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SHORT COMMUNICATION

The use of a clock reaction to measure the porosity of coatings on iron

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1. Introduction

The techniques for measuring the porosity of electrodeposits have been critically summarized by Clarke [1]. The measurement of porosity is ambiguous in that some methods measure the total area of the base metal exposed (obtaining a porosity index) while other methods count and locate the number of pores. Since pores are not uniform in size these two approaches do not necessarily give numbers that are proportional to each other.

Because of an interest in the role of additives in producing and controlling porosity our laboratory has looked at the possibility of developing a rapid simple method for measuring porosity [2]. These methods, because of our interest, have been primarily concerned with measurements related to the total amount of base metal left unplated.

Catalytic methods of analysis, a common procedure in enzymatic analysis, have been developed as a very sensitive method of determining the concentration of a number of substances [3].

In this technique one determines the concentration of a substance by measuring the increase in the rate of a reaction for which the substance is a catalyst. Since a number of porosity tests depend on the production of corrosion products of the base metal it was decided to investigate the possibility of utilizing a catalytic method to determine the concentration of these products. There are two possible advantages to catalytic methods:

1. The sensitivity of the technique may allow the determination of porosity using short corrosion times. In fact, ultimately one would wish to use reactions that are catalysed by the bare substrate metal since this would require no corrosion.
2. The existence of several clock reactions open the possibility of measuring porosity by using only a watch.

It was decided to initiate the study with an investigation of the possibility of utilizing a clock reaction.

2. Experimental details

The clock reaction chosen for study was the oxidation of thiosulphate by peroxydisulphate coupled by iodide with starch used as an indicator for the presence of iodine.

$$\begin{array}{rc}
 & S_2O_8^{-2} + 2I^- \rightarrow I_2 + 2SO_4^{-2} \\
 & I_2 + 2S_2O_3^{-3} \rightarrow 2I^- + S_4O_6^{-2} \\
\hline
\text{Net} & S_2O_8^{-2} + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2SO_4^{-2}
\end{array}$$

The time for this reaction to occur is measured by determining the time elapsed until the appearance of a blue colour. At this time the thiosulphate has been depleted. This reaction is known to be catalysed by several metal ions including iron(II). Thus corrosion of the exposed iron substrate would produce iron(II) which would accelerate the reaction and decrease the time to the appearance of the blue colour. The decrease in this time will be related to the amount of exposed iron.

The study of the effect of paint coatings was made by coating the iron with nail polish.

The study of copper electrodeposits was made by plating previously buffed, washed and dried 1 cm^2 shim steel foils. The plating solution contained 7.5 g cuprous cyanide, 13.1 g potassium sodium tartrate and 9.6 g sodium carbonate in 500 ml of solution.

The coated samples were placed in a solution composed of 1 ml 0.1M KI, 1 ml 0.01M $Na_2S_2O_3$, 1.0 ml 0.2% starch, 2.5 ml 0.1M KNO_3 and 2.5 ml 0.25M HCl, and allowed to corrode under a nitrogen atmosphere for various times. After corrosion the metal foils were removed and 2.00 ml of 0.42M potassium peroxydisulphate ($K_2S_2O_8$) was added to the solution and the time was measured to the appearance of the colour.

Synthetic pores were created by pressing different numbers of wooden toothpicks against

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the substrate during the plating or painting process.

3. Results and conclusions

3.1. *Establishment of appropriate experimental conditions*

It was first necessary to establish that there was a significant difference between the catalytic activity of the corrosion products from copper and those from iron. The induction time (the time until the solution turned blue) was measured as a function of the corrosion time for electroplated foils of copper and iron. In order to accelerate the corrosion rate so that reasonable decreases in induction time could be obtained with relatively short corrosion times a 1 cm^2 platinum foil electrode was attached to the test foil. The effect of corrosion time on induction time is shown in Fig. 1. It can be seen that, within experimental error, platinum had no effect on the induction time. Copper did decrease the induction time but the decrease was small when compared to that of iron. The attachment of platinum to the metal strip caused little change in the effect of copper and the results plotted in the figure are the averages of the experiments with and without the platinum attached. The fact that the change in induction time caused by copper essentially stops changing with time on exposure of the metal to the solution, coupled with the fact that the attachment of the dissimilar metal, platinum, to the copper does not appreciably change the characteristics of the curve indicates that the copper affects the induction time by some surface effect rather than by the production of a corrosion product. It can be seen that the platinum markedly accelerates the effect of the iron as would be expected from a corrosion mechanism. From these studies a corrosion time of 120 s was selected for the porosity testing since it was felt that at this time there was enough differentiation between the copper and the iron to be used for the tests.

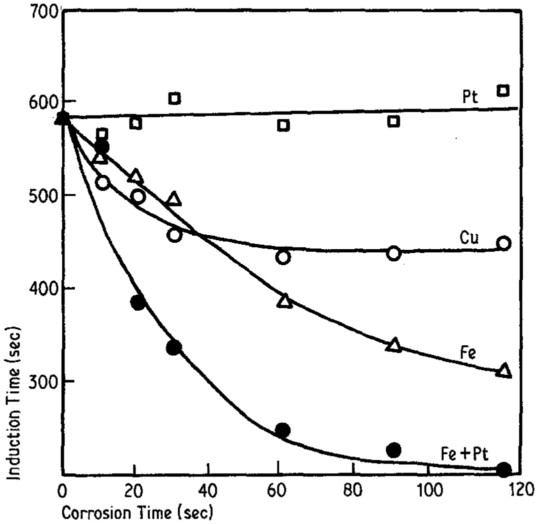

Fig. 1. The effect of corrosion time on the time for the appearance of colour (induction time) on 1 cm^2 foils.

