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ELECTRODEPOSITION PAINTING OF METAL SUBSTRATES: PINHOLING IN SU--ETC(U)
AUG 78 J A GAGLIARDI, D J WHELAN

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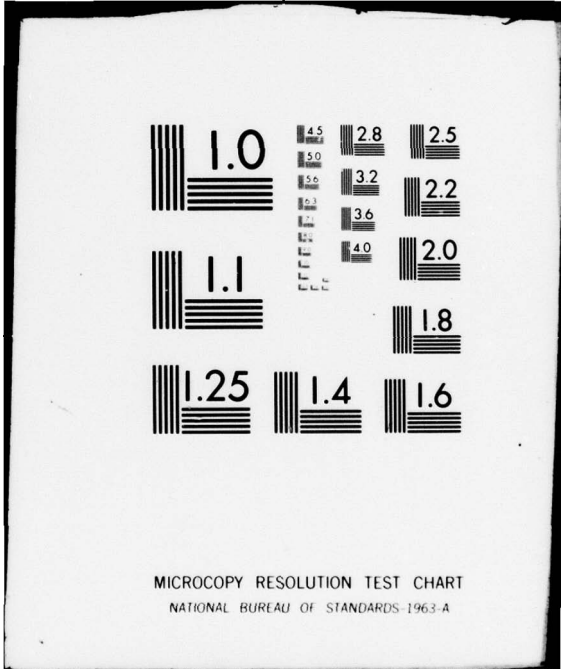
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ELECTRODEPOSITION PAINTING OF METAL SUBSTRATES:
PINHOLING IN SURFACE FILMS

John A. Gagliardi and Daniel J. Whelan

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PINHOLING IN SURFACE FILMS

10 John A./Gagliardi and Daniel J./Whelan

11 Aug 78
12 17p.

ABSTRACT

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DOCUMENT CONTROL DATA SHEET

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<p>1. DOCUMENT NUMBERS:</p> <p>a. AR Number: AR-001-353</p> <p>b. Series & Number: TECH.NOTE MRL-TN-415</p> <p>c. Report Number: MRL-TN-415</p>	<p>2. SECURITY CLASSIFICATION:</p> <p>a. Complete document: UNCLASSIFIED</p> <p>b. Title in isolation: UNCLASSIFIED</p> <p>c. Abstract in isolation: UNCLASSIFIED</p>
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3. TITLE:

ELECTRODEPOSITION PAINTING OF METAL SUBSTRATES: PINHOLING IN SURFACE FILMS

4. PERSONAL AUTHOR(S):
 GAGLIARDI, John A. and
 WHELAN, Daniel J.

5. DOCUMENT DATE:
 AUGUST, 1978

6. TYPE OF REPORT & PERIOD COVERED:

7. CORPORATE AUTHOR(S):
 Materials Research Laboratories

8. REFERENCE NUMBERS:
 a. Task: DST 77/004;
 DEF 99/015 (AIR)
 b. Sponsoring Agency:

9. COST CODE: 274740, 271580

10. IMPRINT (Publishing establishment)
 Materials Research Laboratories,
 P.O. Box 50, Ascot Vale, Vic.3032
 AUGUST, 1978

11. COMPUTER PROGRAMME(S):
 (Title(s) and language(s)):

12. RELEASE LIMITATIONS (of the document):

Approved for Public Release

12-0. OVERSEAS: N.O. P.R. 1 A B C D E

13. ANNOUNCEMENT LIMITATIONS (of the information on this page):

No Limitation

14. DESCRIPTORS:
 Electrodeposited coatings; Electrodeposition; Organic coatings;
 Pinholes; Defects; Electrophoretic coating.

15. COSATI CODES: 1103, 1308

16. ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):

In the electrodeposition painting of mild steel panels, defects are induced at higher electrodeposition voltages. Of these defects, pinholing appears to be the most serious and it occurs even after the surface has been coated at lower voltages with a thin, uniform coating. It probably originates from the conversion of electrical energy into heat energy which causes local boiling of occluded solvent in the film deposited on the work piece.

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ELECTRODEPOSITION PAINTING OF METAL SUBSTRATES:

PINHOLING IN SURFACE FILMS

1. INTRODUCTION

One of the most attractive features of electrodeposition painting of a metal substrate is that of good coverage over the whole surface. This leads to improved durability and corrosion resistance, over and above what is often achieved from similar types of paints applied by alternative coating techniques. The ability of an electrodeposition bath to extend paint films into recessed areas is called its 'throwing power' and is determined by the nature of the bath, the nature and geometry of the substrate and by variations in the coating technique [1]. Quantitative estimates of this parameter have been proposed, most of them relating to the relative thickness of the deposited film in exposed and recessed parts of the test piece [1].

