Corrosion Performance of Zn Alloy Precoated Steels for Automotive Body*

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Synopsis

The corrosion performance of one-side precoated steels for automotive body was investigated and new precoated steel suitable for exterior panel use was evaluated by several kinds of corrosion testing. Ni-Zn alloy electroplated steel may be more effective for insufficiently painted portion. Application of Fe-Zn alloy plated steel may provide effective corrosion resistance of portions where paint film may sufficiently applied. Electroplating Fe-rich Fe-Zn alloy as outer layer provides superior paint adhesion. Finally summary of our philosophy in terms of corrosion performance of precoated steel is depicted.

I. Introduction

Recently intense interest has been shown towards methods for protecting automotive body panels from corrosion with the increasing demands for safe automobile and for saving of resource as well. Corrosion types of automotive body panels can be classified into three forms as shown in Table 1.

- 1) Perforation of closed sections, where finishing processes such as degreasing, phosphating and painting can not be applied sufficiently and salts and mud easily accumulate as well,
- 2) Contact corrosion of hemmed portions, and
- 3) Cosmetic corrosion on exterior body surface caused by collision with sands, stones and rocks on roads.

Corrosion protection of automobile body has been investigated by steel sheet producers, paint manufacturers and chemical conversion producers, and automotive manufacturers through the following approaches:

- 1) Application of precoated steel,
- 2) Improvement of chemical treatment processes and electropaint systems, and

- 3) Improvement in body design.

At present, many kinds of precoated steels, as following, have been proposed for increasing corrosion resistance of automotive body:

- 1) electrogalvanized steel,
- 2) γ -phase Ni-Zn alloy electroplated steel,
- 3) galvanealed steel, and
- 4) Zn-rich primer coated steel (Zincrometal).

Use of precoated steels varied with car manufacturers in accordance with their philosophy on corrosion protection. Car manufacturers require steel sheet producer to develop new precoated steel with thin layer coating of superior corrosion resistance which have also good paintability, formability and weldability. In addition, application of two-side precoated steel sheets suitable for exterior panel use has been investigated. In present study, the corrosion behavior of one-side precoated steel are investigated as described above, and in addition a tentative proposal on new precoated steel sheets suitable for exterior panel use is advanced.

II. Corrosion Resistance of Precoated Steels without Paint Film

Inside-out perforation occasionally occurs in portions which is inaccessible to chemical treatment and painting. In this case, corrosion protection against perforation may depend on corrosion rate of precoated layer. At first, corrosion resistance of as-received precoated steels was evaluated by several methods.

Figure 1 shows the results of corrosion weight loss at the early stage of salt spray test of 5 % NaCl solution, which is a common method to evaluate corro-

Table 1. Corrosion forms of automotive body.

Form of corrosion	1. Perforation of panel	2. Corrosion of hemmed portion	3. Cosmetic corrosion on body surface
Portion	Inside of door and rocker panel	Hemmed portion of hood and door	Visible parts of fender and door
Cause	1. Insufficient chemical treatment and painting 2. Accumulation of corrosive substrate	1. Impracticable painting 2. Galvanic corrosion 3. Crevice corrosion	1. Damage by small stones and sands 2. Defects of paint film
Actions	1. Improvement of chemical treatment process and electropaint system 2. Application of precoated steel 3. Body design change	1. Thorough sealing 2. Application of procoated steel	1. Improvement of paint system (anti-chipping paint) 2. Application of precoated steel

* Received March 18, 1983. © 1983 ISIJ

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CR: Cold rolled steel
GA: Galvannealed steel (45 g/m²)
EG: Electrogalvanized steel (40 g/m²)
AEG: Fe-Zn alloy electroplated steel (20 g/m²)
SZ: Ni-Zn alloy electroplated steel (20 g/m²)

Fig. 1. Corrosion weight loss of as-received specimens in salt spray test.

sion resistance. Weight loss of cold rolled steel and electrogalvanized steel gradually increased with exposure time. Corrosion rate of Ni-Zn alloy and Fe-Zn alloy decreased as corrosion proceeded. Ni-Zn alloy electroplated steel revealed much lower corrosion rate.

