Closed-loop Zinc Plating From Chloride Baths

Sergey S. Kruglikov, Elena S. Kruglikova, Ksenia V. Kazakova
S.S. Kruglikov Consultants, Moscow, Russia

Conventional treatment of waste water from zinc plating line is not efficient due to the formation of ammonia complexes soluble in alkaline media. A new approach is based on the removal of 98-99% zinc ions directly from the reclaim tank by plating out at low cathode current density. Platinized titanium is used as an anode and is placed into a membrane half-cell with a cation-exchange membrane which prevents the discharge of chloride ions and the evolution of chlorine gas. Zinc deposited at the cathode is returned into the plating tank by periodic anodic stripping.

For more information, contact:
Prof. Sergey S. Kruglikov
Bolshaya Spasskaya, 33-107
Moscow, 129090, Russia
Fax: +7-495-609-29-64
Mob. Phone: +7-916-616-96-99
E-mail: skruglikov@mail.ru

Introduction

Plating baths containing ammonium salts are widely used in industry. A typical example is zinc plating bath which contain about 200g/l of ammonium chloride. Its major advantages are high deposition rate, good throwing power and high quality of zinc deposits achieved in the presence of proprietary organic additives.

On the other hand, these baths are responsible for certain problems related with the treatment of rinse water. Conventional technology based on the precipitation of zinc hydroxide after the addition of alkali to waste water is not effective in the presence of appreciable amounts of ammonium compounds due to the formation of ammonia complexes with zinc ions which are stable and soluble in alkaline media. Preliminary removal of ammoniac from waste water after the addition of alkali needs additional operations, equipment and the consumption of energy. Therefore more economical approach to the whole problem is desirable especially for zinc plating lines with not very large output.

Removal of zinc ions from rinse water by the electrodeposition (i.e. by plating out) can be considered as one of possible ways to prevent the access of zinc to waster treatment units. However there are two following obstacles:

1) Zinc ions practically are not discharged at the cathode, if their concentration is in the range of milligrams or tens of milligrams per liter.

2) Major anode process is the formation of oxygen-chlorine mixture.

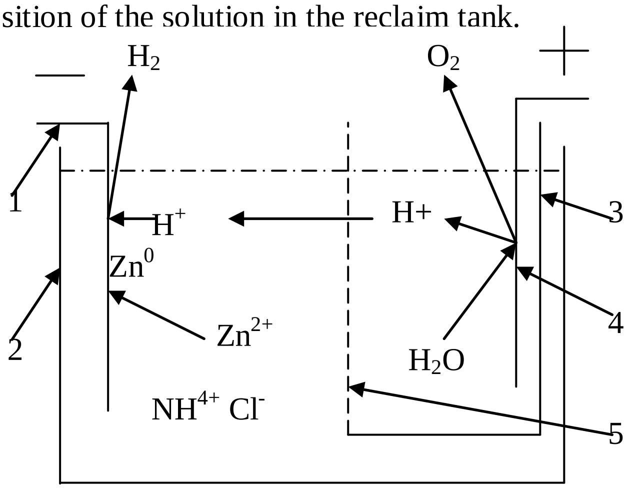
Therefore removal of zinc ions should be made at a stage, where their concentration is sufficient for their discharge. Such a stage may be the rinsing of zinc-plated parts in a reclaim tank. In order to prevent the discharge of chloride ions the anode should be separated from the rinse water in the reclaim tank by a cation-exchange membrane, so the anolyte may be maintained continuously free of chlorides.

Experimental Procedure

Experiments were made with following solutions:

1.	Zn^{2+}	50 g/l
	NH_4CL	220 g/l
	H_3BO_3	20 g/l
	Organic additive	40 g/l
2)	Zn^{2+}	1-3 g/l
	NH_4Cl	220 g/l
	H_3BO_3	20 g/l
	Organic additive	40 g/l

Solution 1 is a typical example of a bath used in industry. Solution 2 can be considered as "rinse water" in the reclaim tank in the zinc plating line where the solution 1 is used in zinc plating tank. Fig. 1 illustrates the formation of the composition of the solution in the reclaim tank.



1, cathode;2,reclaim tank;3, anodic cell;4,anode;5,cationic membrane

Fig.1 . Operation of the reclaim tank in zinc plating line.

According to the principle of a steady-state process a continuous input of the solution dragged from the plating tank into the reclaim tank will result in a gradual increase in the concentrations of all components which are not consumed in the course of the electrolysis. These components include ammonium chloride, boric acid and organic additive. Their concentrations continue to rise up until they approach corresponding values in the plating tank.

These considerations are not valid for zinc ions. In a steady-state process the input of them is equal to the rate of their consumption by the discharge at the cathode. Depending on the efficiency of the cathodic discharge the steady-state concentration of zinc ions in the reclaim tank may be higher or lower. Therefore a particular value of 1-3 g/l was taken for the experiments, representing the conditions in the reclaim tank.

Experiments with solutions 1 and 2 were carried out in a two-chamber cell with a cationic membrane. Before the electrolysis a 200-230 ml portion of solution 1 or 2 was placed into the cathode chamber and same amount of sulfuric acid (200 g/l) was placed into the anode chamber. Platinized titanium was used as an anode. A nickel plate with 50 cm^2 area was used as a cathode and in some experiments with solution # 2 the cathode made of thin stainless steel wire (0.2 mm in diameter) was also used with an overall surface area of about 1 dm^2.

Results and Discussion

The process of gradual removal of zinc ions from the solution #1 is represented in Fig.2.

