Cratering in Electrodeposition Coating of Cationic Paint on Galvannealed Steel Sheet*

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Synopsis
Cratering phenomenon in cathodic electrodeposition coating was investigated and the cratering mechanism was discussed. It occurs when part of the paint film undergoes a thermal change due to the spark discharge on the cathode. The thermal change generates nuclei that hinder the leveling of the deposited paint.

Graters tend to form on galvannealed steel sheet. Its Zn-Fe alloy coating layer has nonuniform electrical resistance and conductivity compared with other types of steel sheet. Therefore it is easily subjected to local current concentration which causes spark discharge when the electrodeposition voltage is high. Methods to suppress the spark discharge are also studied.

I. Introduction
Cathodic electrodeposition coating has been proved to possess a good corrosion resistance and throwing power, and has been widely used in the automobile industry.1-3 In cathodic coating, however, a film defect like pinholes or cissing (Photo. 1) sometimes occurs, which is not formed in anodic electrodeposition. This phenomenon is called cratering, a lot of small pits of 0.1 to 1 mm in size can be observed on the surface of the paint film. When many such craters are formed like pockmarks, the appearance of the painted surface is not beautiful. It is known that cratering is remarkable on a galvannealed steel sheet especially at high electrodeposition coating voltage.4-8

Craters not only impair the paint appearance, but also reduce the corrosion resistance of the coating. Therefore it is necessary to prevent their formation. As a first step, the cratering mechanism has to be clarified. Froman and Franks6-7 reported that hydrogen gas generated during electrodeposition coating caused voids formation in the deposited film, which are not filled up during the baking process. These unfilled voids become craters. This mechanism, however, cannot sufficiently explain why cratering easily occurs on a galvannealed steel sheet and why crater density varies depending on electrodeposition conditions.

To clarify the cratering mechanism in cationic electrodeposition coating, the authors investigated the following items: (1) electrodeposition current, (2) structure and properties of crater, and (3) paint deposition and curing process.

II. Experimental

1. Steel Sheet Specimens
Materials used were cold-rolled steel sheets (hereinafter called CR), galvannealed steel sheets (GA), galvanized steel sheets (GI) and zinc-rich primer coated steel sheets (ZM) for automotive use. Before electrodeposition coating, the test panels (0.8×70×150 mm) were phosphate-treated by a dip method or a spray method.

2. Cationic Electropaints
Two kinds of cationic electropaint were used; an epoxy-based resin and an epoxy-polyamide-based resin. Both are blocked isocyanate type. One was obtained from an automobile coating line tank and the other was prepared in the laboratory.

3. Electrodeposition Coating Method
The electrodeposition unit shown in Fig. 1 was used. The paint was stirred in the deposition vessel at a controlled temperature. One side of the test panel was cathodically electropainted in the vessel by applying a predetermined voltage. A SUS 304 stainless steel panel served as the anode. The area ratio of the anode to the cathode was set at 2/1. The standard anode-cathode distance was 15 cm. In some cases the electrodeposition coating was performed with the distances of 5 cm, 25 cm and 50 cm. A rectifier with a ripple percentage of 5 % or less was used for the DC power source. The applied voltage was varied from 160 to 320 V. By a coulombstatic method the coating thickness was controlled between 20 μm to 25 μm. Depending upon the applied voltage and the anode-cathode distance the electrodeposition time ranged from 2 to 5 min.

After electrocoating, the painted panel was washed
with tap water and deionized water (in both cases, sprayed at a pressure of 1.2 kgf/cm²). Then it was baked at 180 °C for 25 min.

4. Measurements and Analysis

Variation of electrodeposition current with time was measured and recorded with an electromagnetic oscillograph (Yokogawa Type 2915). The surface morphology of deposited paint film was observed under a scanning electron microscope (SEM). The softening and flowing behavior of the paint film during baking process were observed under an optical microscope by heating the deposited paint on a hot plate.

Chemical analysis of baked film was conducted using a grating type infrared spectrophotometer (IR, JASCO IRA-2) and a gel permeation chromatograph (GPC, water: ALC/GPC 244, column: Shodex A803).

Two parts of the film, cratered and non-cratered parts, were analyzed and their compositional differences were discussed.

