

Shellac Film Coating on Metal Sheets by Electrochemical Polymerization

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SYNOPSIS

The electrolysis of shellac in the aqueous ammoniacal solution leads to formation of adherent films onto different metal anodes such as Fe, Cu, Pt, and Pb. The yield of deposited films increases with the time of electrolysis and current levels and is dependent on the nature of electrode materials. Therefore, the film thickness is well controlled by the impressed current level and electrolysis time. The addition of methylacrylamide to the shellac solution gives more adherent and smoother coatings onto the metal sheets than those obtained in the absence of the monomer. The film formation also takes place potentiodynamically. A plausible reaction mechanism of the shellac coating is suggested. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

There are two different electrolytic methods to coat metal surfaces for protection against corrosion. One is the electrocoating method where a preformed ionizable polymer is deposited on the substrate from solutions or suspension of a polymer by electrophoretic means. The other is a direct electrochemical polymerization method where coating on metal surfaces takes place with polymers formed electrochemically *in situ*.

In both methods, synthetic polymers are generally utilized.^{1,2} There are several reviews¹⁻³ and patents⁴⁻⁹ on electrocoatings to protect metals from corrosion by the electrochemical polymerization of organic monomers *in situ*. Shellac is one of the earliest resins that was attempted to be applied in electrocoating.^{10,11} However, no detailed information appears to exist in the literature on the anodic electrocoating of shellac on metals. In this paper, we describe shellac film coating on metal sheets by the electrochemical polymerization method in the aqueous ammoniacal solution of shellac with or without a monomer. Shellac is a natural resin of animal origin and has a rare combination of very desirable properties.^{12,13}

EXPERIMENTAL

Materials

Dewaxed and decolorized shellac was used. This type of shellac was prepared by filtering off the wax from a chilled alcohol solution of seed lac and then removing the color by adsorption with activated carbon. A solution of dewaxed decolorized shellac (4 g) was prepared in 25 mL of aqueous ammonia (2N) solution by warming at 50°C in a constant temperature bath.

Coating Method

The solution of shellac was taken into a simple H-shaped electrolytic cell where anode and cathode compartments were divided by a fine fritted glass disc 2 cm in diameter. The cell was thermostated at 30°C and electrolysis was carried out at a fixed current using Al, Fe, Cu, Pt, and Pb electrodes. The area of the electrode was 2 cm². The electrolysis at different electrode potentials was conducted with a CV-27 BAS (Bio Analytical System, U.S.A.) cyclic voltammetry system equipped with a BAS X-Y recorder in a single-compartment three-electrode cell under a N₂ atmosphere. The working electrode was a platinum microelectrode, the counter electrode was a platinum wire, and the reference electrode was a

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saturated chemical electrode (SCE) that was isolated from the cell by a KCl bridge.

RESULTS AND DISCUSSION

When the shellac solution was subjected to electrolysis at a fixed current of 50 mA, a strong adhering shellac film on the anode surface began to form immediately while the cathode remained clear. The anode was taken out from the electrolytic cell and the film was peeled off with a sharp razor. It was thoroughly washed with water, dried, and then weighed to a constant weight. The coating yield of film/cm² deposited on different metal electrodes is presented in Figure 1, which shows that the film yield increases with electrolysis time and is dependent on the nature of the electrode materials. The coating on Al, Fe, and Cu is technologically important. The coating yield increased linearly with increase of impressed current levels, as is evident from Figure 2. Therefore, the film thickness is well controlled by the current level and electrolysis time. The electrodeposited shellac was insoluble in common solvents such as methanol, ethanol, acetone, and *N,N*-dimethylformamide.

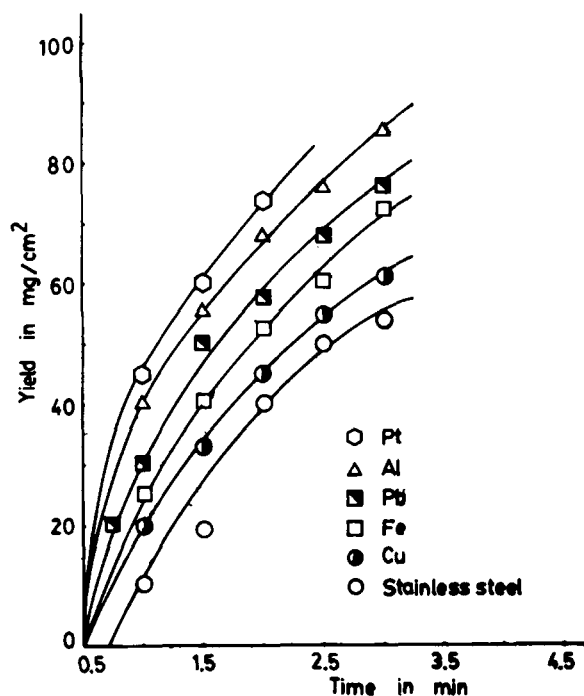


Figure 1 Weight of films of shellac (4 g in 25 mL of 2*N* aqueous ammonia) formed on different metal anodes, as indicated, at 50 mA and 30°C.

