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# The resistance of electrodeposited layers of rubber and resins

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The electrical resistance per unit deposition charge per unit area ($p$, $\Omega\ C^{-1}\ cm^{-2}$) has been calculated from current–time data for the anodic deposition of polymers in the following systems: (a) resin deposition on mild steel and copper coated mild steel, (b) rubber deposition on mild steel and aluminium, and (c) two resin systems of two concentrations on mild steel and brass. The values of $p$ are analyzed in detail and it is concluded that $p$ can be qualitatively related to the electrical conductivity of the electrode material and the adhesion of the electrodeposits, taking into consideration the different mechanism for the stability of rubber latex and the resin system. For a given value of $p$, electrodeposits on aluminium are 40% more adherent than those on mild steel. Further, for the same adhesion, values of $p$ are lower by about 20% when aluminium is used instead of mild steel as the anode. It has also been concluded that the study of $p$ versus the current density during the electrodeposition of the resins is a convenient and useful method of approach to the study of electrophoresis in its practical application to the preparation of electro-coatings of industrial value.

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## 1. Introduction

The resistance of organic electrodeposits per unit area per unit charge for the deposition process ($\Omega\ C^{-1}\ cm^{-2}$) is a useful concept. Its value for electrodeposited rubber from rubber latex [1] has been shown to be of the order of 26 Ω.

In this paper the method of calculation is extended to resin systems using mild steel, copper coated mild steel and brass anodes. The relevant equation for calculating the resistance (Ω) per coulomb per unit electrode area (1 cm²) is

$$p = \frac{2V}{(I_0)^2}\left(\frac{1-x}{1+x}\right)\left(\frac{1}{x}\right)\left(\frac{1}{t}\right). \qquad (1)$$

$I_0$ is the initial current ($t = 0$) (A), $I$ is the current at time $t$, $x = I/I_0$ and $V$ is the cell voltage.

In situations where experimental data on $I_0$ and $V$ are not available and when the values of $V$ and $t$ are the same, the values of $p$ for two metals (1 and 2) can be compared.

$$\left(\frac{p_1}{p_2}\right) = \left(\frac{I_2}{I_1}\right)^2 \frac{[(1-x)/(1+x)]_1(1/x_1)}{[(1-x)/(1+x)]_2(1/x_2)} \qquad (2)$$

where $I_2$ and $I_1$ are the relative values of the initial current at the chosen common value of $V$ for the two metals 1 and 2.

The derivation of Equation 1 is given in the Appendix.

## 2. Experimental procedures and results

The values obtained for $p$ in the following systems are given in Tables 1 and 2.

(a) Electrodeposition at 30 V (d.c.) from a 5%

*Table 1. Values of p for cases a–d obtained by substitution in Equation 1 for cases a–c and in Equation 2 for case d. (Data source: Figs. 1 of [2, 5])*

| $t$ | *Value of p* ($\Omega\ C^{-1}\ cm^{-2}$) | | | |
|---|---|---|---|---|
| (s) | *case a* | *case b* | *case c* | *case d* |
| 5 | 75·3 | 75·3 | 71·1 | 19·7 |
| 10 | 127 | 76·9 | 90·4 | 16·7 |
| 15 | 127 | 71·9 | 90·2 | 13·5 |
| 20 | 132 | 71·2 | 93·1 | 12·3 |
| 30 | 131 | 70·4 | 90·2 | 10·3 |
| 40 | 130 | 68·9 | 93·2 | 10·8 |
| 60 | 98·2 | 62·7 | 81·8 | 8·9 |