In general, electropaint is dispersed in water which contains some organic solvent. The organic solvent evaporates gradually by aging. Its concentration in water was measured using a gas chromatograph (Hitachi 063).

The electrical resistance of the tested sheet surface was measured by the DC four-terminal method. SEM absorbed electron beam images of the surface were also observed, which gave an estimation of the uniformity of the surface conductivity.

III. Results

1. Conditions for Crater Formation

1. Influences of Electrodeposition Coating Conditions (Applied Voltage, Anode-Cathode Distance and Bath Temperature)

A cationic paint obtained from an automobile coating line was electrodeposited on GA under various voltages and anode-cathode distances at a constant bath temperature. And the cratering density on the surface was measured. As shown in Fig. 2, a high voltage and a short anode-cathode distance brought about a high crater density. The bath conductivity ranges from 1200 to 1400 µS/cm. This low conductivity results in a relatively high IR drop. Therefore the anode-cathode distance can be considered to affect the crater density in the same way as the applied voltage.

Electrodeposition coating was also carried out on GA under various voltages and bath temperatures with a constant anode-cathode distance. As shown in Fig. 3, the voltage for crater formation decreased with increasing bath temperature. This can be explained by the dependence of bath conductivity on temperature, shown in Fig. 4.

Summarizing the results, the following methods are effective in depressing cratering in electrodeposition coating.

i) Lowering the applied voltage
ii) Increasing the anode-cathode distance
iii) Lowering the bath temperature

In this experiment as the standard operation conditions, the anode-cathode distance of 15 cm and the bath temperature of 28 °C were chosen.

Fig. 1. Electrodeposition coating unit.

Fig. 2. Relationship between the anode-cathode distance and the crater density. (Zinc phosphated GA, Epoxy paint, Bath temp.: 28 °C)

Fig. 3. Relationship between bath temperature and crater density. (Zinc phosphated GA, Epoxy paint, Anode-cathode distance: 15 cm)
2. Dependence of Crater Density on Steel Sheet and Paint

Figure 5 shows the relationship between the voltage at which cratering begins and the crater density. Crater density varies depending on the kind of steel sheet. On the contrary the epoxy-based paint and the epoxy-polyamide-based paint have almost the same tendency for cratering.

Craters were not formed on any type of steel sheet at low applied voltages. As the voltage was increased, cratering occurred first on GA (at 220 V), then on ZM (at 250 V), and further on GI (at 280 V). On CR, craters were observed only when voltages higher than 300 V were applied.

3. Influence of Zinc Phosphate Treatment

Both zinc phosphated and non-phosphated GA were electrodeposition coated, and the crater density was counted. Spray method and dip method were used for zinc phosphate treatment. Results are given in Fig. 6. The three specimens in Fig. 6 have almost the same crater density. It means that the phosphate coating scarcely affected cratering. Therefore, the cratering tendency of GA can be attributed to the nature of the steel sheet itself.

4. Effect of Paint Aging (Behavior of Organic Solvents)

Various organic solvents are added to a cationic electropaint to adjust the dispersibility and film leveling property of resin.3 Table 1 gives an example of the solvent composition of a paint used in an automobile coating process. As can be seen in Table 1, monoethers of ethylene glycol (cellosolves), carbitols and ketones are the main solvents. MIBK is added to adjust viscosity during resin synthesis and paint preparation. After the paint bath has been prepared it is vaporized gradually. The effect of solvent content in the paint on cratering was investigated.

A cationic electropaint was prepared from the original paint liquor in the laboratory. Then it was subjected to aging in an open vessel at room temperature. During the aging, GA was electro-coated at given intervals and the variation of solvent content was measured with a gas chromatograph. Figures 7 and 8 show the results.

The coating thickness and the cratering behavior varied with the aging time. Just after the bath preparation the paint film was deposited up to the thicknesses greater than the designed value (25 μm) without forming craters. As aging proceeded craters began to appear. The paint thickness decreased and after 20~25 h it reached the designed value of 25 μm. It was found that, as shown in Fig. 8, MIBK decreased gradually with aging and could be scarcely detected after 24 h. There was no substantial change in the amounts of butyl cellosolve, ethyl cellosolve and carbitol. At the time when MIBK evaporated out, the coating thickness reached the predetermined value and cratering began to occur. Thus it is likely that the MIBK is mainly attributable to cratering.