In a previous communication from these laboratories [2], brief mention was made of the relative throwing power of various water-borne anionic electrodeposition paints. In general, it was found that :

- (i) initially, there was a rapid build up of paint on the metal substrate followed by a slower deposition reaction, and
- (ii) surface defects, in the form of pinholing and cratering, occurred in the films when the initial deposition was carried out at higher voltages. The physical phenomena contributing to these defects were described in the original report [2].

Using freshly prepared baths of an electrodeposition paint, Baycryn White 36/6, formulated at MRL, films with good hiding power, gloss, adhesion and scratch resistance were deposited on mild steel test panels. At a deposition voltage of 60 volt, applied for five minutes, a film thickness of 45-48 μm (ca 2 mil) was achieved over the whole panel (Ref. 2, Table 5 and Fig. 7), the surface area of the coated panel being 130 cm^2 .

Improved durability and corrosion protection are normally obtained with thicker coatings from a given formulation (Ref. 2, Section 3.6) and increased relative throwing power into recesses is obtained at higher voltages [2-4]. Accordingly, an extension to this original work was

suggested [5], namely, to carry out the electrodeposition painting of metal substrates in several stages, by increasing the voltage gradually as the thickness of the deposited film increased. Under these conditions, it was envisaged that, once the initial coating was deposited over the whole substrate and the rate of build up of paint thickness decreased, thicker films could be obtained by increasing the voltage without adversely affecting the film properties.

In this work, however, it was found that, while heavier films were deposited in this way, they were deposited unevenly and were badly pinholed.

2. EXPERIMENTAL

2.1 Electrodeposition Paint

The electrodeposition paint, Baycyl 36/6, used in this work was formulated as described in the earlier report [2]. The electrodeposition resin, Baycyl L461/W, was from a stock supplied by Bayer (Australia) Ltd.

(1) Ingredients

Baycyl L461W (55% in isobutanol)	160 g
NN-dimethylethanolamine	4.7 g
Rutile titanium dioxide (Tioxide RCR6)	36.0 g
Isodecanol	6 ml
Distilled water	250 ml

(2) Preparation

The resin, base and pigment were milled overnight with distilled water, 250 ml, and isodecanol, 6 ml. The paint was then thinned with distilled water, 750 ml. The pH of the mixture was adjusted to pH 8.1-8.2 by the addition of further amine as required.

The solids content of the bath was about 10.3 per cent and the pigment:binder ratio of the paint in the bath was 0.41:1.

2.2 Substrates

Rectangular panels, 15 cm × 6.7 cm × 0.1 cm, were cut from mild steel. All panels were sanded to present a bright surface and rubbed clean with a moist cloth to remove the fine dust of metal adhering to the surface, dried, degreased and desmuted by rubbing with mineral turpentine. This procedure conforms to Australian Standards AS 1580 (May 1975), 'Pretreatment of Metal Test Panels'.

2.3 Electrodeposition

The same procedure as adopted earlier was used in this work [2].

A stainless steel panel formed the cathode and the test panel formed the anode. The distance between the anode and the cathode was 5 cm. All electrodepositions were run under programmed voltage-increase conditions. After deposition, the panels were carefully washed with clean water to remove loosely adhering excess paint which resulted solely from contact of the panel with the bath.

The washed panels were air-dried overnight and then baked at 140-150°C for thirty minutes.

2.4 Physical Measurements

Film thickness was measured using the Fischer Permascope 'Non-Destructive Film Thickness Tester', Type ES and gloss (60°) was measured on a Gardiner PG-5500 Glossmeter.

3. RESULTS

Table 1 summarises the variation in the mass of film deposited on to the test panels from a freshly prepared bath of Baycryn White 36/6 at a deposition voltage of 60 volt. The surfaces all show a consistently high gloss and uniform film thickness, (Table 1), the smooth finish of which can be seen from a representative photomicrograph (Figure 1).

Earlier work [2] had shown that, at deposition voltages in excess of 70 volts, thicker films were produced under constant voltage deposition conditions but these films contained certain blemishes, the most serious being pinholing.

In electrodeposition, two causes are usually cited for pinholing :

- (i) rupture of the deposited film by oxygen liberated at the anode during the electrolytic reaction which accompanies the electrocoating process, and
- (ii) rupture of the deposited film by changes in the physical parameters of the surface which occur during the deposition process and the generation of heat from this process.

It was suggested [5] that the tendency towards pinholing may be aggravated when the initial electrodeposition reaction is carried out at higher voltages. In this situation, there is a high current density across the metal test piece and rapid generation of oxygen at the anode occurs. It was argued that once the initial surge of current diminished, the subsequent build up of paint film should proceed more slowly to deposit a smooth surface, free of pinholes and that thicker films could then be built up on the initial film by gradually increasing the applied voltage. This tacitly assumed that pinholing was caused primarily by gas evolution from the electrolysis reaction.

