

KINETICS OF SHELLAC FILM COATING SHEETS USING ELECTROCHEMICAL POLYMERIZATION TECHNIQUE

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Abstract:-

The electrolysis of shellac in the aqueous ammoniacal solution leads to formation of adherent film onto different metal anode 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 coating 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.

Keywords:- Shellac, methylacrylamide, monomers, cyclic voltammograms

Introduction

There are two different electrolytic methods to coat metal surface 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 reviews and patents on electro coating to protect metals from corrosion by the electrochemical polymerization of organic monomer *in situ*. Shellac is one of the earliest resins that was attempted to be applied in electro coating. However no detailed information appears to exist in the literature on the anodic electro coating of shellac on metals. In this paper we describe shellac film coating on metals sheets electrochemical polymerization method in the aqueous ammoniacal solution of shellac with or without monomer. Shellac is a natural resin of animal origin and has a rare combination of very desirable properties.

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 and decolorized Shellac (4g) was prepared in 25 ml aqueous ammonia (2N) solution by warming at 50⁰ C in 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 2cm in diameter. The cell was thermo stated at 30⁰ C and electrolysis was carried out at a fixed current using Al, Fe, Cu, Pt, and Pb, electrodes. The area of electrodes was 2cm². 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 under a N₂ atmosphere. The working electrode was a platinum

microelectrode, the counter electrode was a platinum wire, and the reference electrode was a 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 in a fixed current of 50mA a strong adhering shellac film on the anode surface began to form immediately while the cathode remains clear. The anode was taken out from the electrolytic cell and the film was peeled off with the sharp razor. It was thoroughly washed with water, dried and then weighed to a constant weight. The coating yield of film/cm² deposit on different metals electrodes is presented in Figure -1, which shows that the film yield increases with electrolysis time and is dependent on the nature of electrode materials. The coating on Al, Fe, and Cu, is technologically important. The coating yield increases linearly with increase of impressed current level 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

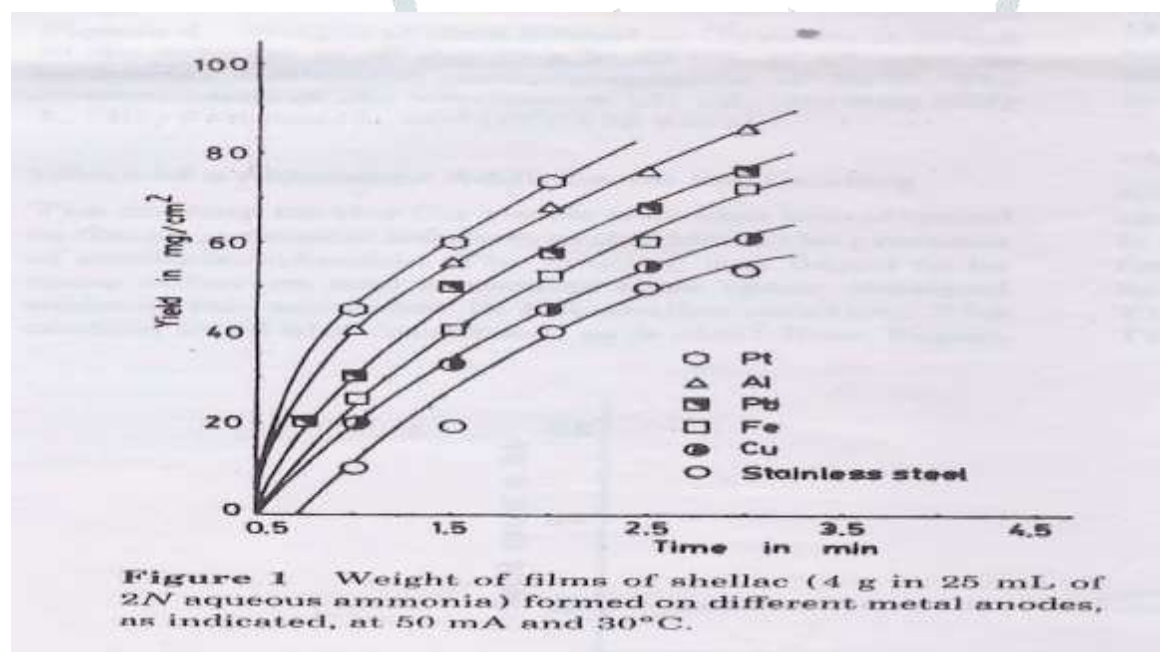
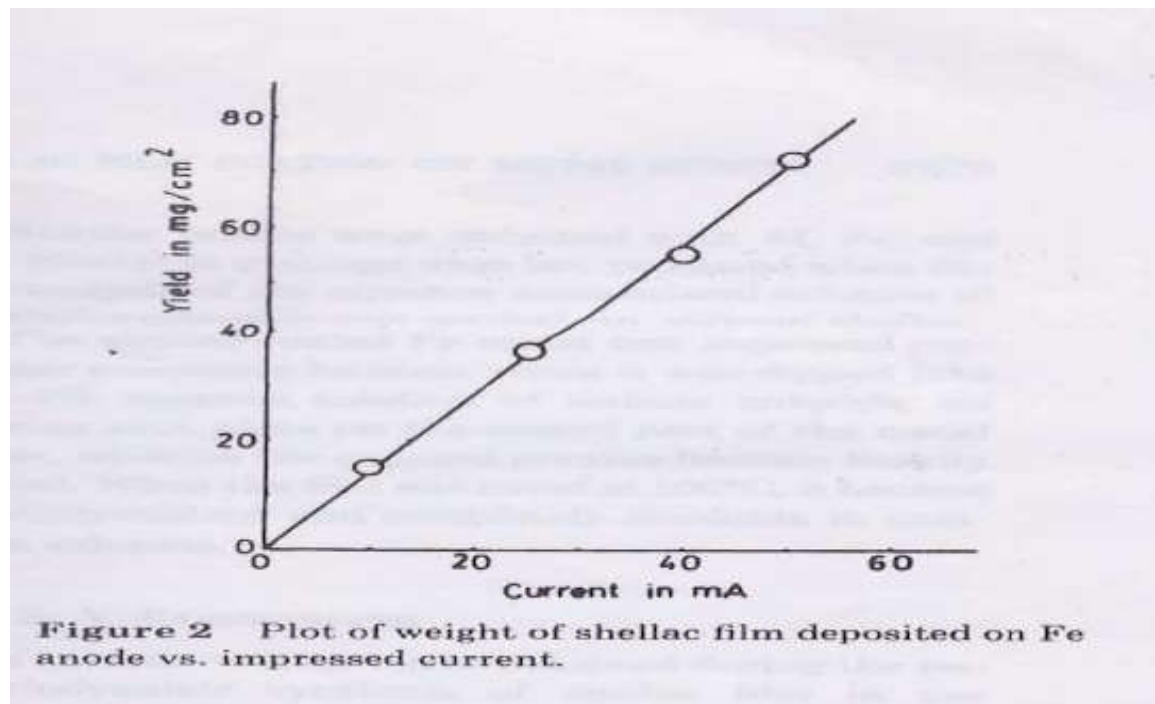


