiving water bodies.

(2) For an electroplating shop that needs to control its waste, it is beneficial to the shop to re-examine its manufacturing processes in order to minimize the pollution discharge. This may involve the change of plating bath composition, use of better rinsing methods, etc.

(3) With respect to wastewater treatment, there is no universal treatment method that can encompass the specific characteristics of wastewater and constraints of every plating shop. It will definitely be advantageous for an electroplater to engage the services of a consulting engineer to carry out treatability tests on the wastewater of concern to establish the most cost-effective treatment solutions.

References

[1]*Handbook of Chemistry and Physics*. 50th Ed., Chemical Rubber Co., Cleveland, Ohio, 1963.

[2]*Handbook of Analytical Chemistry*. McGraw-Hill, New York, 1963.

[3]Hoeness and Johnson. *Ionic Equilibrium as Applied to Qualitative Analyses*. Holt Rinehart & Winston Co., New York, 1954.

[4]Lanouette, K. H. Heavy Metals Removal. *Chem. Engineering*, Oct, 1977, Deskbook Issue, 73.