To test this hypothesis, an initial deposition was carried out at 60 volts (varying periods) and then the voltage was increased stepwise to a final voltage of 80 volt, the voltage sequence being as follows: 60 volt (1, 3 or 5 min), 65 volt (1 min), 70 volt (1 min), 75 volt (1 min), 80 volt (1 min). On completion the films were washed, dried overnight and stoved at 140-150°C, as described earlier.

Typical results are presented in Table 2 and in Figures 2 and 3.

In all cases, heavier films were deposited under these conditions on the mild steel panels, surface area 126 cm² (Table 2), but once the electro-deposition voltage exceeded 70 volt [2], excessive pinholing occurred (Figures 2 and 3). This pinholing was very similar to that produced in defective stoved finishes by boiling off trapped solvent.

The results described in Table 2 and illustrated in Figures 1-3 were typical of those obtained in this investigation and they confirmed the conclusions of the earlier report [2], that the most satisfactory coatings thrown on to small test panels were obtained from freshly prepared baths at 60 volts. At this voltage, the build up of paint occurs very quickly, the current decreases from 300 mA to less than 1 mA within forty five seconds and maximum evolution of oxygen occurs at the anode [2]. This is the period when film 'blow off' by electrolytic gas evolution would most likely occur but, in the small panels used in this study, it was never observed under these conditions.

As mentioned above, however, pinholing becomes a problem at higher voltages.

In electrodeposition, much heat is generated in the deposited film and, if this heat is not dissipated, the rise in film temperature may be sufficient to produce boiling of the liquid contained in the film [4]. At higher voltages, this conversion of electrical energy into heat is accentuated, particularly as film thickness increases. Hence, at least in the coating of small objects, the electrodeposition voltage needs to be kept below the voltage at which film rupture occurs, even after a substantial, insulating film thickness has been deposited slowly and uniformly over the whole surface.

The rupture voltage, like 'throwing power', will presumably be determined by the substrate under consideration, by the nature of the bath and by variations in the coating techniques.

4. APPLICATION

Optimum conditions for operating an electrodeposition bath do vary for different test pieces. Many commercial installations in the U.S.A. and in Europe operate at 200-250 volt quite successfully, depositing thin films, usually of the order of 25-50 micron (1-2 mil). The electrodeposition time necessary varies from substrate to substrate, typically being from one minute (for metal doors) [5] to five minutes (for automobile chassis) [6].

For much smaller workpieces much lower electrodeposition voltages will be necessary to achieve satisfactory surface coverage, because, in these cases, there is a more rapid build up of film and a faster rate of generation of heat within the film.

While heat generated within the film during deposition may, in certain instances, improve the flow of the film and assist the coalescence of the depositing film, it can also have adverse effects. If the build up of heat is too rapid and the heat cannot be dissipated readily from the workpiece, the temperature of the deposited film rises and solvent boiling can occur, causing pinholing or massive film rupture ('blow off').

Aspects of this problem have been analysed mathematically [4,6]. The results obtained confirm the practical result expressed in this paper for small workpieces, that an optimum deposition voltage exists where a homogeneous, uniform coating is deposited, this voltage varies from substrate to substrate and depends on the surface area of the workpiece and on the accessibility of the surface to the depositing medium.

Unpublished work from these laboratories on the coating of partly closed steel containers further supports these results; more uniform coatings on both the inside and outside surfaces are obtained when these containers are coated at 80 volts than are obtained at 60 volts, using Baycrl 36/6 but, above 85 volts, pinholing, non-uniform coverage and surface roughness occur. The internal and external surface areas of these containers are 95 cm² and 125 cm², respectively.

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T A B L E 1

CONSTANT VOLTAGE DEPOSITION

BAYCRYL WHITE 36/6

Deposition Voltage: 60 Volt

Substrate: Mild Steel Panels

Deposition Time (min)	Film Thickness (micron)	Mass deposited per unit area (g cm^{-2})	60° Gloss (%)
5	44-46	6.92×10^{-3}	61-64
3	39-40	6.23×10^{-3}	58-64
2	33-35	5.16×10^{-3}	62-66

- Conditions:
- (a) Freshly prepared bath, pH 8.1, 21-22°C
 - (b) Surface area covered: 126 cm²
 - (c) With Baycrl White 36/10, higher glosses were obtained, (up to 82%), but adhesion and scratch resistance were less satisfactory, (Ref. 2).