Figure - 2



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.

Effect of 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 obtained with Al, Fe, and Pt. Electrode coating 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 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^o C, it became thermo resistant and completely insoluble in common solvents.

Figure – 3

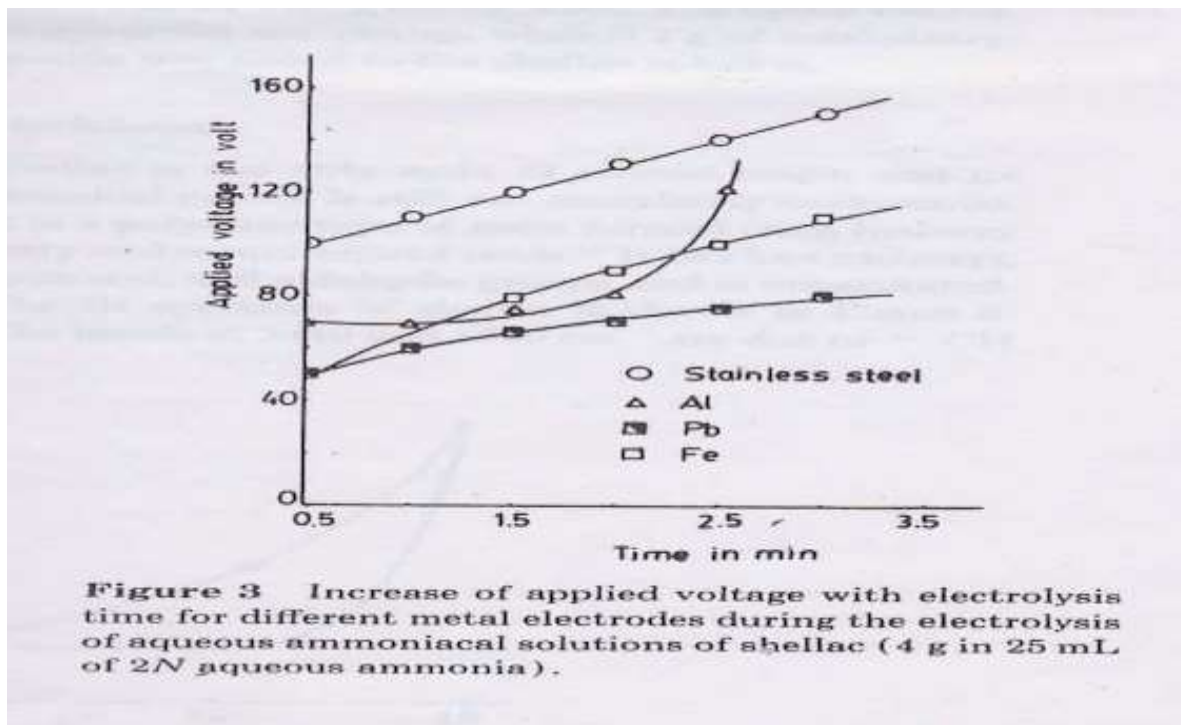
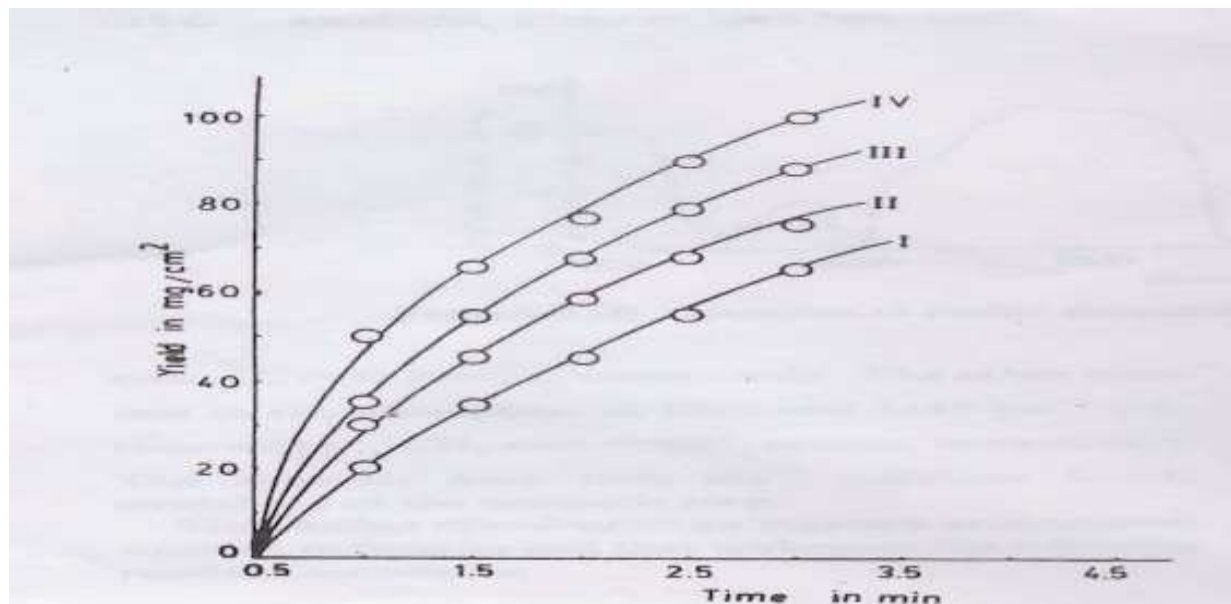


Figure – 4



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 1.0V 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. The repeated cycles, the working microelectrode becomes coated with a brown mass. The cyclic voltammogram did not change when 0.2g of methylacrylamide was added to the shellac solution.

