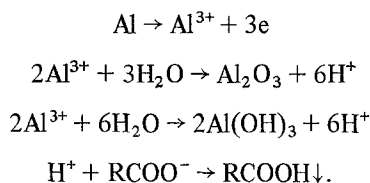# The mechanism of electrodeposition of acrylic resin on aluminium

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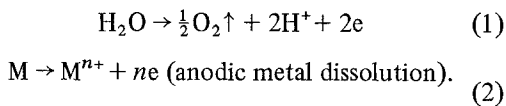
A mechanism for the electrodeposition of acrylic resin on aluminium is proposed, based on experimental studies of acid value, anodic gas evaluation and anodic film resistance. The mechanism can be expressed as

$$Al \rightarrow Al^{3+} + 3e$$

$$2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+$$

$$2Al^{3+} + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+$$

$$H^+ + RCOO^- \rightarrow RCOOH\downarrow.$$

This is different from the mechanism for zinc and steel, where it is metal ions from anodic dissolution which neutralize the macro-ions and cause a deposit on the anode surface.

1. Introduction

Electrodeposition of polymer films on metal surfaces is currently of great commercial interest because of its low cost and pollution-free nature, and because it produces a uniform coating with good adhesion, even in high-speed coating operations [1]. For a water-dispersible, anionic resin system, the polymers used usually contain acid groups. When neutralized with a base, such as diethylamine, a salt of the polymer is formed which can ionize in water to form positively charged ions and negatively charged macro-ions. The electrodeposition process using this resin system with steel or zinc as the anode [2–5] has the following anodic reactions:

$$H_2O \rightarrow \tfrac{1}{2}O_2\uparrow + 2H^+ + 2e \qquad (1)$$

$$M \rightarrow M^{n+} + ne \text{ (anodic metal dissolution).} \qquad (2)$$

These are followed by neutralization of the macro-ions

$$RCOO^- + H^+ \rightarrow RCOOH\downarrow \qquad (3)$$

$$nRCOO^- + M^{n+} \rightarrow (RCOO)_nM\downarrow \qquad (4)$$
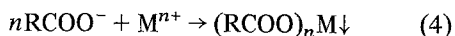
and perhaps the Kolbe reaction for the macro-ions.

Studies of the mechanism of electrodeposition on aluminium are scarce. Yeates [1] incorrectly regarded Al as an insoluble anode; Bushey [6] identified the presence of an aluminium oxide film. In this work, we propose a mechanism for the electrodeposition of acrylic resin on an aluminium surface.

2. Experimental

2.1. Materials

The acrylic resin used was XC-4010, supplied by American Cyanamid. It had an acid value of 1.60 meq g^{-1} of solid, an OH value of 2.43 meq g^{-1} of solid and a solid content of 73–76% [7]. The solvent in the resin was 2-ethoxyethanol. The curing agent used for XC-4010 was Cymel-303 (hexamethoxymethylmelamine), also from American Cyanamid, which had a solid content of 98% [8]. All other chemicals used were of reagent grade.

The solutions for electrodeposition were prepared by mixing resin and curing agent in various ratios with water and diethylamine to make a solution of 6.9% solid content. The amount of

diethylamine added was just sufficient to make a clear solution. Sheet metals to be coated were: aluminium (No. 1100, produced by Taiwan Aluminum and containing 99% Al, 0.2% Cu, 0.05% Mn and 0.1% Zn); steel (JIS G3141, containing 98% Fe, 0.1% C, 0.04% P and 0.04% S); stainless steel (SUS 303, containing 74% Fe, 18% Ni, and 8% Cr); platinum (about 99.9% Pt) and zinc-coated steel, which was used as zinc.

2.2. Equipment

The d.c. power supply used was a home-built model and had a maximum output of 5 A and a voltage range of 0–400 V. It was operated in two ways, at constant voltage or constant current. Voltages and currents during electrodeposition were recorded by a combined voltage and current recorder built by Rikadenki Kogyo, Japan, Model DB-2. The electrodeposition cell had dimensions of 75 mm × 35 mm × 20 mm (about 50 cm³). The cathode used was a platinum gauze, and the anode was the metal to be coated. The distance between them was 1 cm.