*Table 2. Values of p for case e*

| *Resin system* | *Concentration and anode material* | *mean c.d.* ($10^{-6}$ A m$^{-2}$) | *p values* ($\Omega$ C$^{-1}$ cm$^{-2}$) | *p* × *c.d.* | *p/c.d.* |
|---|---|---|---|---|---|
| castor oil<br>+ maleic anhydride [10] | standard [10]<br>mild steel | 2·81 | 2·98 | 8·37 | 0·943 |
| castor oil<br>+ maleic anhydride | standard<br>brass | 1·59 | 91·3 | 145·2 | 57·4 |
| castor oil<br>+ maleic anhydride | $\frac{2}{3}$ standard<br>mild steel | 2·25 | 1·65 | 3·71 | 0·733 |
| sodium hydroxide<br>resin system [11] | standard [11]<br>mild steel | 1·28 | 4·32 | 5·53 | 3·38 |
| sodium hydroxide<br>resin system | $\frac{2}{3}$ standard<br>mild steel | 3·80 | 64·4 | 244·7 | 16·9 |

aqueous resin bath over mild steel; anode area = cathode area = 8·75 cm$^2$.

(b) Deposition under the same conditions from the same bath over (1 $\mu$m) copper coated mild steel.

(c) Over (10 $\mu$m) copper coated mild steel.

(d) Deposition from rubber latex over aluminium and mild steel. Anode area = 9 cm$^2$ and anode/cathode ratio = 20.

(e) Deposition from two different resin systems using two bath compositions and a small volume of the bath ($\simeq$ 300 ml). The experimental conditions from which the values of *p* have been evaluated are summarized in Table 3.

The electrodeposits were prepared on mild steel and copper plated mild steel under the following experimental conditions: Alkyd resin concentration, 5 wt% (prepared as per procedures

*Table 3. Experimental conditions from which the values of p have been evaluated*

| *Resin system employed* | *Voltage of deposition* (V) | *Average anode c.d.* ($10^{-6}$ A m$^{-2}$) | *Anode material and its skin surface* | *t* (s) | $I_0$ (mA) | *x (fraction of the initial current at time t seconds)* | *Range of values of p evaluated* ($\Omega$ C$^{-1}$) |
|---|---|---|---|---|---|---|---|
| castor oil + maleic anhydride resin system [9] of standard concentration ($\simeq$ 10%), bath volume used 300 ml | 30–100 | 1·53–7·33 | mild steel plates, 7·5–15 cm$^2$ | 9–150 | 225–750 | 0·1–0·692 | 0·31–6·89 |
| castor oil + maleic anhydride<br>$\frac{2}{3}$ standard concentration | 30–50 | 1·38–3·83 | mild steel plates 7·5–16·25 cm$^2$ | 31·8–70·6 | 175–625 | 0·25–0·57 | 0·25–0·57 |
| castor oil + maleic anhydride<br>standard concentration | 50 and 100 | 0·7–3·70 | brass plates of area 5·75 cm$^2$ | 18–90 | 50–300 | 0·23–0·60 | 0·48–3·70 |
| sodium hydroxide resin system [11]<br>standard concentration | 20–100 | 0·55–2·99 | mild steel plates, 5 and 19·3 cm$^2$ | 18–180 | 30–800 | 0·43–0·85 | 0·1–4·0 |
| sodium hydroxide resin system<br>$\frac{2}{3}$ standard concentration | 30, 60 and 80 | 0·7–8·50 | mild steel plate, 5 cm$^2$ | 15·7–88·5 | 45–600 | 0·21–0·7 | 1·54–113·6 |

[8] available in our laboratory); deposition voltage, 30 V; distance between electrodes, 5·6 cm; baking temperature of the deposit, 200° C; baking time, about 2 hours.

The copper deposition prior to resin electrodeposition, as and when needed, was effected to the predetermined thickness by first striking the copper in a cyanide solution followed by plating in an acid sulphate bath; the required solutions for both conformed to the best available compositions in the laboratory.

The bond strength values for the resin deposits were measured by the sandwich pull-off techniques [13] using the Hounsfield tensometer. This involves gradually increasing tension on the surface of the paint through an attachment until failure occurs either within the film (cohesive) or at the interface (adhesive). The attachment to the paint film is made through a high strength adhesive like a CIBA araldite/hardener system which does not interact with the paint film and affect the adhesion of the film to the substrate.