In Fig. 2, the results of corrosion depth which are evaluated by Dry & Wet cycle test are shown. This cycle test consists of immersion in 5 % NaCl solution at 35 °C and drying by 50 °C hot air. 1 cycle consists of 1 h wet and 1 h dry periods. Corrosion depth of cold rolled steel increased linearly.

Corrosion rates of precoated steels varied with coating weight and alloy component of plated layer. Perforating corrosion occurred once coated layer dissolved and corroded away from the substrate. Therefore corrosion rates were nearly the same for all materials after occurrence of perforating corrosion. Ni-Zn alloy electroplated steel shows good property of corrosion protection in spite of light coating weight. Corrosion depth after 10 cycles of corrosion cycle test-1, which consists of combination of salt spray, drying and salt immersion, is shown in Fig. 3. The linear relationship between corrosion depth and coating weight can be seen for all materials. Ni-Zn alloy electroplated steel showed a gradual slope. Corrosion behavior of as-received materials varied with the evaluation method. It is necessary to develop an acceleration method which simulates the actual environments of automobile corrosion. In these methods as described above, Ni-Zn alloy electroplated steel showed the highest corrosion resistance. The difference of corrosion resistance at early stage may be caused by the protective effect of corrosion products on the surface and the surface enrichment of alloying elements such as Ni and Fe.^{1,2)}

III. Corrosion Resistance after Painting

1. In the Case of Specimens Insufficiently Electropainted

For the evaluation of inside corrosion in door, side-sill and others that is not electropainted sufficiently,

CR: Cold rolled steel
EG: Electrogalvanized steel (40 g/m²)
GA: Galvannealed steel (45 g/m²)
SZ: Ni-Zn alloy electroplated steel (20 g/m²)

Fig. 2. Corrosion depth of as-received precoated steels in Dry & Wet cycle test.

AEG: Fe-Zn alloy electroplated steel
SZFO: Ni-Zn alloy/Fe-Zn alloy double layer electroplated steel.

Fig. 3. Relation between corrosion depth and coating weight of as-received specimens. (after 10 cycles of corrosion cycle test-1).

specimens cathodically electropainted with about 5 μ m film in thickness were provided after immersion phosphating.

(Electropaint: Power Top U-30 from Nippon Paint Co.)

(Phosphate chemicals: Granodine #SD2000 from Nippon Paint Co.)

Perforation may occur when blistering occurs and advances. Figure 4 shows the relation between ratio of blistered area and corrosion depth after 75 cycles of corrosion cycle test-2 which consists of the following test condition:

After 60 cycles blistering of cold rolled steel appeared on the whole surface and then perforation was observed after 75 cycles. Zincrometal (ZM) showed few blister and no corrosion depth even after 75 cycles. Occurrence of blister on Ni-Zn alloy electroplated steel was a little similar to ZM, but pitting type corro-

(): Coating weight (g/m²)
ZM: Zn-rich primer coated steel (Zincrometal)

Fig. 4. Corrosion behavior of cathodically electropainted specimens with thin paint film.

sion was observed. Fe-Zn alloy plated steel showed fast occurrence of blister and deeper corrosion depth. Corrosion depth of galvanized steel (60 g/m²) was equal to that of Ni-Zn alloy plated steel (20 g/m²).

2. In the Case of Specimens Sufficiently Electropainted

Specimens were first subjected to zinc phosphate treatment using an immersion technique and cathodically electropainted with about 20 μ m film in thickness. The evaluation of the blistering width at cross cut scribes was carried out by salt spray test. The results are shown in Fig. 5. Galvanized steel and electrogalvanized steel subjected to heat treatment (EGA) after plating showed wider creepage width than other materials. Blister width of Fe-Zn alloy electroplated steel and Ni-Zn alloy electroplated steel was comparable to that of cold rolled steel. ZM revealed the best corrosion performance among all specimens.

