

The adsorption of addition agents in acid zinc plating

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In this paper, authors have studied the adsorption behaviour of a wide variety of addition agents by galvanostatic polarisation technique, capillary electrometer and impedance measurements in acidic zinc plating bath. A suitable correlation has been arrived at between the techniques studied.

Key words: Adsorption, zinc plating, addition agents

INTRODUCTION

Plating solutions, in addition to major ingredients, contain small amounts of organic substances. These are intentionally added to plating solutions to produce beneficial changes in the character of deposit. These agents are chosen to provide improved brightness, fine grain structure, better corrosion resistance, improved throwing power and levelling power [1]. They mostly consist of organic compounds containing nitrogen, sulphur and oxygen. These addition agents are classified as brighteners, levellers, wetting agents and stress relievers depending upon the effects produced on the deposit. The mechanism of their action is not yet fully understood. Among the theories proposed, two are significant. One is based on adsorption and the other on complex formation. Other theories postulated are ion pairing, hydrogen evolution etc.

The use of organic compounds as additives in acidic zinc plating can be traced back as early as 1907. Behaviour of a wide variety of compounds is reported [2]. In this paper authors have selected eleven addition agents from the literature, taking care to include various functional groups to study their behaviour.

EXPERIMENTAL

Addition agents selected for this study are thiourea, β naphthalene sulphonate, gelatin, dextrin, β naphthol, benzaldehyde, glucose, cetyl trimethyl ammonium bromide (CTAB), tetraethylene pentamine and pyridine. The concentration of addition agents was fixed at 1 g/L. The plating bath consists of zinc sulphate 240 g/L, sodium acetate 15 g/L and aluminium sulphate 30 g/L. pH of the bath was maintained at 3.5 ± 0.2 . Mild steel was used as cathode in all the techniques. The procedure for carrying out the electrocapillary studies and calculation of interfacial tension are discussed elsewhere [3]. Galvanostatic polarisation was carried out by exposing an area of 1 cm^2 and the current was from 1 to 100 mA.cm⁻². AC impedance measurements were

carried out at the potential corresponding to a current density of 10 mA cm^{-2} . The real and imaginary parts of the cell impedance were measured for various frequencies (10 mHz to 10 KHz). Charge transfer resistance value and double layer capacitance were calculated from the Nyquist diagram.

RESULTS AND DISCUSSION

Electrocapillary measurements

Measurements of adsorption of several organic molecules on different faces of single crystal and on polycrystalline electrode showed that zinc belongs to 'mercury' like electrode [4]. According to Antropov's concept of 'null potential', the data obtained for adsorption of organic compounds on mercury can be extended to other metals also. It is found from the studies that sulphur containing compounds adsorb on the positive side of the electrocapillary maximum because of lone pair of electrons in the sulphur atom. Due to the presence of π -electron interaction of the naphthalene ring in naphthalene sulphonate, the adsorption was found to be more than thiourea. Among the colloids, gelatin shows maximum adsorption and dextrin shows very little adsorption. This may be due to more complexing tendency of gelatin. Among the oxygen containing compounds glucose shows no adsorption, as water molecules are more polarisable than glucose. Pyridine shows very little adsorption as it forms salts with strong acids. Adsorption is found to be maximum for CTAB due to the interaction of positively charged ammonium cations with negatively charged metal surface and also due to the larger size of the cation.

Polarisation studies

Except thiourea, all other compounds increase the cathodic polarisation to an appreciable extent. Maximum polarisation was observed with benzaldehyde. The depolarising action of thiourea is due to the incorporation of undecomposed thiourea in the zinc deposit [5]. The

increase in electrode polarisation for all other cases is due to adsorption which blocks the active sites for deposition.

Impedance measurements

Impedance diagram for all compounds obtained showed a capacitive loop at high frequencies and an inductive loop at low frequencies. The charge transfer resistance values increase in the following order:

Thiourea < Glucose < Naphthalene sulphonate < Pentammine < Pyridine < dextrin < CTAB < Naphthol < Benzaldehyde.

The same trend was observed for polarisation behaviour also. Thus there is a good correlation between the polarisation behaviour and charge transfer resistance values. Double layer capacitance value for gelatin is very much less than other compounds because of fine grained structure obtained with gelatin.

CONCLUSION

Adsorption behaviour of the additives clearly showed that there is a correlation between adsorption, polarisation behaviour and charge transfer resistance.

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