The values of $p$ as a function of time of deposition (Table 1) and current density (Table 2) have been analysed by a technique recently developed by the author [3, 4].

The values of $p$ are summarized in Tables 4 and 5 to facilitate comparison and discussion. $p$ depends on the bath system, anode metal and depositing conditions. For the same anode metal (mild steel) $p$ is about 3·9 smaller for rubber latex than for when the resin system is used for the electrodeposition experiments. This can be attributed to differences in surface charge density ($\sigma$, C m$^{-2}$) of the depositing particle entities in the two systems. The particle size [14] of rubber latex is ($3{\cdot}29 \times 10^{-7}$ m) whereas the size of the resin particle [15] entities is smaller ($0{\cdot}05$–$1{\cdot}0 \times 10^{-7}$ m). The mechanism [6] of stability of the two systems, however, is not the same and this can contribute to differences in the surface charge density of the two resin systems. Differences in hydration number of the depositing entities occur when the surface charge densities of the depositing entities are not the same. When the charges on such electrodepositing particles are neutralized at the electrode, marked differences in electrical resistance of the electrodeposits can occur. There is scope for further detailed investigations using one metal under constant depositing conditions, from different resin bath systems containing depositing particles of different surface charge densities.

It is difficult to relate $p$ to the electrical conductivity of the anode material, as aluminium (a better conductor than mild steel) increases the value of $p$ (Table 4) in rubber latex whereas copper (better conductor than mild steel) decreases the value of $p$ in the resin system (Tables 4 and 5). The strong oxide layer over the aluminium may

*Table 4. Comparative study of the values of p*

| *Nature of the depositing bath system* | *Anode material* | *Value of p* ($\Omega$ C$^{-1}$ cm$^{-2}$) | *Remarks and data reference* |
|---|---|---|---|
| Aqueous resin bath system | mild steel and copper coated (10 μm) mild steel | 102 | |
| | mild steel and copper coated (1 μm) mild steel | 43 | |
| rubber latex bath system | mild steel | 26 | Table 2 of [1] |
| | aluminium | 343 | the average value of ratio of $\frac{p_{\mathrm{Al}}}{p_{\mathrm{m.s.}}}$ values = 13·2 (compare case d of Table 1)<br>the $p_{\mathrm{Al}}$ value will be $26 \times 13{\cdot}2 \doteq 343$ |

*Table 5. Relation between p and bond strength of electrodeposits*

| *Anode metal* | *Bond strength* [7] (psi) *of electrodeposits* | *Value of p* $(\Omega\ C^{-1}\ cm^{-2})$ | *Remarks and data reference* |
|---|---|---|---|
| aluminium | 3770<br>2185<br>3235<br>2695<br>3135 | 343<br>(compare Table 4) | value from rubber latex system in which adherent electrodeposits are possible [8] |
| mild steel | 1715<br>3630<br>1760<br>1800 | 102<br>(compare Table 4) | value from resin system in which adherent electrodeposits are possible [9] |
| | 0 | 26<br>(compare Table 2 of [1]) | rubber deposits over mild steel are peelable |

be the cause of the difficulty in relating $p$ to the electrical conductivity of the anode material.

It is possible to relate $p$ to the bond strength values of the electrodeposits [7]. An analysis of the available results (Table 5) indicates that electrodeposits on aluminium are 40% more adherent than those on mild steel. Further for the same adhesion, the values of $p$ are lower by about 20% when aluminium is used as the anode material in place of mild steel.

## 3. Discussion of the results

A thin coating of copper over mild steel (thickness $\hat{=}$ 1 μm) influences the value of $p$ greatly; $p$ is reduced by a factor of 2·4 (compare Tables 4 and 5). Thicker coatings (10 μm), however, have no further effect on the value of $p$. The higher electrical conductivity of copper (as compared with mild steel) may cause a very high rate of charge neutralization and dehydration in the first layers. This would cause the first layer of the electrodeposits to have a high resistance and this may further delay deposition.