Furthermore in Fig. 6, relation between the maximum corrosion depth and the blistering width at cross cut scribes after 100 days exposure of Dry & Wet cycle test is shown. For ZM, the creepage from scribe was slightly wider than that of cold rolled steel, and the corrosion depth was about half as much as cold rolled steel. Electrogalvanized steel showed the same depth as ZM, and the creepage was remarkably wider. Concerning with Ni-Zn alloy electroplated steel and galvanized steel, the width of blistering from scribe line was the same as that of cold rolled steel. This blister width of galvanized steel was much narrower than that in Fig. 5.

Moreover the resistance against corrosion of specimens which had been electropainted, seal-coated and top-coated was evaluated to investigate corrosion under exterior paint film. As may be seen in Fig. 7, both corrosion depth and creepage width after 100 days Dry & Wet cycle test decreased and the difference of corrosion depth between ZM and other pre-coated steels increased in comparison with results obtained from corrosion testing with cathodically electropainted specimens shown in Fig. 6. Evaluation of

EGA: Electrogalvanized steel followed by thermal diffusion

Fig. 5. Corrosion behavior at scribed line on cathodic electropaint film after 60 days salt spray test.

Fig. 6. Corrosion behavior at scribed line on cathodic electropaint film after 100 day Dry & Wet cycle test.

Fig. 7. Corrosion behavior at scribed line on 3-coat paint film after 100 day Dry & Wet cycle test.

G90: Hot-dip galvanized steel (135 g/m²)

Fig. 8. Corrosion depth at scribed line on cathodic electropaint film after 60 cycles of corrosion cycle test-1.

corrosion depth of specimens which were cathodically electropainted up to about 20 μ m thickness were also employed by corrosion cycle test-1.

Corrosion depth at scribed line of paint film after 60 cycles is shown in Fig. 8. Perforation occurred on ZM as well as on cold rolled steel. Galvanized steel showed excellent corrosion performance when

sufficiently painted. However galvanized steel is thought to be limited to formability because of manufacturing process. Therefore Fe-Zn alloy layer which has both good corrosion performance as galvanized in spite of lighter coating weight and good formability similar to cold rolled steel has been investigated. A new precoated steel with Fe-Zn alloy layer produced by electroplating which would not alter the mechanical property of cold rolled steel as substrate has been developed.³⁾ Fe content in Fe-Zn alloy is about 20 % which is larger than that of galvanized steel. The content was determined by electrochemical measurement. Corrosion performance in as-received and insufficiently electropainted state was mentioned previously.

Figure 9 shows the result of corrosion resistance at scribed line after cathodic electropainting. After 60 cycles of corrosion cycle test-1, complete perforation was observed in cold rolled steel specimens. On the contrary Fe-Zn alloy electroplated steel with coating weight of about 20 g/m² showed the same corrosion resistance as that of galvanized steel (45 g/m²). In addition, Fe-Zn alloy electroplated steel showed narrower paint film creepage than galvanized steel.

Ni-Zn alloy electroplated steel insufficiently painted, as well as in case of as-received, showed better corrosion resistance than other precoated metals. When specimens were sufficiently electropainted better corrosion resistance was observed in Fe-Zn alloy plated steel.

3. Contact Corrosion

As automotive body was an assembly of several kinds of precoated steel, some precoated steel sheets were jointed to cold rolled steel by spot welding, then they were cathodically electropainted after immersion phosphating and the corrosion behavior of the specimens cut over the paint film was evaluated.

Figure 10 shows the results of 100 day Dry & Wet cycle test. Adhesion failure of paint film on cold rolled steel side connected to galvanized steel and electrogalvanized steel occurred widely. Width of this adhesion failure was narrower for specimens connected to Ni-Zn alloy plated steel.

These results were consistent with results obtained through the measurements of galvanic currents between a precoated steel and cold rolled steel in 5 %

NaCl solution as shown in Fig. 11. Precoated steel was phosphated only, whereas cold rolled steel was cathodically electropainted after phosphating. Paint film thickness was adjusted to vary step-wise as in illustrated in Table 2. Galvanic current which flows in direction to dissolve precoated steel gradually in-

Fig. 10. Contact corrosion behavior after 100 day Dry & Wet cycle test.

Fig. 11. Changes of galvanic current.

Table 2. Paint failure occurred by galvanic corrosion.