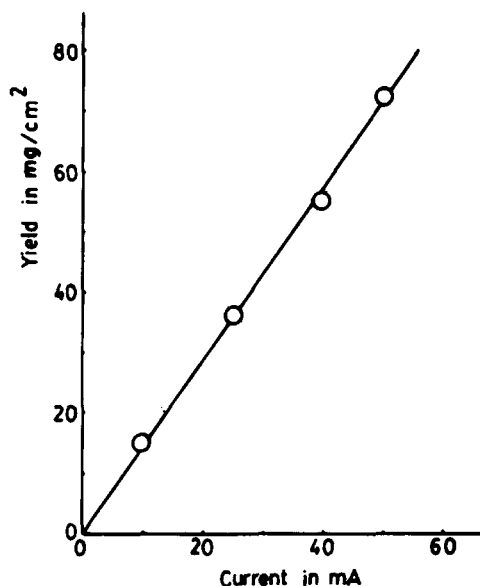


Figure 2 Plot of weight of shellac film deposited on Fe anode vs. impressed current.

The buildup of the film on the anode caused the increase of cell resistance and, consequently, the applied initial voltage increased with the time of electrolysis, as shown in Figure 3. The continued electrolysis for a longer period of time caused the current drop.

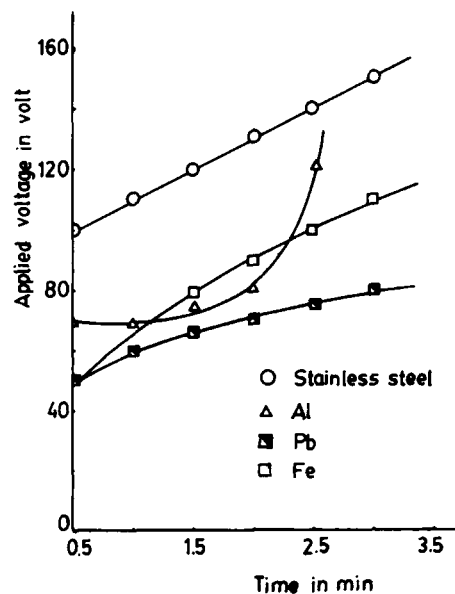


Figure 3 Increase of applied voltage with electrolysis time for different metal electrodes during the electrolysis of aqueous ammoniacal solutions of shellac (4 g in 25 mL of 2*N* aqueous ammonia).

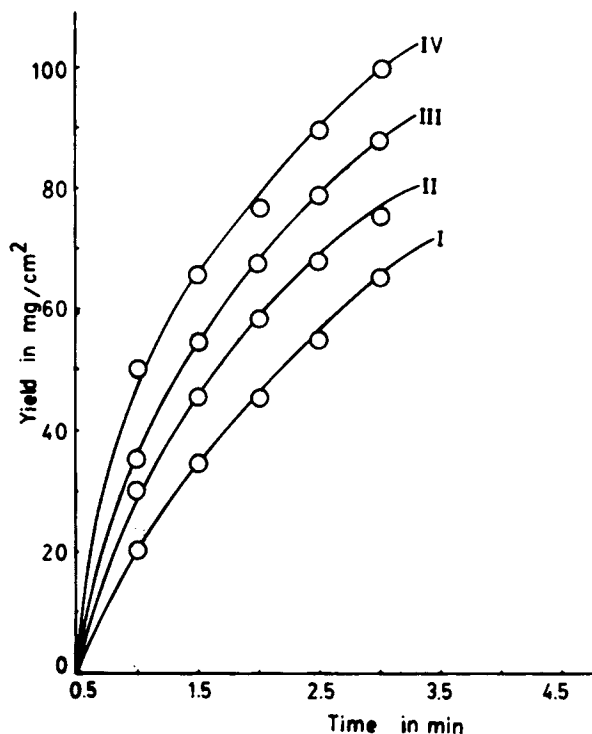


Figure 4 Weight of films formed on Cu anode at 50 mA in the solution of shellac (4 g in 25 mL of 2*N* aqueous ammonia) containing methylacrylamide at 30°C. The concentration of the monomer is (I) nil, (II) 0.59 mol/L, (III) 0.90 mol/L, and (IV) 1.18 mol/L.

