Waste Treatment for Discarded Electroplating Baths

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Abstract

In the process of Silver-plating on various metallic hardware, the electrolyte is essentially comprised of high content of cyanide ions 120 g/L along with salts of Silver metal and other required ingredients. Spent Silver plating bath needs specific treatment to destroy cyanide ions beyond detectable limit of 0.1 ppm before putting into common stream of wastewater drain. Oxidation of cyanide under alkaline condition is attempted using Sodium hypochlorite solution (10-12% W/V) to reduce cyanide content below detectable limit through the formation of bicarbonate and gaseous nitrogen. Complete destruction of cyanide ion is confirmed and allowed to release in the main stream of wastewater.

Keywords: cyanide, treatment, effluent, electroplating bath.

Introduction

Silver electroplating is carried out on various substrates majorly aluminium, kovar, invar and other such metals, which are being used for different components of electronics packages. In electroplating, silver corresponding cyanide salt along with other chemistry is used. This bath contains silver potassium cyanide, sodium or potassium cyanide and sodium carbonate. This bath contains a very high concentration of cyanides up to 90-120 g/L, silver 30-34 g/L and sodium carbonate 30 g/L. Plating is carried out batch wise from this bath. Silver metal concentration goes down than the required concentration, bath is replenished with silver plating salt. Silver is consumed from bath and carbonates concentration are increased more than 100 g/L. After long term usage, the plating efficiency decreases and results in defective plating. Dusty silver deposits are observed. At this time the bath is said to be exhausted. So it is advisable to stop the use of this exhausted bath and shift to new one. This whole bath containing high concentration of cyanides is of around 50-200 litres capacity. The main problem occurs over here is that, the existing effluent treatment plant is not designed for high concentrations of cyanides. So to prevent shock loading conditions and avoid other operational problems, we stored all these exhausted baths separately, instead of disposing this waste to treatment plant. Its dilution would require huge amount of water to bring it to safe dispose limit. This created a requirement to develop a separate treatment technique for the cyanides. It is necessary to treat cyanides before treatment of heavy metals because cyanides may interfere in heavy metal removal by forming metal complexes. Also according to central pollution control board (CPCB) standards for electroplating sector, cyanide concentration shall not be more than 0.2 mg/L. So it becomes very important to treat the cyanides in order to meet the standards.

This paper provides basic information about the treatment of extremely toxic cyanide wastes. Basic system guidelines are described along with typical operating parameters. The main objective of effluent treatment is to protect the environment from pollution and fulfil the Government's standards for emission or discharge of environmental contaminants.

Several methods are described in literature about treatment of cyanide effluent which includes use of ozonation alone and conjugation with UV radiation, biologically active species, biosorption-biodetoxification, hydrogen peroxide, photochemical process, sodium hypochlorite, calcium hypochlorite [1] , sulfur dioxide, precipitation by adding heavy metals, ion exchange, activated carbon, aldehydes, per oxygen compounds and bio oxidation [2-11].

Amongst oxidants chlorine is preferred because it is readily available and the least expensive but excess chlorine can produce cancer-causing substances by reacting with other effluent compounds. Ozonation is a

J. Electrochem Soc. India Vol.(73) 7&8 - 2024, page No. 267-280

second choice and is preferred by industries because its excess converts to oxygen, but it requires ozonator and oxygen cylinder to produce ozone. Considering safety measures to store highly flammable oxygen cylinder and hazardous smell of ozone, it was avoided to choose ozonation. Alkaline chlorination is the most popular and preferable treatment for cyanide waste in plating effluent treatment plants. It generates minimum waste. 10-12% Sodium hypochlorite was chosen based on easy availability and less hazardous properties compared to others.

Literature is available for treatment of cyanide up to concentration of 1 g/l. But there are no references found for treatment of cyanides in the concentrations ranging from 2 to 120 g/l. In this study it is exercised to treat cyanides in this higher concentration range.

2. Materials and method

Technical grade 10-12% sodium hypochlorite, 10% sodium hydroxide, pH meter, ORP meter, thermometer, pumps and reaction tanks were sourced from local supplier. During all experiment personal protective equipments such as protective apron, hand gloves, respirator mask with filter cartridge and eye goggles were used to ensure operator safety. The experiments were performed under exhaust hood with high suction capacity.

Samples were taken for discarded plating baths of silver. Initial and final silver concentration, pH, carbonate (if any) and cyanide content were analyzed by using potentiometric titretor according to guidelines [7].