The above conclusion is supported by the general observation that the presence of an underlayer of copper on the mild steel improves the adhesion of the electrocoating to the substrate. As the thickness of the copper coat increases, the copper gets dispersed well into the surface of the mild steel. Since 5 μm copper coated mild steel gives the same rate [2] of fall of current as 10 μm and a 10 μm coating gives the same value of $p$ as mild steel (compare Tables 4 and 5), it is concluded that more data with respect to copper coating thickness in the range 1–5 μm will be of interest in relating the specific conductivity of the metal to $p$.

$p$ values of aluminium are about 13 times larger than those of mild steel for deposition from rubber latex (see Table 4). Since adherent electrodeposits of rubber are possible on aluminium, unlike on mild steel, a low value of $p$ may mean a porous deposit with less adhesion. The observed larger adhesion of rubber latex on aluminium may be due to the strong oxide layer on the aluminium surface.

When rubber latex and resin, deposited on mild steel are compared (Table 5) values of $p$ are higher with the resin system than with rubber latex; the higher values can be associated with the greater adhesion in the case of the resin system. Since it is possible to obtain larger values of $p$ with resin systems, a well-dispersed water-soluble resin in rubber latex may prove to be a suitable method to prepare adherent rubber deposits on mild steel.

The results in Table 2 indicate that the values of $p$ are dependent on the nature of the anode material, the current density (c.d.) employed in the experiments, the nature and the concentration of the resin chosen for the bath. The sodium hydroxide resin system is different in nature from the castor oil bath system. Dilution of the baths in both cases and deposition on mild steel gives ($p$/c.d.) values, which decrease in one case and increase in the second. In the case of the castor oil–maleic anhydride resin system, marked changes in the values of ($p \times$ c.d.) and ($p$/c.d.) are observed when brass is used as the anode material.

## 4. Conclusions

The study of the variation of $p$ versus current density during the electrodeposition of resin is a convenient and useful approach in investigations of electrophoresis. When applied to practical laboratory problems in the preparation of electrocoatings of industrial value. $p$ variations with current density can be used in the design [12] of electrical systems for large-scale resin deposition (bath sizes of the order of 1500 litres), using laboratory data of deposition from small volumes ($\simeq$ 500 ml).

## Appendix

The derivation of Equation 1 is as follows.

Current ($I$) at any time $t$ is given by

$$I = \frac{V}{R_b + R_f}$$

where $V$ is the applied voltage, $R_b$ the bath resistance and $R_f$ the resistance of the film. This is rewritten as

$$\left(\frac{1}{I}\right) = \left(\frac{R_b}{V}\right) + \left(\frac{R_f}{V}\right) \qquad (3)$$

and $$\left(\frac{R_b}{V}\right) = \left(\frac{1}{I_0}\right)$$

where $I_0$ is the current at time $t = 0$, that is the initial current. $R_b$ will not change during deposition as no bulk changes in bath concentration are involved during electrodeposition.

Defining $x = (I/I_0)$ and $R_f = pQ$ where $Q$ is the charge passed through the system during time $t$, from Equation 3

$$p = \left(\frac{V}{Q}\right)\left(\frac{1-x}{x}\right)\left(\frac{1}{I_0}\right). \qquad (4)$$

For short intervals of time of the order of 5–20 s (Table 1)

$$Q = \left(\frac{I_0 + I}{2}\right)t = \frac{I_0(1+x)}{2}t$$

or

$$\frac{1}{Q} = \frac{2}{I_0(1+x)t}. \qquad (5)$$

Substituting Equation 5 into Equation 4

$$p = \frac{2V}{(I_0)^2}\left(\frac{1-x}{1+x}\right)\left(\frac{1}{x}\right)\left(\frac{1}{t}\right)$$

which is Equation 1. Equation 1 is in a convenient form to evaluate $p$ at different values of $t$ when experimental data is available in the form of the fraction of the initial current ($x$) versus time $t$ and also when values of voltage $V$ and $I_0$ are available.

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