2.3. Procedure

Prior to electrodeposition, the sheet metals were polished, then rinsed with distilled water, degreased with alkaline cleaner, immersed in 10% sulphuric acid at room temperature for 5 min, rinsed with distilled water, immersed in 10% nitric acid at room temperature for 2 min, rinsed with distilled water, and finally dried in air [1].

After electrodeposition, the coated sheet metals were rinsed with distilled water and dried in air. The coated polymer film was then washed with ethanol before the acid value of the film was determined by titration with 0.1 N KOH in methanol. To determine the amine content, 5 cm³ of bath solution was added to 20 cm³ ethanol with two drops of bromocresol green as indicator. This was then titrated with 0.1 N HCl until its colour changed from blue to bistre. The acid and amine contents were expressed as meq acid and base respectively per gram of solid [1].

To determine the Al content in the deposited film, the film was washed with acetone, dried in air and burned in a crucible at 600° C for 6 h to leave a residue of Al_2O_3. In order to confirm

Table 1. Ratios of acid values of the films coated on various metals to that of XC-4010

Metal	Acid value ratio
Aluminium	0.995
Steel	0.890
Zinc-coated steel	0.703
Stainless steel	0.925

whether the residue was Al_2O_3, the following steps were taken: the residue was dissolved in 1 cm³ distilled water with one drop HCl, the pH value was adjusted to 4–5 with 6 N NH_4OH aqueous solution saturated with NH_4Cl, and 1 cm³ 0.25% aluminon was added. The solution was heated at 100° C for 10 min and a deep red colour showed the residue to be Al_2O_3.

3. Results and discussion

To simplify the study of the mechanism of deposition of acrylic resin on aluminium, the curing agent was not added to the solution. The studies included investigations of the acid value, the anodic gas and the anodic film resistance.
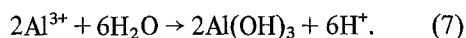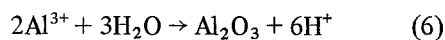
3.1. Acid value

Ratios of the acid value of XC-4010 to those of the films coated on various metals at a constant current of 124 mA are listed in Table 1. It shows that both steel and zinc have dissolved anodically to an appreciable extent and that some of the macro-ions have been neutralized with metal ions and deposited on to the neutral metal surface. But the polymer film on aluminium contains only a minor amount of metal salt and most of the macro-ions are neutralized with hydrogen ions. What then is the source of hydrogen ions? Because the voltage applied was far above the voltage required to electrolyse water (Equation 1), we cannot at this stage exclude it as a possible source of hydrogen ions in resin deposition.

3.2. Anodic gas

No appreciable gas evolution occurred from the aluminium anode at 100 V. In order to check that the experimental technique was correct, steel was

used to replace the aluminium, while keeping the other experimental conditions the same. Gas evolution occurred, indicating that the experimental technique was correct. This would indicate that Reaction 1 and the Kolbe reaction did not occur and that the hydrogen ions were not generated by Reaction 1. Ellinger [10] measured the weight loss of the metal anode for various metals during electrodeposition and found that steel, nickel, copper and silver had appreciable weight loss, but that aluminium gained weight. Bushey [6] recorded the presence of an aluminium oxide film after electrodeposition. Thus we propose the anodic reaction of aluminium to be:

$$Al \rightarrow Al^{3+} + 3e \qquad (5)$$

$$2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+ \qquad (6)$$

$$2Al^{3+} + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+. \qquad (7)$$

The aluminium is first dissolved to form Al^{3+}, this then reacts with water to form Al_2O_3 and/or $Al(OH)_3$ to release H^+. The H^+ then reacts with the macro-ions to form the deposited resin film. Al_2O_3 is a densely packed material which deposits on the surface of the aluminium, while $Al(OH)_3$ is a gel-like material which could swell with a certain amount of resin.

Measurements under conditions of constant current ($3.1 \, mA \, cm^{-2}$) and at a voltage greater than $150 \, V$ showed that a small amount of gas (in comparison to that in the case of steel) was generated. This was probably due to passivation by an Al_2O_3 and water electrolysis on the oxide. Measurement of the Al content of the resin film indicated that only $0.06 \, wt\%$ was Al. This small amount of Al could be due to $Al(OH)_3$ or Al^{3+} neutralized with macro-ions.