For electroplating silver baths total volume was 400 litres. Silver present in the baths was plated out on SS304 plates at higher current densities. Initial and final silver content was analysed by using x-ray fluorescence spectrometer. Initial cyanide concentration of baths was 120 grams/ litre. The whole treatment was done as per directions given in reference [3]. In one batch 100 litres of solution was taken in 500 litres bath. Reaction was completed in 4 batches. Sensors were arranged for continuous monitoring of reaction. Dosing pumps were arranged for dosing of base (10% sodium hydroxide), oxidant (10-12% sodium hypochlorite) and acid (10% nitric acid). Each part of cyanide requires 9.56 parts of chlorine to oxidize it to carbon dioxide theoretically. The actual requirements exceeded the stated stoichiometric values. So, during experiment 10 gm of sodium hypochlorite was used for each 1 gram of cyanide present in the effluent. Monitoring cyanide waste water treatment by ORP measurement electrode is quite useful indicative method for demonstrating whether proper quantities of treatment chemicals have been added. Following steps were followed for waste treatment of cyanide. The reaction was carried out at room temperature of 30-35°C. Effluent treatment plant schematic diagram for cyanide containing effluent is given in figure 1.

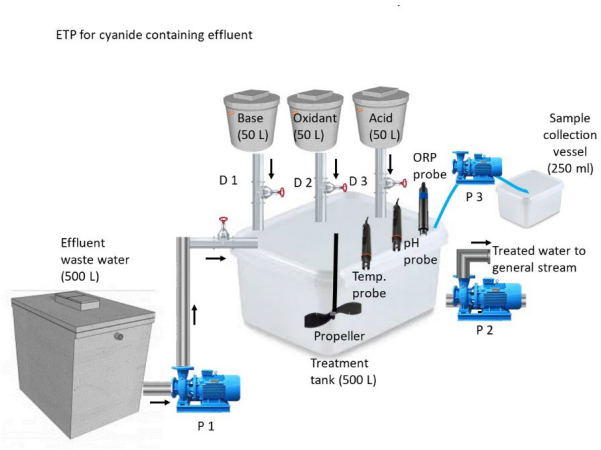


Figure 1 Effluent treatment plant schematic diagram for cyanide containing effluent

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

1st stage:

(a) $NaCN + NaOCl + H_20 \rightarrow CNCl + 2NaOH$

(b) $CNCl + 2NaOH \rightarrow NaCNO + NaCl + H_20$

Initial value of sample pH and ORP values lies between 11-12 and 0 to -400mV respectively. ORP set point was +300 mV. The rise in ORP is easily observable with consequent addition of hypochlorite which further supports the reaction progression.

2nd stage:

$2NaCNO + 2NaOH + 3NaOCl \rightarrow 2Na_2CO_3 + 3NaCl + N_2 + H_20$

Reaction was done at pH in the range of 8.5 to 9.5. ORP set point was +750 mV. Ideal reaction time was 2 hours. If pH drop was observed, 10% sodium hydroxide was added to maintain pH 9-9.5.

Overall:

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

At the end of reaction, pH nearly comes to 8-9.5 and ORP comes up to +650 to +750 mV. Carbonate increased in the solution gradually with time which also supports the completion of reaction. Ensured removal of cyanide by titration. The treated solution was alkaline. So it was neutralized to meet discharge limits. Nitric acid was used to lower pH. But before adding acid it was confirmed that all the cyanide was converted to bicarbonate and nitrogen, otherwise it would produce hazardous hydrogen cyanide gas while coming in contact with acid. Discarded treated solution.

3. Results

For electroplating silver discarded baths, silver was recovered by plating on SS304 plates at current density of 40-50 amperes per square feet at room temperature. Initial silver content was 28 g/L and after recovery silver content was 1.5 g/L. Theoretically, it should require 47 kg of sodium hypochlorite but practically it required 50 kg of sodium hypochlorite for complete removal of cyanide. This can be due to loss of chloride content from sodium hypochlorite during storing and reaction. The solution was treated with sodium hypochlorite for cyanide removal. Treatment was continued until cyanide was below detectable level. Initially the solution was having pH 12. The treatment was carried out batch wise. After cyanide removal solution was having pH above 10, which was neutralized by nitric acid to get pH between 6-8. ORP changes during the reaction is given in figure 2.

