

Development of Multi-functional Conversion Coatings by Inorganic Polymer for Electrical Appliances

TSUCHIMOTO Kazuaki*¹ MATSUDA Takeshi*² MATSUZAKI Akira*³

Abstract:

As electrogalvanized steel sheets, EG, for electrical appliances, multi-functional conversion coatings were developed in order to meet recent requirements for additional as well as and higher functions to enable manufacturers to use EG with fewer processes. This conversion coatings achieved high corrosion resistance and high conductivity by applying “eNanoTM coat”^{*4} technology. The “eNano coat” has two film formation concepts. First is using a neutral treatment solution to maintain conductive points by preventing dissolution of the convex parts of zinc crystals. Second is high barrier layer by inorganic polymer with a thin film. Furthermore, JFE Steel has commercialized multi-functional conversion treated steel sheets with a high anti-fingerprint property, paint adhesion, press formability and galling resistance by blending the optimum organic resin and lubricants in the composite coating.

Product name: Eco FrontierTM JN2^{*5}

1. Introduction

As electrogalvanized steel sheets (EG) for use in electrical appliances and OA products, multi-functional conversion coated steel sheets with various functions have been demanded in response to the heightened need for omission of post-processes in order to reduce the manufacturing costs of EG users. For example, accompanying the progress of digital electrical appliances in recent years, shield boxes are provided inside the housings of digital electrical appliances to prevent leakage of electromagnetic waves. However, if the electrical conductivity of the conversion coated steel sheets

that make up the box is inadequate, connections are made via nickel gaskets or other conductive materials in some cases. In order to reduce manufacturing costs by omitting these conductive materials, there is a high need for steel sheets with both high corrosion resistance and conductivity. In the press forming process, high lubricity that enables use without oil coating and does not cause cracking or galling during forming is required so that the oiling and degreasing processes can be omitted. Moreover, an anti-fingerprint property is also necessary for easy handling by users and excellent appearance of final products.

Figure 1 shows the relationship between the corrosion resistance and electrical conductivity of conventional chromate-free coatings. Although conductivity is improved by reducing the thickness of the coating, at the same time, corrosion resistance deteriorates. Therefore, both corrosion resistance and conductivity are properly satisfied by optimal control of the film thickness. In parts with high corrosion resistance requirements, corrosion resistance was secured by increasing the thickness of the conversion coating, but in this case, it was difficult to obtain satisfactory conductivity at a low cost without using conductive materials, etc.

As described in this report, a multi-functional conversion coated steel sheet with a combination of corrosion resistance, electrical conductivity, an anti-fingerprint property, paint adhesion, press formability and galling resistance was commercialized by adding the optimum organic resin and high-lubricity material to the composite coating, based on the technology of the inorganic polymer coating “eNanoTM coat”^{*4}, which satisfies both corrosion resistance and electrical con-

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*¹ Senior Researcher Deputy Manager,
Coated Products Research Dept.,
Steel Res. Lab.,
JFE Steel



*² Senior Researcher Manager,
Coated Products Research Dept.,
Steel Res. Lab.,
JFE Steel



*³ Dr. Eng.,
General Manager,
Functional Material Research Dept.,
Steel Res. Lab.,
JFE Steel

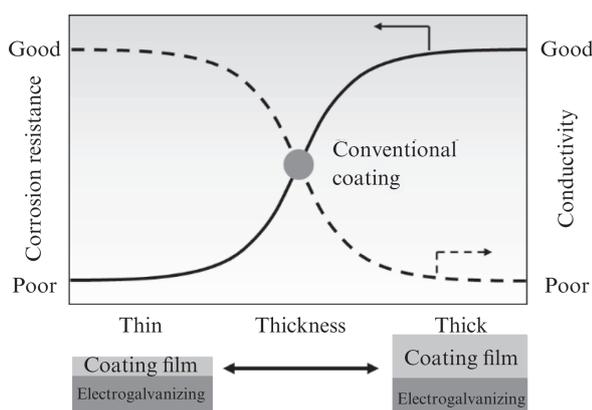


Fig. 1 Relationship between corrosion resistance and conductivity

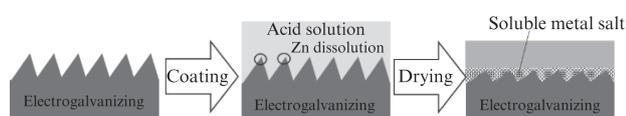


Fig. 2 Film formation mechanism of conventional chromate-free coating

ductivity combined.

2. Compatibility of High Corrosion Resistance and Conductivity

2.1 Conventional Chromate-free Technology

In the conventional chromate free coating, a barrier effect equivalent to that of a hydrated chromium oxide cross-linked film is realized by reacting the zinc coating and the acid component in the conversion treatment solution and forming a reaction layer of insoluble metal salts (Fig. 2). In particular, in composite coatings of a water-soluble organic resin and phosphoric acid, it is known that corrosion resistance is improved by the formation of a reaction layer comprising phosphoric acid and zinc at the interface with the Zn plating¹⁻³⁾. However, when the reaction layer was formed by insoluble metal salts, conduction points could not be secured and it was difficult to maintain high conductivity because the acid component dissolved the convex parts of the electroplated Zn crystals. Thus, there were limits to the compatibility of corrosion resistance and conductivity with the film composition concept of the conventional chromate-free coating.