3.3. Electrical resistance due to aluminium oxide

Lebras [2] has used the relation between applied voltage and current to calculate electrical resistance during electrodeposition. He divided the resistance into two parts, the resistance due to the bath solution and that due to the film, to demonstrate the change of film resistance with time. Using a similar approach, but also considering the oxide resistance, one can divide the total resistance into three parts:
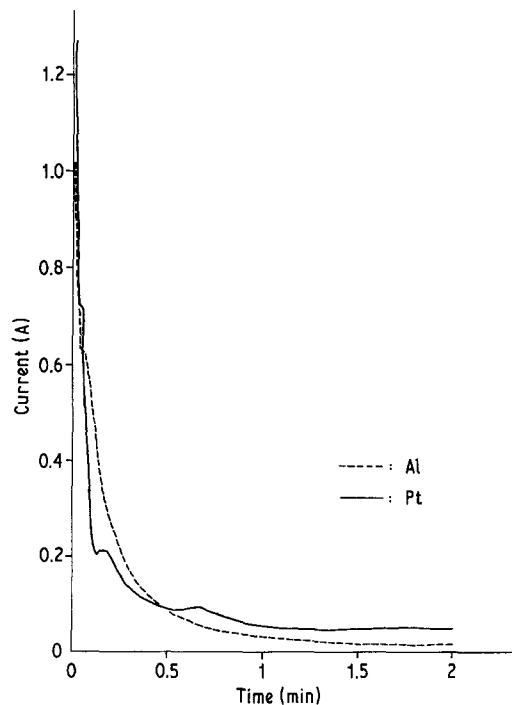

Fig. 1. Current variations of Al and Pt anodes during deposition at a constant voltage of 100 V (anode surface area: 40 cm^2).

$$R_{total} = R_{oxide} + R_{film} + R_{bath}$$

$$= R_{oxide} + R_{bf}. \qquad (8)$$

Since R_{bath} is about $80–100 \, \Omega$ and is small in comparison to R_{film} or R_{oxide}, R_{bath} and R_{film} can be combined in the term R_{bf}. Since Pt does not form an oxide film, we use the R_{bf} of Pt as that of the other metals. The results of measurements are plotted in Figs. 1–3.

Fig. 1 shows the variation of current with time at a constant voltage (100 V). It can be seen that the initial current of Pt is higher than that of Al. This can be attributed to the formation of Al_2O_3 or $Al(OH)_3$ immediately after immersion of Al in the bath solution, which would increase the electrical resistance. For zinc and steel, the current–time curves were similar to those for Al and Pt.

Fig. 2 shows the variation of deposition voltage with time for a constant current of 143 mA. These curves represent total resistances versus time using the relation $V = RI$. Each curve shows a two-stage deposition; the first stage was complete within about the first 20 s, and the second stage within a further 20 s. This two-stage deposition probably
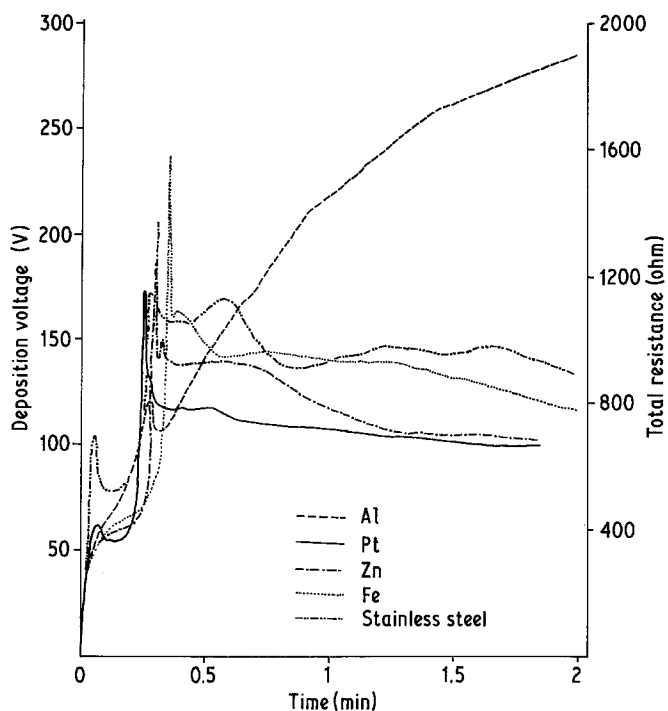
means a two-layer film deposition. The peak in each curve was due to insufficient capacity of the power supplier. The total resistances after 1 min are in the order: Pt < Zn < Fe < stainless steel < Al. During deposition, the surface of the stain-