2. Microstructure of Graters

Craters have an appearance similar to that of coating defects such as pinholes and cissings. In order to study the microstructure the inside of craters was observed with SEM. A foreign substance shown in Photo. 2 was found at the bottom of every hole. It should be a nucleus for cratering. The nuclei to appear. The paint thickness decreased and after 20~25 h it reached the designed value of 25 μm. It was found that, as shown in Fig. 8, MIBK decreased gradually with aging and could be scarcely detected after 24 h. There was no substantial change in the amounts of butyl cellosolve, ethyl cellosolve and carbitol. At the time when MIBK evaporated out, the coating thickness reached the predetermined value and cratering began to occur. Thus it is likely that the MIBK is mainly attributable to cratering.
were found regardless of the types of steel sheet and paint. Although the size was different from one nucleus to another, there was a correspondence between the crater size and the nucleus size.

These nuclei could be more clearly seen on the surface of a deposited paint film before baking. Photograph 3 shows an example of crater formed on GA. Round nuclei can be observed in the paint. In Photo. 4 nuclei formed on ZM are shown. At the crater the paint film has concave surface and zinc coating layer is exposed. The diameter of a nucleus varies from 1 to 10 μm.

It can be concluded that the structure of craters is different from that of pinholes and cissing, which are attributable to the paint wettability.

3. Electrodeposition Current and Deposition Process

In electrodeposition that resulted in cratering, a sound was generated and spark discharge could be observed on the cathode surface. The sound was similar to that generated when a hot object is thrown into water. It can be heard 1 to 2 sec after the start of electrolysis and continued for several seconds. The spark discharge could be observed by the naked eye near the liquid surface of the paint. It could be more clearly seen on various parts of the steel sheet when a pigment-free clear paint (opalescent) was used.

Current–time relationships at the early stage of electrodeposition were measured with an electromagnetic oscillograph. The result for GA is given...
in Fig. 9(1). The current began to oscillate about 1 sec after the start of electrolysis. The starting time of oscillation coincided with that of spark discharge. A similar current oscillation occurred also on ZM that is also susceptible to cratering (Fig. 9(2)). For CR and GI, which have small cratering tendency, the current oscillation was scarcely observed, as is shown in Fig. 10.

The deposited paint on GA and CR was investigated with SEM. As shown in Photo. 5, at the early stage the cationic paint was deposited in the form of fine meshes. In the paint film on GA, large circular deposits appeared after 2 sec, which corresponded to the starting time of current oscillation. Then they increased in number and grew in size gradually. In the paint on CR, however, such circular deposits were not present and the mesh structure grew with time. When the painted GA was taken from the bath carefully and observed with SEM, a lot of foams were found, as shown in Photo. 6. These foams had the same size as the circular deposits. Therefore it was concluded that the circular deposits in Photo. 5 were depressed foams, which had been formed by H₂ gas generated on the cathode. Each of them contained some nuclei.

4. Properties of Nucleus

From these experimental results it was presumed that nuclei were formed by a local thermal reaction.
of the paint due to the spark discharge. In order to prove it the difference in properties between the nuclei and the normally deposited paint was studied.

As is apparent from Table 2, the solubility of the nuclei in solvent is different from that of the normally deposited paint. All the solvents easily dissolved the normally deposited paint. However, except for tetrahydrofuran they could not easily dissolve the nuclei.

Photograph 7 shows the surface of GA where the paint film was removed by dissolving with DMF. Nuclei remain in the almost original form on the substrate.

1. Infrared Spectrographic Analysis (IR)

The nuclei were separated from the paint with the methods shown in Fig. 11 and were analyzed using IR and GPC. Figure 12 shows IR spectra of the nucleus on GA. The nucleus has an absorption band at the wave number of 1388 cm⁻¹ which appears neither in the IR spectra of the original paint liquor nor in that of the normally deposited paint. It has a strong band for aliphatic CH₂ and CH₃ stretches (2960, 2920 and 2848 cm⁻¹).