Table 1 Condition of chemical conversion treatment

Sample	Solution pH	Coating matrix
i	Acidic	Phosphoric acid + Resin
ii	Neutral	Resin
iii	Neutral	Silicate + Metal salt

2.2 “eNano™ Coat”^{*4} Technology Satisfying High Corrosion Resistance and Conductivity

2.2.1 Sample preparation and evaluation method

In order to clarify the factors that affect the corrosion resistance and conductivity of the conventional chromate-free coating, a sample having a composite coating of an organic resin and phosphoric acid (sample i) and for comparison, a sample having a single component resin coating using conversion treatment solution with a neutral pH (sample ii) were prepared. Next, to realize compatibility of high corrosion resistance and high conductivity, sample iii (“eNano coat”) with an original inorganic polymer coating developed by JFE Steel Corporation⁴⁾, which consists of a silicate binder and metal salt inhibitor, was prepared using a conversion coating solution with a neutral solution pH. The conversion treatment conditions of the three samples are shown in Table 1.

The substrate for all samples was an electrogalvanized steel sheet (EG) with a thickness of 0.6 mm and a Zn plating weight of 20 g/m². The samples were prepared by applying the conversion treatment solution to this substrate with a bar coater, followed by drying by induction heating under conditions of an achieved sheet temperature of 140°C and heating time of 5 s.

The corrosion resistance of the samples was evaluated by a salt spray test (SST) conforming to JIS Z 2371. Conductivity was evaluated by measuring the surface resistance with a LORESTA™⁶ GP manufactured by Mitsubishi Chemical Analytech Co., Ltd. and a 4-pin probe (ASP type). Surface resistance was evaluated by performing these measurements 10 times with a 4-pin probe load of 300 g, and considering the number of times that it was possible to achieve 10⁻⁴ Ω of less as the conduction ratio.

The concavity and convexity of the electroplated Zn crystals was investigated by SEM observation. In order to confirm the morphology of the surface layer of the coatings, the accelerating voltage was adjusted to 0.5 kV.

Polarity measurements were performed using a platinum counter electrode and an Ag/AgCl reference electrode in an aerated 2% NaCl solution at ambient temperature. Polarity measurements were carried out at a sweep speed of 1 mV/s after immersion in salt water for 24 h.

*6 LORESTA is a registered trademark of Mitsubishi Chemical Analytech Co., Ltd. in Japan.

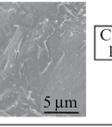
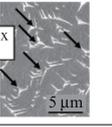
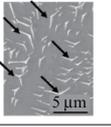
Sample	eNano coat		
	i	ii	iii
Treatment solution	Acidic	Neutral	Neutral
Corrosion resistance (SST 72 hr)			
(White rust)	Good (Slightly)	Poor (Entirely)	Excellent (Nothing)
SEM image			
Conductivity (Conductive ratio)	Poor (30%)	Good (100%)	Good (100%)

Fig. 3 Corrosion resistance and conductivity of conventional and newly-developed coatings

2.2.2 Results and discussion

Figure 3 shows photographs of the appearance, surface SEM images and the conduction ratios of the resin-phosphoric acid coating (sample i) and the single component resin coating (sample ii) after a 72 h SST. Sample i showed satisfactory corrosion resistance, as virtually no white rust had occurred after the 72 h SST, but the entire surface of sample ii was covered with white rust. On the other hand, the conduction ratio of sample i was 30%, which was poor in comparison with sample ii. Thus, sample i failed to satisfy both high corrosion resistance and conductivity. Comparing the respective coating structures and their performance, in the surface SEM image of sample i, almost no convex parts of the Zn crystals could be observed, and based on this, it is thought that conductivity decreased due to the loss of conduction points. Accordingly, in sample i, dissolution of the Zn crystals by the phosphoric acid used as the acid treatment solution is considered to be the main cause of reduced conductivity and increased corrosion resistance. On the other hand, in sample ii, convex parts of the Zn crystals were confirmed in the SEM image, and this sample showed satisfactory conductivity. Although conduction points were retained because dissolution of the Zn crystals was suppressed by using a neutral conversion treatment solution, it is thought that corrosion resistance decreased because a reaction layer of insoluble metal salts was not formed^{5,6}. Based on these results, in order to satisfy both high corrosion resistance and high conductivity, it is necessary to form a barrier layer equivalent to the reaction layer of insoluble metal salts while also maintaining the convex profile of the Zn crystals, and it was suggested that use of a neutral conversion treatment solution is an effective approach for maintaining the convex profile of the Zn coating crystals.

