Electron conducting organic coating of mild steel by electropolymerization

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The aim was to coat mild steel with an electron conducting polymer in order to replace any possible electrochemical corrosion of the metal by another electrochemical reaction occurring on top of the film. In view of potential industrialization, electropolymerization of a water soluble monomer was studied. In most cases, this was achieved by oxidation, and the substrate had to be passivated. Polyaniline was obtained in nitric acid solution. Films had a good structure but were brittle and powdery on the surface. Except on tin free steel, they were insulating. Polypyrrole was a better candidate. Prepared from a Na₂SO₄ solution, films were conductive, ensured good corrosion resistance of the substrate but they were brittle and adhesion to the substrate was not high. Furane, thiophene and iron substituted vinylpyridine complex were tried without success. Further research should consider copolymerization of pyrrole with other monomers.

1. Introduction

The aim of this research was to develop a new process to protect mild steel against corrosion. It is well known that corrosion is largely an electrochemical phenomenon. Electrochemical reactions occur at interfaces between an electronic conductor and an ionic conductor. Accordingly, if it is possible to completely cover mild steel with a continuous film of a chemically inert but electron conducting substance, corrosion of the substrate will be avoided, because any electrochemical reaction will occur at the surface of this film without involving the substrate. Other advantages of such an electron conducting film are to allow further electrochemical treatment at its surface, such as electrophoretic painting. Also, reactive metallic powders could be included in the electron conducting film or placed at its surface to achieve sacrificial protection of the substrate without the need for an intimate contact between the metallic grains or with the substrate.

In this paper, electropolymerization is considered as a method to obtain adherent and cohesive electron conducting films. It involves a solution of organic monomer, the transfer of an electron between the substrate and a monomer and the charged monomer leading to the polymerization reaction. For such a process to give a continuous cover of the substrate, the polymer must be insoluble in the electrolyte and the polymerization reaction may not proceed in a direction perpendicular to the substrate.

This process is very different from electrophoresis: in electropolymerization, the polymer is obtained in situ by an electrochemical process, whereas in electrophoresis, the polymer is present in the solution at the beginning of the process.

A literature survey reveals that different monomer solutions can be considered to obtain adherent and electron conducting films. Three types of monomer are especially interesting [1, 2]: benzenic substituted derivatives, heteroaromatic compounds and organo-metallic complexes.

Among benzenic substituted derivatives, aniline can be electropolymerized by oxidation [3-20]. Electronic conductivity of the film varies from 10⁻¹³ to 10⁻¹⁰ Ω⁻¹ cm⁻¹. Properties depend largely on the support electrolyte: in acid solution, semi-conducting films are obtained on noble metals, but in water-methanol solutions at high pH non conducting films are obtained on mild steel. Phenol can also be electropolymerized by oxidation of phenolate anions at high pH, giving polyoxyphenylen. With an inorganic base very thin and adherent films are obtained. With saturated amines polymerization occurs towards the bulk of the solution. Unsaturated amines wet films are obtained with a poor coverage of the substrate.

Heteroaromatic polymers can easily be obtained by electrochemical oxidation. For pyrrole [21-33], with an organic electrolyte containing acetonitrile and perchlorate ions, polymers are highly conductive: for example 10⁻¹⁰ Ω⁻¹ cm⁻¹, probably because some perchlorate ions act as doping agents. Inorganic acid solutions can also be used. Again, some anions are
were examined in cross section after cementation, showing where copper metal nuclei were generated. Neutral copper sulphate solution at 37 g dm\(^{-3}\) Cu\(^{2+}\) or 37 g dm\(^{-3}\) Cu\(^{2+}\) at room temperature. Some samples by copper cementation after 5min immersion in a $2.310^{\text{u}}$.

Electrochemical behaviour of the films was also studied. Electronic properties were characterized by polarization curves of coated steel samples in 10\(^{-2}\) M sulphuric acid. This also allowed determination of the redox properties of the film and evaluation of the kinetics of the O\(_2\)/OH\(^{-}\) reaction on this film. The electronic nature of conductivity of the films was also checked by electrophoretically depositing zinc from a 80 g dm\(^{-3}\) H\(_2\)SO\(_4\), 60 g dm\(^{-3}\) Zn\(^{2+}\) solution. In this case, results depend not only on conductivity but also on hydrogen overpotential on the film. Accordingly, copper electrodeposition was also studied. To avoid cementation, a cyanide solution was chosen: 74.5 g dm\(^{-3}\) CuCN, 92 g dm\(^{-3}\) NaCN, 30 g dm\(^{-3}\) NaOH, at 20°C and 6 A dm\(^{-2}\) cathode current density. Anaphoretic painting was also checked on a Levis industrial bath at pH 8.9 containing 11.2% solids after drying half an hour at 160°C. Anaphoresis occurred for 2 min at 250 V. It was followed by curing for ten minutes at 190°C.

The electrolytic cell was very simple: a closed 500 ml vessel allowing work under an inert atmosphere, without agitation. The electrodes were 55 mm x 90 mm sheet coupons, 1 mm thick for stainless steel and 0.25 mm for mild steel. They were placed vertically at 20 mm distance and the exposed surface was 13 cm\(^2\). The temperature was kept constant at 20 ~ C. Anaphoresis occurred for 2 min at pH 8.9 containing 11.2% solids after drying half an hour at 160°C. Anaphoresis occurred for 2 min at 250 V. It was followed by curing for ten minutes at 190°C.

The thickness of the films was determined by three different methods. The first involved weighing 20 samples obtained under the same conditions and measuring the density of the films by sink or float in organic liquids of various densities. The second method was by compressing a certain number of coated samples between two thick steel blocks and observing the cross section after metallographic polishing. The third was based on a conventional magnetic induction thickness measurement apparatus (FORSTER Monimeter S2.310).

The porosity of the films on mild steel was measured by copper cementation after 5 min immersion in a neutral copper sulphate solution at 37 g dm\(^{-3}\) Cu\(^{2+}\) or in acid copper sulphate solution (192 g dm\(^{-3}\) H\(_2\)SO\(_4\), 37 g dm\(^{-3}\) Cu\(^{2+}\)) at room temperature. Some samples were examined in cross section after cementation, showing where copper metal nuclei were generated.