Figure – 5

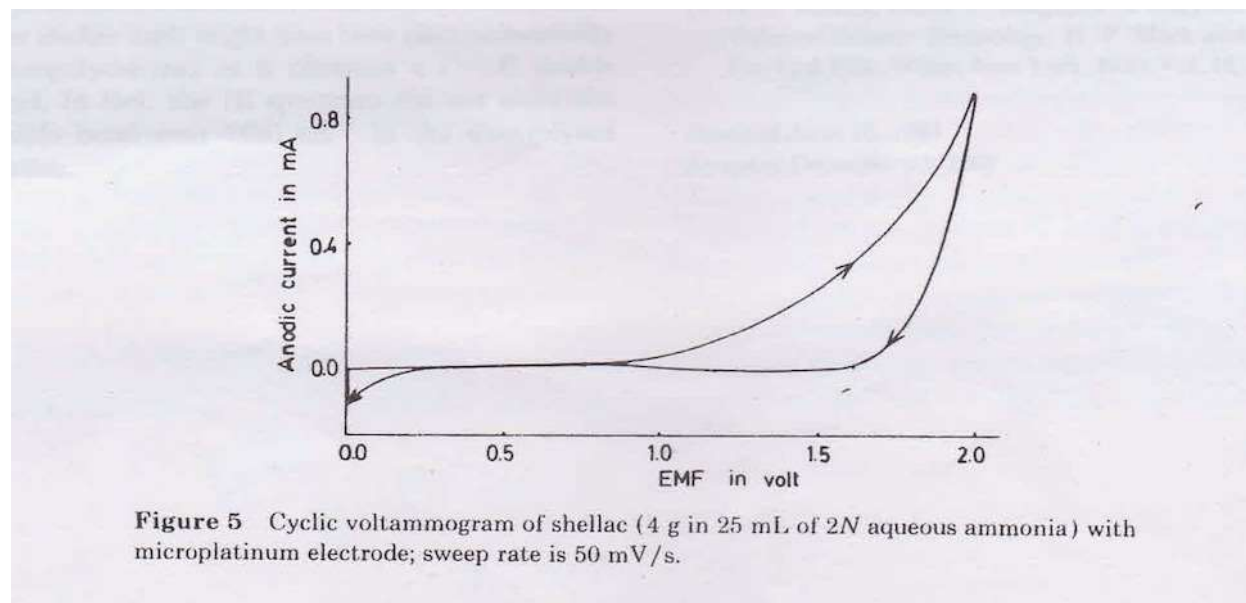


Figure 5 Cyclic voltammogram of shellac (4 g in 25 mL of 2N aqueous ammonia) with microplatinum electrode; sweep rate is 50 mV/s.

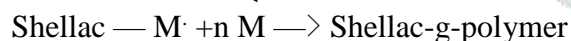
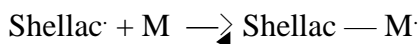
Mechanism:

Shellac is the only resin of animal origin and its chemical nature is still not completely understood. In polyester type of resin formed from hydroxyl fatty and sesquiterpene acids. It has free carboxyl, hydroxyl, and aldehydic groups and is unsaturated. The IR spectrum of shellac is shown in figure-6. The band at 3440 and 1700cm^{-1} are due to $-\text{CH}$ and $>\text{C}=\text{O}$ groups, respectively. The other maxima in the absorption at 2940 and 1440cm^{-1} corresponds to $>\text{CH}_2$ and $>\text{CH}_3$ groups, respectively. The shoulder near 1630cm^{-1} indicates $\text{C}=\text{C}$ stretching in the aromatic ring.

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



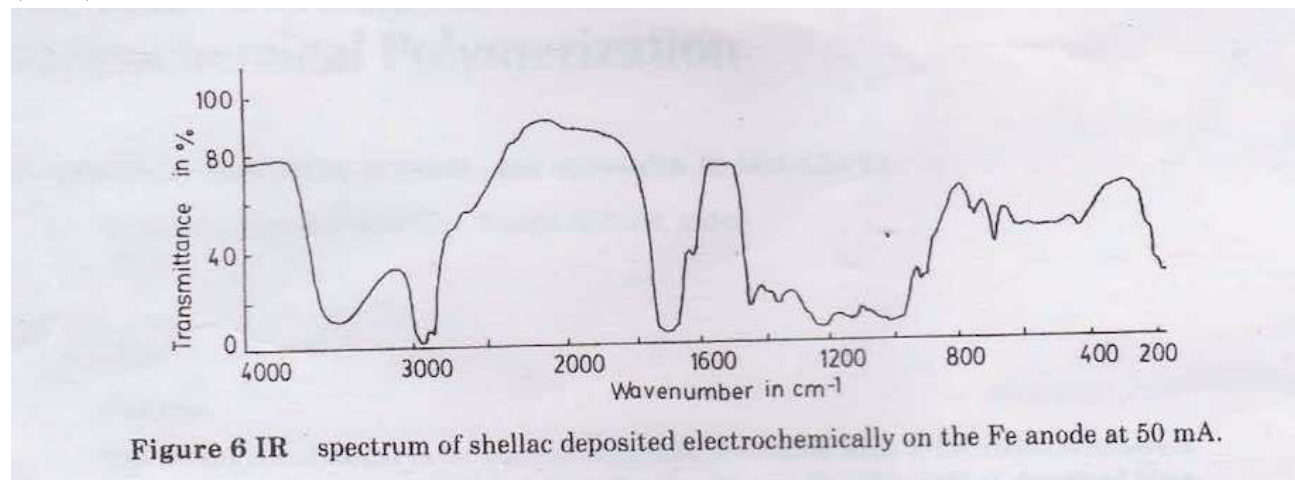
The shellac radical so formed may react with the monomer molecules:



In the absence of 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 $\text{C}=\text{C}$ double bond. In fact the IR spectrum did not show the double bond near 1630cm^{-1} in the electrolyzed shellac.

Figure - 6

(1979)



Acknowledgements:

I thank to H. O. D. Chemistry, H. D. Jain College, V. K. S. University Ara for providing necessary facilities

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