Fig. 3. Variation of oxide resistance of Al during electrodeposition at a constant current of 143 mA (calculated from Fig. 2).

less steel showed the presence of red oxide. The resistance for Al continuously increased with time, indicating a continuous growth of aluminium oxide. For Zn, Fe and stainless steel, the oxides also formed during deposition, but ceased to grow after 0.5–1 min.

Fig. 3 shows that R_{oxide} for Al during deposition increased with time. This clearly implies that the amount of aluminium oxide increased with time after 0.5 min. For the constant-current experiment, the weights of film deposition on Al and Pt were 0.1819 and 0.3459 g respectively. Although the film thickness on Al is thinner than that on Pt, its resistance is higher, This strongly indicates the presence of aluminium oxide.
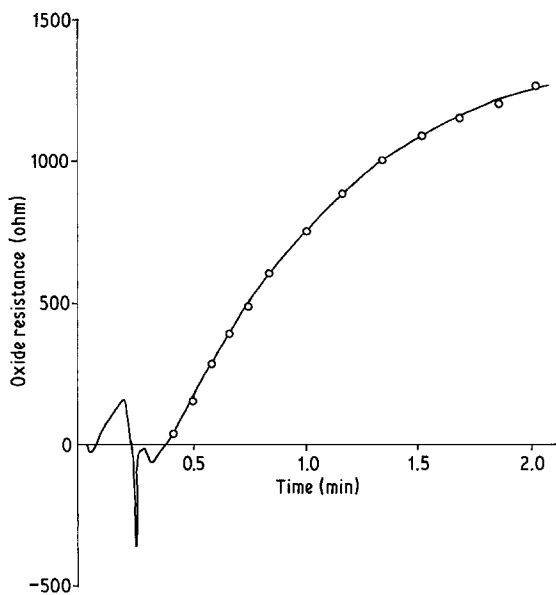
3.4. Depositions with curing agent

Mixing the resin XC-4010 and curing agent Cymel-303, with acid values of 1.608 meq g^{-1} of solid and 0 meq g^{-1} of solid, respectively [7, 8], in various ratios, it was found that the acid value of the resin before and after mixing remained unchanged. Using the solutions for electrodeposition on Al anode, it was found that the coulometric efficiency III [11] (defined in Table 2) remained unchanged under constant voltage oper-

Table 2. Coulometric efficiency of bath solution with various ratios of resin to curing agent, for constant voltage electrodeposition. Al sheet, 60 mm × 30 mm × 1 mm; applied voltage 80 V; electrodeposition time 2 min

Run	Resin/curing agent weight ratio	Solid content (%)	Amine content	Degree of neutralization (%)[†]	Acid value of deposited film	Weight of deposited film (g)	Resin content in deposited film (%)	Coulometric efficiency II[‡]	Coulometric efficiency III[§]
1	10/0	8.14	136.6	85	160.5	0.0469	99.8	0.01275	0.01084
2	6.0/4.0	7.43	96.6	100	136.7	0.0425	84.4	0.01055	0.01055
3	5.1/4.9	7.36	69.7	86	122.3	0.0580	75.5	0.01318	0.01133
4	4.0/6.0	7.31	57.7	89	121.9	0.0607	75.3	0.01265	0.01126

† Degree of neutralization = amine content/acid value.
‡ Coulometric efficiency II = number of grams of resin deposited per coulomb.
§ Coulometric efficiency III = coulometric efficiency II × degree of neutralization.

ation, as shown in Table 2. In other words, for the same degree of neutralization, the amount of resin deposited per coulomb was a constant value, about $0.011\,g\,C^{-1}$, indicating that the curing agent did not consume any electricity and was carried towards the anode by the macro-ions through physical linkage. Thus addition of the curing agent had no effect on the electrodeposition mechanism.

4. Conclusion

From the discussion above, it is appropriate to propose that the mechaism under normal operating condition procedes by Reactions 5–7 followed by Reaction 3.

Acknowledgement

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