2. Gel Permeation Chromatography (GPC)

According to GPC measurements, the nucleus has a larger molecular weight than the normally deposited film. In Fig. 13 the hatched portion corresponds to the increase in molecular weight. The peak near THF-25 ml indicates the increase for epoxy resin. The increase was estimated to be approximately 3000 using a calibration curve for DGBEA (Diglycidil Ether of Bisphenol A) type epoxy resin. While the

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Normally deposited paint film</th>
<th>Nuclei</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>30 s</td>
<td>2 min</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>Δ</td>
<td>Δ</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Δ</td>
<td>Δ</td>
</tr>
</tbody>
</table>

O: Soluble   Δ: Little soluble   ×: Insoluble

Table 2. Solubility in solvent of deposited paint film and nuclei. (Immersion time: 30 s and 2 min)

Fig. 11. Methods for analyzing nuclei.

Fig. 12. Infrared ray absorbing spectra of the nucleus on GA.

Fig. 13. Results of GPC measurement.
molecular weight of normal paint was calculated to be about 900.

5. Behavior of the Paint during Baking

The softening and flowing process during baking was observed for the paint deposited on GA and CR. As the temperature reached 60 °C the paint began to soften and flow, which indicated that the leveling was started. On GA the leveling near the nuclei did not proceed smoothly. Although small nuclei were covered gradually with the paint, large ones remained uncovered until the curing reaction was completed. They repelled the flow of surrounding paint. As the result, craters were formed. Photograph 8 shows the change in the surface of the paint film on GA during baking. On the other hand on CR, the leveling was completed in a short time and cratering did not occur.

It was also found that H₂ gas contained in the film escaped out when the paint film was fused and did not cause crater.

6. Electrical Resistance

The electrical resistance of the surface of GA, GI, CR and ZM was measured by the DC four-terminal method. Results are given in Table 3. ZM which has an organic film showed the highest resistance. The resistance decreased in the order of GA, CR and GI.

Photograph 9 shows absorbed electron beam images of the surfaces of GA, CR and GI. GA has many white areas where the absorbed electron beam is strong. This corresponds to nonuniform electrical characteristics. GI and CR did not show the nonuniform absorption. GA has a Zn–Fe alloy coating layer, according to X-ray diffraction analysis shown in Fig. 14. The Zn–Fe layer consists of δ₁, γ and η phases. These Zn–Fe alloy phases were prepared by electroplating and their electrical resistances were measured by the same method. A columnar electrode with a diameter of 3 mm was used for measurement. The following values were obtained under the electrode force of 10 kg, δ₁ layer: 0.43 mΩ, γ layer: 0.53 mΩ, η layer: 0.08 mΩ. It seems that the nonuniform composition of the Zn–Fe layer leads to the nonuniform surface conductivity.

<table>
<thead>
<tr>
<th>Type of steel sheet</th>
<th>GI</th>
<th>CR</th>
<th>GA</th>
<th>ZM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode force</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(dia. 3 mm)</td>
<td></td>
<td></td>
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<tr>
<td>10 kg</td>
<td>0.033</td>
<td>0.224</td>
<td>0.434</td>
<td>7.18</td>
</tr>
<tr>
<td>20 kg</td>
<td>0.024</td>
<td>0.077</td>
<td>0.200</td>
<td>4.72</td>
</tr>
</tbody>
</table>

* a columnar electrode

(a) As deposited
(b) Being leveled
(c) Cured

Photo. 8.
Microscopy of paint flow and leveling.

CR
GI
GA

500 μm

Photo. 9.
Absorbed electron beam images of steel sheet surfaces.

Table 3. Electrical resistance of steel surface. (mΩ)

Fig. 14. Mechanism of cratering.
IV. Discussion

1. Cratering Process

From the experimental results, the cratering process in the cathodic electrodeposition coating is summarized as follows:

(1) Just after the start of electrolysis, \( \text{H}_2 \) gas generation and paint deposition begin, and the steel sheet cathode is covered with porous paint film and gas layer. If electrodeposition is performed at a high voltage, spark discharge occurs locally on the steel surface.