	CR	Precoated Steel
CR-ZM		
CR-SZ		
CR-GA		
CR-EG

Corrosion depth: 60 cycles of corrosion cycle test-1
Creepage width: 47 days of salt spray test

Fig. 9. Relation between corrosion depth and creepage width.

creased with exposure time. Rating of materials can be described as follows:

electrogalvanized steel > galvanized steel
> Ni-Zn alloy electroplated steel > ZM

It seems that Zn powder in coating film only serve to improve the weldability and does not sacrificially protect cold rolled steel.⁴⁾ Galvanic corrosion behavior of Ni-Zn alloy plated steel was similar to that of ZM. This corrosion resistance of Ni-Zn layer is caused by Ni enrichment in corrosion products as corrosion proceeds.¹⁾ Electrogalvanized steel showed the highest galvanic current which could reasonably explained by the high sacrificial protectivity of Zn layer. Adhesion failure of paint film on cold rolled steel side as shown in Table 2 agreed with the results in Fig. 10.

4. Paint Adhesion

Paint adhesion initial occurs at the initial stage of underfilm corrosion, and thus better paint adhesion eventually provides better corrosion resistance. Especially, it is an important property of precoated steel for exterior body panel to assure good appearance. Difference of paint adhesion among precoated steels, however, could not be observed, when phosphated specimens were only cathodically electropainted with about 20 μm thickness. Paint adhesion can be evaluated usually utilizing specimens which are electropainted, seal-coated and top-coated with total film thickness of about 90 μm. Specimens were scribed as

checker of 2 mm width (11×11 lines) and the adhesive tape was applied and removed under the following conditions:

- 1) As painted
- 2) After immersion in warm de-ionized water (40 °C or 50 °C) for 240 h.

General tendency of paint adhesion is shown in Table 3, though there is difference between specimens from different painting conditions and from different lots. No peeling of paint was found for all types of steels for test 1). Precoated steels except for ZM, did not show sufficient paint adhesion for test 2). It is assumed that phosphophyllite which was apt to precipitate on cold rolled steel by zinc phosphating was influenced the paint adhesion. This assumption is supported by the measurements of paint adhesion and P-ratio as shown in Fig. 12. P-ratio of hopeite $Zn_3(PO_4)_2 \cdot 4H_2O$ and phosphophyllite $Zn_2Fe(PO_4)_2 \cdot$

Table 3. Results of paint adhesion.

Substrate	Peeled area of paint film (%)	
	Test 1)	Test 2)
Cold rolled steel	0	0
Electrogalvanized steel	0	76
Galvanized steel	0	100
Ni-Zn alloy electroplated steel	0	44
ZM	0	0

(a): P-ratio
(b): the paint adhesion after immersion in de-ionized water at 50 °C for 240 hr

Fig. 12. Influence of Fe content of Fe-Zn alloy on (a) P-ratio and (b) the paint adhesion after immersion in de-ionized water at 50 °C for 240 hr.

AEGF: Zn-Fe alloy/Fe-Zn alloy double layer electroplated steel
Photo. 1. SEM micrographs of zinc phosphate crystal on precoated steels.

Table 4. Summary of our philosophy in terms of corrosion performance of precoated steel.