T A B L E 2

PROGRAMMED VOLTAGE DEPOSITION

BAYCRYL WHITE 36/6

Voltage Programme	Film Thickness (micron)	Mass deposited per unit area (g cm ⁻²)	60° Gloss (%)	Surface Description
(a)	39-40	6.23×10^{-3}	58-64	Satisfactory
(b)	58-62	8.94×10^{-3}	56-60	Slight pinholing
(c)	96-109	12.33×10^{-3}	47-63	Severe pinholing

NOTES:

(a) Deposition conditions: 60 volt/3 min

(b) 60 volt/3 min + 65 volt/1 min --- 75 volt/1 min

(c) 60 volt/3 min + 65 volt/1 min + -- 80 volt/1 min

(d) Mild steel panels. Surface area coated 126 cm²

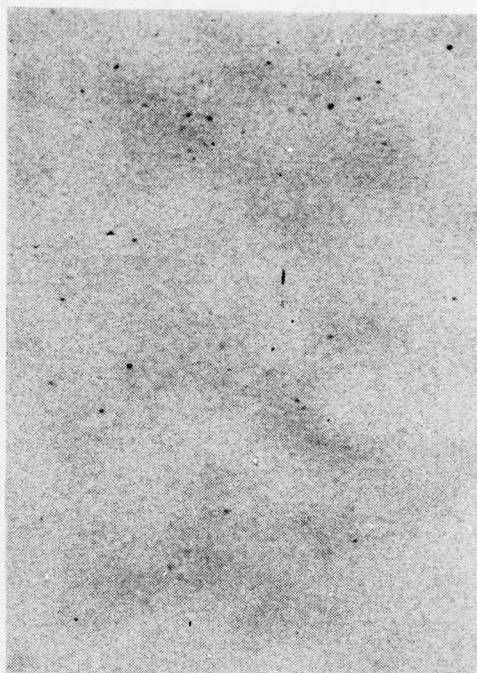


FIG. 1

Micrograph (x25) of Baycryn White 36/6 Coatings deposited on Steel Panels

FIG. 1 - Deposition voltage of 60 V applied for five minutes.
Film thickness 44-46 micron, Gloss (60°) 62 per cent.

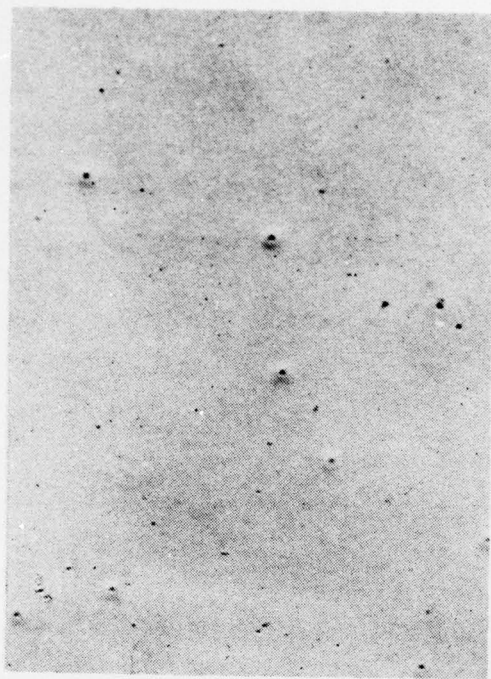


FIG. 2

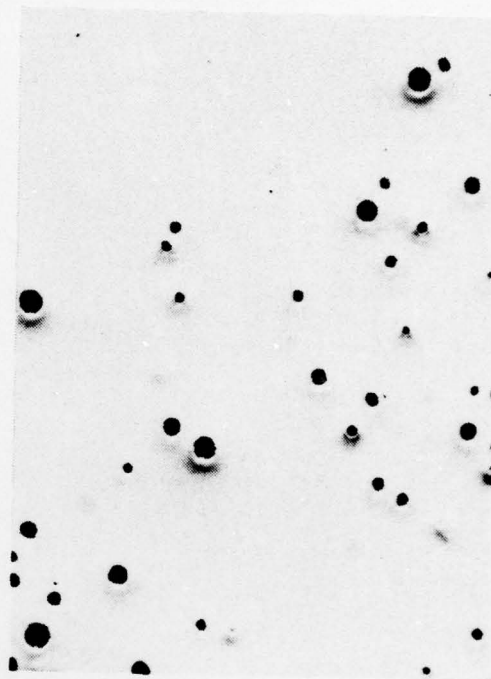


FIG. 3

Micrographs (x25) of Baycryn White 36/6 Coatings deposited on Steel Panels

FIG. 2 - Programmed deposition: 60 V for three minutes followed by stepwise increases in voltage to a final voltage of 75 V applied for one minute.

FIG. 3 - Programmed deposition as above, the final voltage being 80 V applied for one minute.

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