3.2. *The effect of area on the induction time*

If the rate of corrosion is proportional to the area of exposed iron

$$\frac{\mathrm{dFe(II)}}{\mathrm{d}t} = k_1(\text{area iron}) \tag{1}$$

then the amount of iron(II) produced after corrosion for a specified length of time will be proportional to the area of iron exposed to the solution.

It is known that the rate law for the clock reaction under these conditions is:

$$\frac{-\mathrm{d}[S_2O_3^{-2}]}{\mathrm{d}t} = k_2[S_2O_8^{-2}][S_2O_3^{-2}][Fe^{+2}] + K_3[S_2O_8^{-2}][S_2O_3^{-2}] \tag{2}$$

If one uses a fixed amount of $S_2O_8^{-2}$ and $S_2O_3^{-2}$, with other conditions fixed, the time for the colour to appear should follow the equation

$$\frac{1}{\text{time}} = k_2'[Fe^{+2}] + k_3'$$
$$= k_2''[\text{area of Fe}] + k_3' \tag{3}$$

A determination was made of the effect on the induction time of the area of iron exposed to the solution by using different area shim steel foils. Fig. 2 shows a plot of the area of iron vs the reciprocal of the induction time. It can be seen that in agreement with theory it is a linear plot showing that the induction time can be used to measure the surface area of iron exposed to the solution.

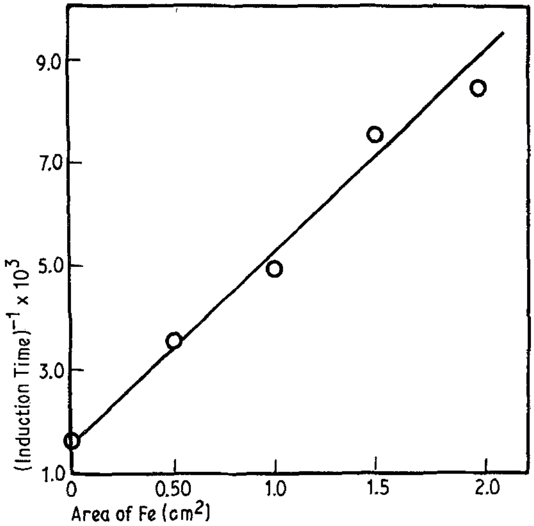

Fig. 2. The effect of the area of the iron on the reciprocal of the induction time.

3.3. *The effect of pores on the induction time*

Two types of coatings are used in this study, nail polish and electrodeposited copper. The pores were synthetically produced by holding with clamped toothpicks against the base metal while it was painted or electroplated. The toothpicks used with the nail polish were smaller than the ones used in the electrodeposited experiments.

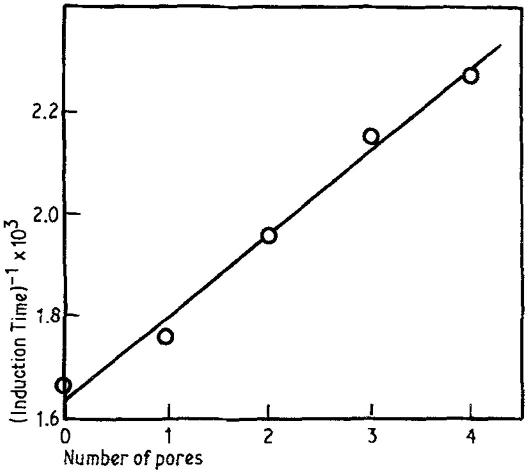

Fig. 3. The effect of the number of macropores in a nail polish coating on iron on the reciprocal of the induction time.

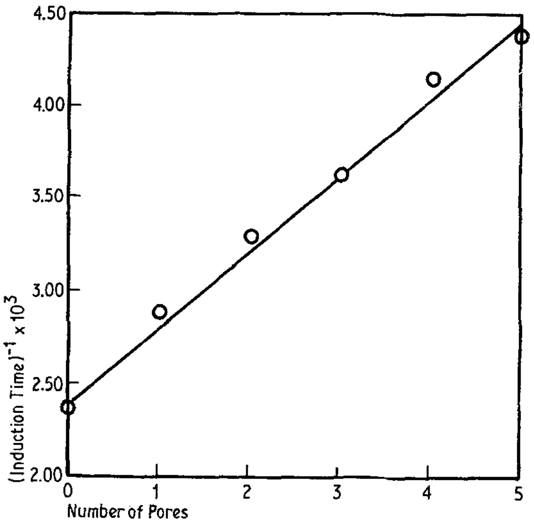

Fig. 4. The effect of the number of macropores in an electrodeposited copper coating on the reciprocal of the induction time.

Figs. 3 and 4 show that in agreement with theory the number of pores is inversely proportional to the measured induction time. This shows that the measurement of induction time in this clock reaction can be used as a convenient method to measure the porosity of coatings on iron. It should be remembered that it measures the total area exposed rather than the number of pores and it suffers from the disadvantages of other corrosion methods. However, it does demonstrate that kinetic methods can be used to measure porosity. There are a variety of kinetic methods available and a number are much more sensitive than the one used in this example.

Acknowledgement

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References

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