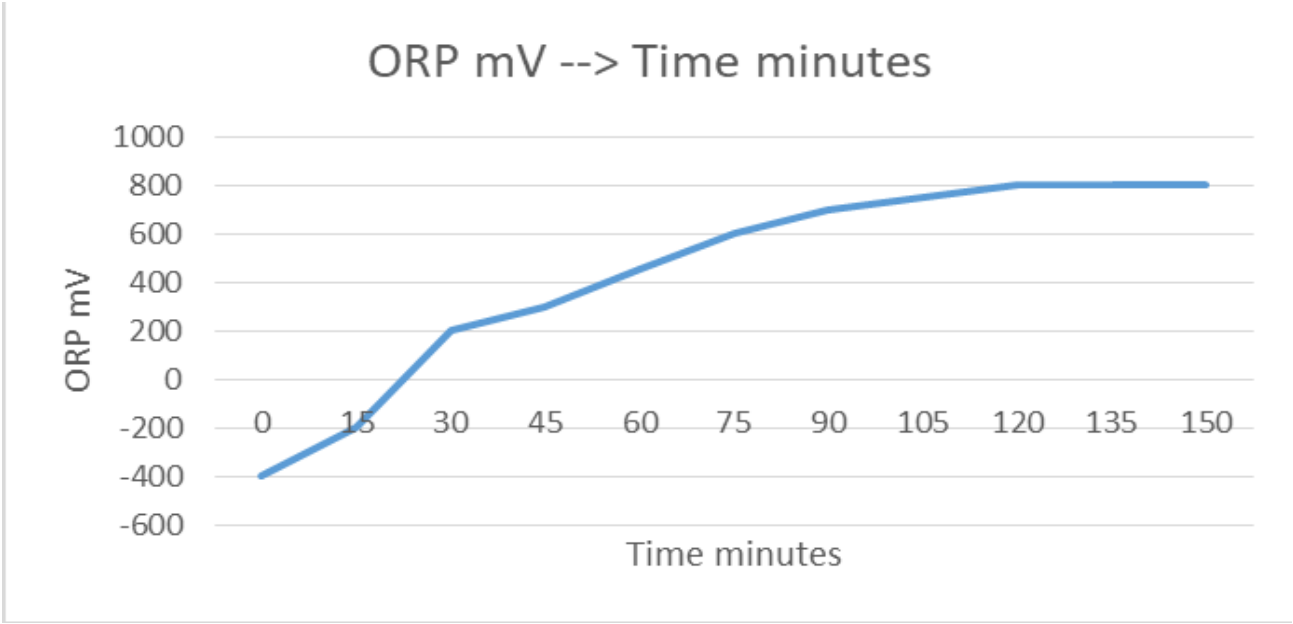


Figure 2 ORP changes during reaction

Details of pH changes during the reaction is given in Figure 3. Initially pH of solution was 12. Sodium hypochlorite was added, cyanide was converted to cyanate, and pH decreased to 9. Here the first step of reaction was completed. Again sodium hypochlorite was added for further conversion of cyanate to nitrogen and sodium carbonate. Gradually pH was decreased. At the end of reaction at about 120 minutes pH came to 8-8.5. All cyanide was destroyed. Remaining solution was treated with nitric acid to get pH between 6.5-6.

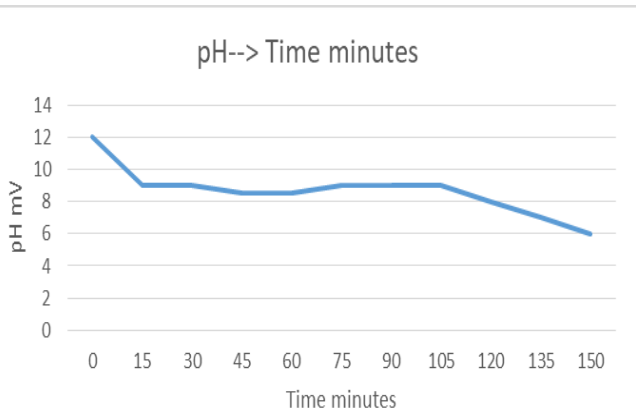


Figure 3 pH changes during reaction

During second stage of reaction bubbling of nitrogen gas was observed in the bath. Generation of carbonate was confirmed by titration.

4.Conclusion

From experiments it can be calculated that for every 100 litters electroplating silver baths having 120 ± 2 g/L cyanide required 7 litters of sodium hypochlorite to neutralize cyanide. The left over solution had pH above 8-9.5 after treatment, which was neutralized by nitric acid. This treated neutral solution was discarded into main stream effluent. During this experiments we found difficulty in storing 10-12% sodium hypochlorite solution at room temperature of 35°C and above. As soon as container is opened, sodium hypochlorite concentration started to come down. It was recommended to use it within 24-30 hours. It is quite important to maintain concentration to at least 8-10% to get efficient oxidation reaction. This process is found very useful and successfully implemented in our facility with semi-automated controls. Advantages of using sodium hypochlorite is that reaction doesn't require complex machinery and setup, process is rapid, technical grade material is easily available as by product from chemical industries, reaction is easily controllable. Disadvantage is that using hypochlorite required careful pH control to prevent formation of toxic cyanogen chloride.

Acknowledgement

The authors appreciate technical help received from STPD colleagues during the course of experiments reported in this paper. The authors gratefully acknowledge guidance received from Head STPD, Shri Ranajit Pal, the inspiration received from Shri Arun Bindal, Group Director, EFMG and best regards to reviewers for spending their valuable time in the evaluation. Sincere thanks to Shri Sumitesh Sarkar, AD SAC, and Director-SAC for their necessary guidance and facilitating us to do this experiment.

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