(2) The spark discharge brings about a thermal reaction of the deposited paint near the discharge point. A part of the paint changes into the nuclei which have different natures from normally deposited film.

(3) These nuclei do not easily fuse into the paint film in the flow process during baking. Large nuclei prevent the inflow of the paint and cause the crater formation. Figure 15 shows this process schematically.

2. Mechanism of Spark Discharge

The spark discharge that occurs across two electrodes in an aqueous solution is utilized as a surface hardening in industry. The mechanism of spark discharge in the electrodeposition coating process can be considered to be the same as that of electrolytic heating in an aqueous solution.

The spark discharge takes place in the gas layer formed on the cathode, and is essentially a gaseous discharge. The gaseous discharge is known to obey Paschen's law. According to it the sparking voltage, \( V_s \), is a function of a product of the gas pressure, \( p \), and the gap length, \( d \), as

\[ V_s = f(pd) \]

Figure 16 gives the relation between \( V_s \) and \( pd \) (Paschen's curves) for various gases in a uniform electric field of parallel-plate electrodes. If the voltage exceeds \( V_s \), a breakage occurs.

In the cathodic electrodeposition coating, the gas layer consists of a mixture of generated \( \text{H}_2 \), steam and solvent vapors. As the first approximation, however, the pattern of Paschen's curve is considered to be the same as the curves for single gas shown in Fig. 16. When gas generation starts, \( pd \) increases as gas bubbles grow in size and \( V_s \) changes accordingly.

In the electrodeposition coating process the voltage applied to the paint film, \( V_d \), is thought to increase gradually with time. This is explained as follows. Until the start of the paint deposition the electrical resistance of the system is determined mainly by that of the paint liquid. However, as the paint film containing gas has a far higher electrical resistance than the paint liquid, the current decreases in the electrodeposition process. This is supported by the current-time curves shown in Figs. 9 and 10. The potential distribution changes for the same reason. \( V_d \) increases as the film grows.

When \( V_d \) becomes larger than the sparking voltage, \( V_s \), the spark discharge begins and breaks the deposited paint. The time of approximately 1 sec before the current oscillation mentioned before must be the time required for \( V_d > V_s \).

According to Fig. 5, GA gives the highest crater density among materials tested. The spark discharge takes place most easily on it. As is shown in Photo. 9, different from other materials it has a non-uniform electrical characteristics and has a lot of small areas with good conductivity. Therefore, when cathodic electrodeposition is performed, current concentration takes place in these areas and spark discharge tends to occur.

3. Measures to Prevent Cratering

Cratering can be prevented by suppressing the spark discharge during electrodeposition. For this purpose, the following measures are effective.

i) To prevent the local current concentration by making the surface conductivity uniform. For GA, the alloy layer can be made uniform by controlling the galvanizing and annealing process. It is also effective to let \( \gamma \) phase of good conductivity to distribute uniformly on the top layer of coating, or to cover the surface with a uniform coating of Fe, Zn, etc.

ii) To release the generated \( \text{H}_2 \) gas from the cathode surface easily. This can be done by adjusting the surface tension of paint, strengthening the stirring in the vessel and vibrating the steel sheet to be coated.
iii) To reduce the applied voltage as mentioned in III. 1.

iv) To prepare a cationic electropaint that ensures a low electrical resistance of the deposited paint film. An electropaint containing large amounts of low boiling point solvents does not cause cratering. This is because the resistance of the deposited paint film is low. A paint designed to produce a thick deposited film of low resistance would be very effective in preventing cratering.

V. Conclusions

The cratering in cathodic electrodeposition coating was investigated and the following results were obtained:

1) Cratering occurs when part of the paint undergoes a thermal change due to the spark discharge on the cathode. Nuclei are generated which hinder the leveling of the deposited paint film.

2) Cratering tends to occur on GA and ZM, and not on GI and CR. The nonuniform surface conductivity of GA causes high crater density.

3) The following measures can be taken to suppress the spark discharge during electrodeposition:

   1) Making the surface conductivity of the steel sheet uniform.

   2) Preparation of a cationic electropaint that results in the deposited paint film of low electrical resistance.

   3) Reduction of the applied voltage.

   4) Allowing generated H₂ gas to leave the cathode surface easily.

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