	1. Perforation of panel	2. Corrosion of hemmed portion	3. Cosmetic corrosion on body surface
Required characteristics	1. Protection of substrate without painting 2. Anti-corrosion of thin film painting 3. Throwing power of cathodic electropaint	1. Small potential difference between steel and precoated layer 2. Sacrificial protection 3. High insulation	1. Corrosion resistance at damaged paint film (red rust, blister) 2. Paint adhesion 3. Paintability (cratering, gloss)
Methods suggested	1. Less noble metal than steel and plating layer of heavy coating weight 2. Less noble alloy than steel and light plating layer of superior corrosion resistance 3. Coating with polymer 4. Multi-layer of plating with light coating weight and coating with polymer	1. Less noble metal than steel 2. Coating with polymer	1. Less noble metal than steel and plating layer of light coating weight 2. Potential close to steel and plating layer of light coating weight 3. Plating layer of light coating weight as a supply of Fe ions (in case of phosphating) 4. Smooth surface and electropaintability close to steel
up-to-date and future countermeasure	1. Hot-galvanized steel: Improvement in weldability 2. Electro-galvanized steel (C.W. 100 g/m ²) ◦Plate layer of light coating weight 3. Galvannealed steel: Formability → Plate layer of light coating weight and electroplate ◦Electroplate Fe-Zn alloy 4. Zn-Ni alloy: Anti-corrosion → Multi-layer Light coating weight ◦Plate Fe-Zn alloy as top layer* 5. ZM: Anti-corrosion in formed parts and weldability → Use of precoated steel as substrates ◦Paint thinner film * in case of outer panel		1. Galvannealed steel ◦Formability, Paintability ◦Plate layer of light coating weight and electroplate ◦Electroplate Fe-Zn alloy 2. Zn-Ni alloy: ◦Red rust ◦Paint adhesion ◦Multi-layer ◦Light coating weight ◦Plate Fe-Zn alloy as top layer 3. ZM: ◦Red rust ◦Formability ◦Paintability ◦Use precoated steel as substrates ◦Paint thinner film

4H₂O is defined from the following equation:

$$P = Ip/(Ip + Ih)^5$$

where, *Ip*: X-ray diffraction intensity of (100) plane in phosphophyllite
Ih: X-ray diffraction intensity of (020) plane in hopeite.

Paint adhesion of multi-layer electroplated steel which consists of Ni-Zn alloy as inner layer and Fe-Zn alloy, of which Fe content is about 80 % and coating weight is about 4 g/m², as outer layer was evaluated. Fe-Zn alloy as outer layer acted as a source of Fe ions to zinc phosphate film. The multi-layer electroplated steel had better paint adhesion than existing precoated steels and showed the same corrosion resistance as single layer. Morphology of zinc phosphate crystal greatly varies as shown in Photo. 1 (p. 971). Zinc phosphate on Fe-rich outer layer is similar to that of cold rolled steel and P-ratio is about

Table 5. Test methods to evaluate corrosion resistance.

1. Salt spray test	Salt spray of 5 % NaCl solution
2. Dry & wet cycle test	Immersion in 5 % NaCl solution ↓↑ Hot air drying
3. Cycle test-1	→ Salt spray of 5 % NaCl solution ↓ Hot air drying ↓ Immersion in 5 % NaCl solution ↓ Drying
4. Cycle test-2	→ Immersion in 5 % NaCl solution ↓ Hot air drying ↓ Humidity

100 %. This Fe-rich outer layer can be electroplated on other precoated steels, where only hopeite crystal is formed by conventional phosphating, which provides superior paint adhesion.

IV. Summary

The corrosion resistance of existing precoated steels for automotive body was investigated and new precoated steels suitable for exterior panel use were evaluated.

(1) Application of Ni-Zn alloy electroplated steel may provide effective protection against corrosion of portions where paint film may not be sufficiently applied.

(2) For sufficiently painted portions, Fe-Zn alloy plated steel may be more effective.

(3) Electroplating Fe-rich outer layer provides superior paint adhesion.

Finally summary of our philosophy in terms of corrosion performance of precoated steel is depicted in Table 4.

Test methods to evaluate corrosion resistance are shown in Table 5.

REFERENCES

- 1) A. Shibuya, T. Kurimoto, M. Nishihara, S. Wakano and T. Kurashige: Proc. ASM-ADDRG Int'l Conf., ASM, Metals Park, (1981), 333.
- 2) Y. Miyoshi, K. Yoshida, T. Azami, T. Kanamaru and S. Kado: *Tetsu-to-Hagané*, **66** (1980), 858.
- 3) T. Watanabe, M. Ohmura, T. Honma and T. Adaniya: SAE Tech. Paper, No. 820424, (1982).
- 4) S. Wakano, S. Matsuo, M. Nishihara, H. Shigematsu and K. Koike: *Sumitomo Metals*, **32** (1980), 322.
- 5) T. Miyawaki, H. Okita, S. Umehara and M. Okabe: Proc. Interfinish '80, The Metal Finishing Soc. Japan, Tokyo, (1980), 303.