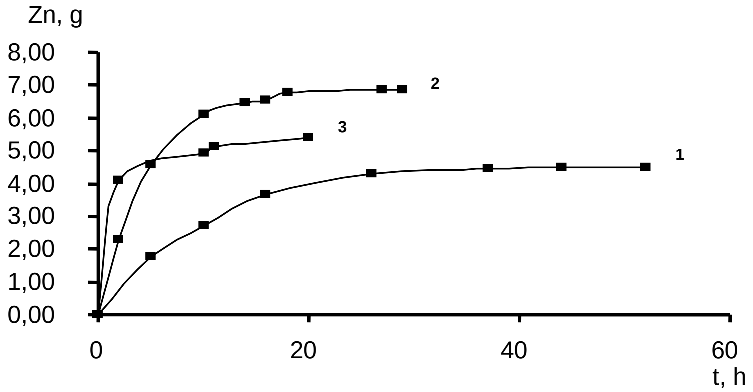


Fig.2 Amount of zinc deposited at the cathode, g.
1. i = 0,6A/dm^2; 2. i = 2A/dm^2; 3. i = 6A/dm^2.

Since the initial concentration of zinc ions is high, the initial parts of the curves in Fig.2 are rectilinear and suggest that higher current density allows to reduce the time necessary for the removal of 50% of zinc ions from the solution. However complete removal needs nearly same time (20-30 hrs) both at high and low current densities. This apparent contradiction is explained by the curves in Fig.3: at higher current densities the specific deposition rate is lower than at lower ones.

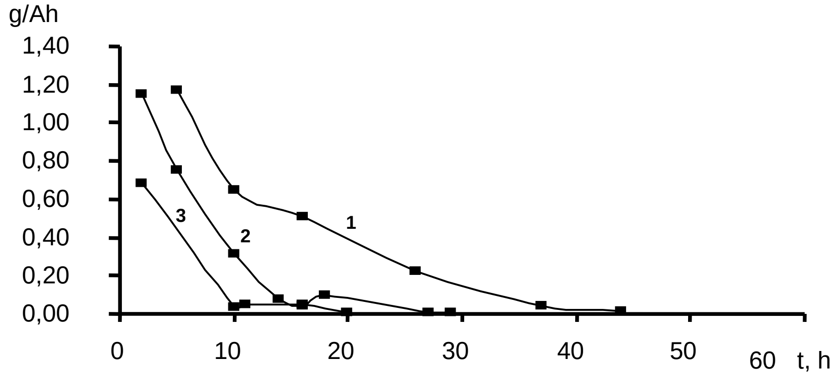


Fig.3 Specific zinc deposition rate, g/Ah
1. i = 0,6A/dm^2; 2. i = 2A/dm^2; 3. i = 6A/dm^2.

Similar relationships are observed for zinc current efficiency (Fig.4).

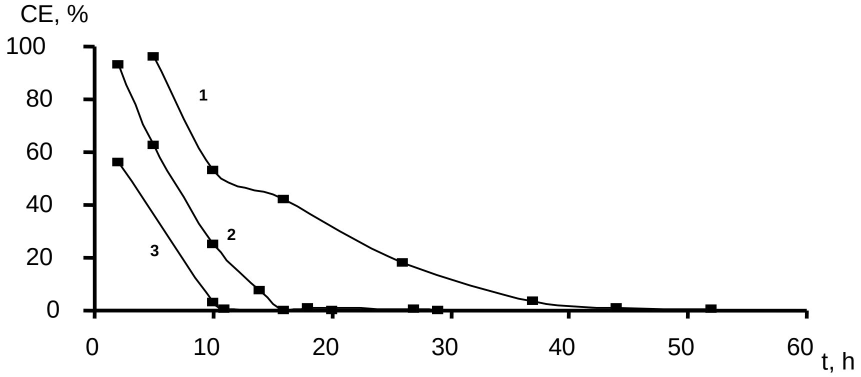


Fig.4 Current efficiency of zinc (%) as a function of time (h).
1. i = 0,6A/dm^2; 2. i = 2A/dm^2; 3. i = 6A/dm^2.

A number of experiments (Table 1) were made with the solution #2 which represents conditions existing in the reclaim tank in a steady-state process, i.e. when the rate of zinc ions input is equal to the rate of their removal by the discharge at the cathode. Wire cathode with large surface area allows to achieve relatively high current per unit volume of the solution (up to 5 A/l) even at low cathode current density (0.2 A/dm^2). Thus in spite of low current efficiency the removal rate is high enough and will allow to maintain low concentration of zinc ions in the reclaim tank. Therefore the input of zinc ions into waste water can be reduced by 98-99%. Zinc deposited at the cathode can be periodically stripped in the plating tank. Waste water from closed-loop zinc plating line will contain mainly non-metal components of plating bath, i.e. ammonium chloride, boric acid and organic additives.

Tabl.1. Current Efficiency at Lower Concentrations of Zn^{2+} (solution #2).

Zn^{2+} concentration, g/l	Cathode current density, A/dm^2	Current Efficiency,%
Flat cathode		
2.2	0.2	4.2
Wire cathode		
2.7	0.2	38
2.7	0.5	16
1.1	1	9.7
1.1	1	6.8

Few units based on this method are now in operation in plating shops in Russia.

Conclusions

1. A membrane cell can be used for the removal of zinc ions from reclaim tanks in zinc plating lines.
2. Cationic membrane reduces to a minimum the anodic discharge of chloride ions.
3. Cathodes with large surface area are preferred to increase the efficiency of the process.