Effect of a Monomer Addition on the Coating

The coating on the Cu anode was also investigated in the ammoniacal solution of shellac in the presence of methylacrylamide. The coating was found to be more adherent and smoother than those obtained without the monomer in the shellac solution. The coating yield also increased, as is clear from Figure

4. Similar results were obtained with Al, Fe, and Pt. Electrode coatings were not produced when the electrolysis of the aqueous ammoniacal solution of methylacrylamide was carried out without shellac.

The shellac-coated Fe metal had improved corrosion resistance because, when it was dipped into the 1% aqueous solution of sodium chloride, no rusting took place on the coated part of the metal sheet, whereas the exposed portion became heavily rusted. When the film was cured at 100°C, it became thermoresistant and completely insoluble in common solvents.

Cyclic Voltammograms

The current-voltage curve obtained during the potentiodynamic synthesis of shellac film in the aqueous ammoniacal solution is presented in Figure 5, which shows that the anodic current began to increase at 1.0 V vs. SCE, suggesting that shellac suffers anodic oxidation. No anodic current was shown when the aqueous ammoniacal solution without shellac was cycled in the range from 0.0 to 2.0 V. On repeated cycles, the working microelectrode became coated with a brown mass. The cyclic voltammogram did not change when 0.2 g of methylacrylamide was added to the shellac solution.

Mechanism

Shellac is the only resin of animal origin and its chemical nature is still not completely understood. It is a polyester type of resin formed from hydroxy fatty and sesquiterpene acids.¹³ It has free carboxyl, hydroxyl, and aldehydic groups and is unsaturated. The IR spectrum of shellac is shown in Figure 6. The bands at 3440 and 1700 cm^{-1} are due to $-\text{CH}$

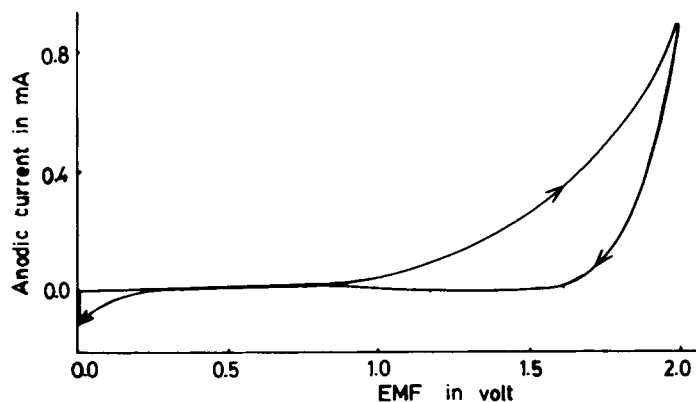


Figure 5 Cyclic voltammogram of shellac (4 g in 25 mL of 2*N* aqueous ammonia) with microplatinum electrode; sweep rate is 50 mV/s.

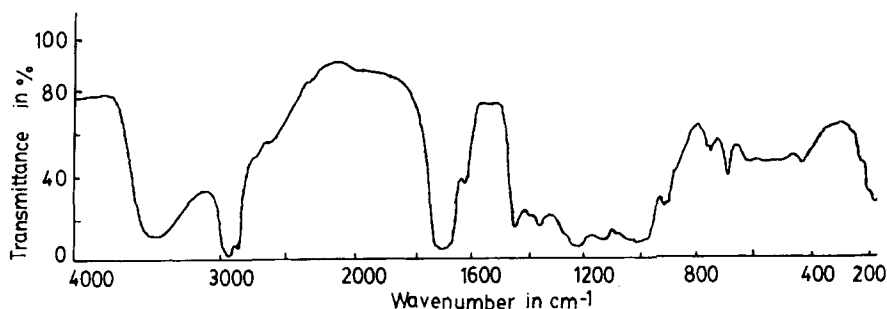
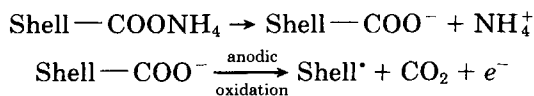


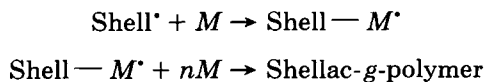
Figure 6 IR spectrum of shellac deposited electrochemically on the Fe anode at 50 mA.

and >C=O groups, respectively. The other maxima in the absorption at 2940 and 1440 cm^{-1} correspond to >CH_2 and —CH_3 groups, respectively. The shoulder near 1630 cm^{-1} indicates C=C stretching of the aromatic ring.

The shellac dissolves in an aqueous ammoniacal solution to form its salt that undergoes the following reaction sequences:



The shellac radical so formed may react with the monomer molecules:



In the absence of a monomer, shellac radicals may dimerize and/or undergo a cross-linking reaction. In presence of a monomer, it forms graft copolymers. The shellac itself might have been electrochemically homopolymerized as it contains a C=C double bond. In fact, the IR spectrum did not show the double bond near 1630 cm^{-1} in the electrolyzed shellac.

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