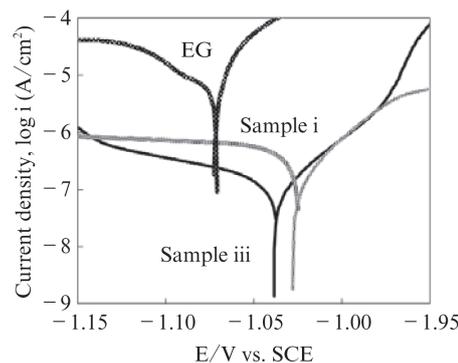


Fig. 4 Polarization curves

Figure 3 shows the corrosion resistance, conductivity and surface SEM image of sample iii, which was produced by using a neutral treatment solution and has an inorganic polymer coating consisting of a silicate binder and metal salt inhibitor. The conduction ratio of sample iii is 100%, which is equal to the conductivity of sample ii. Since remaining convex parts of the Zn plating crystals were observed in the surface SEM image, it is thought that the dissolution reaction of the Zn plating was suppressed by adjusting the pH of the treatment solution to neutrality. On the other hand, as no white rust occurred on sample iii even after the 72 h SST, it was found that this coating can satisfy both corrosion resistance and conductivity at a high level.

The polarization curves of EG and samples i and iii are shown in Fig. 4. In comparison with EG, both the anodic reaction and the cathodic reaction of sample i with the conventional resin-phosphoric acid coating were suppressed. This result is attributed to improvement of the barrier property by the reaction layer of insoluble metal salts. Comparing the reduction current densities of samples i and iii, sample iii showed a lower value. Based on this, it was found that the inorganic polymer coating consisting of the silicate binder and metal salt inhibitor has a higher barrier property than the insoluble metal salt reaction layer.

3. Multi-Functional Conversion Coatings

3.1 Anti-Fingerprint Property by Resin Composite

3.1.1 Sample preparation and evaluation method

Although it was possible to satisfy both corrosion resistance and conductivity at a high level by utilizing the technology of the inorganic polymer coating “eNano coat,” which is produced by using a neutral conversion treatment solution and has a coating consisting of a silicate binder and a metal salt inhibitor,

the anti-fingerprint property and press formability required in steel sheets for electrical appliances are still inadequate. Therefore, development of a multi-functional coating was studied. It is known that a composite coating containing organic resin is effective for imparting an anti-fingerprint property to conversion coatings. Therefore, samples were prepared by applying an acrylic resin, an urethane resin and a phenol resin with a coating weight of 0.5 g/m² each to EG with a bar coater, and drying the samples by induction heating under conditions of an achieved steel sheet temperature of 140°C and heating time of 5 s.

Following this, a sample was prepared under the same conditions by adding a resin with a particularly good anti-fingerprint property to sample iii, and the anti-fingerprint property and paint adhesion property of the samples were evaluated.

The anti-fingerprint property was evaluated by applying white petroleum jelly (Vaseline) to the samples and measuring the color change (ΔE) before and after wiping. Color change was measured in the SCE mode (specular component excluded method) using a spectrophotometer, and was displayed on Lab color space. ΔE is expressed by Eq. (1) when the initial values are L_b, a_b, b_b and those after applying and wiping the Vaseline are L_a, a_a, b_a .

$$\Delta E = \sqrt{(L_a - L_b)^2 + (a_a - a_b)^2 + (b_a - b_b)^2} \dots (1)$$

In order to evaluate the influence of the type of organic resin on the anti-fingerprint property, surface free energy was investigated. Surface free energy (γ_s) was calculated based on the measured value of the contact angles of the samples with water and iodide methylene 20 s after dropping the solution on the samples⁷⁻⁹.

Paint adhesion was evaluated by an adhesion test after immersion in boiling water. After degreasing the samples (Par-Clean N364S, Nihon Parkerizing Company, Limited, 60°C, 2 min spraying), a melamine alkyd resin (DELICON #700, NIPPONPAINT Co., Ltd.) was coated on the samples to a thickness of 30 μ m and baked for 30 min at 130°C. Next, after immersion in boiling water for 2 h, grids of one hundred 1 mm squares were formed on the samples by cutting with an NT cutter. A peeling test was then performed by applying and peeling adhesive tape, and paint adhesion was evaluated by the peeling area ratio of the resin coating.

3.1.2 Results and discussion

The anti-fingerprint property evaluation (ΔE) and the surface free energy (γ_s) of the single component coatings with the various organic resins are shown in

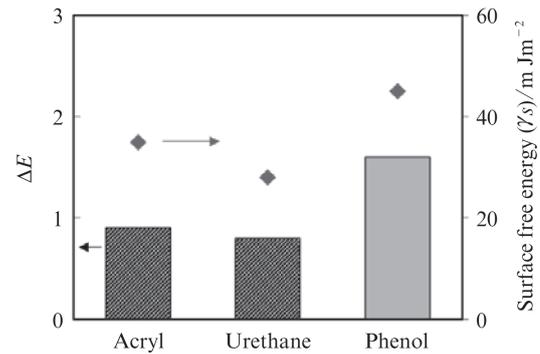


Fig. 5 Anti-fingerprint properties and surface free energy of single component coatings of various organic resins

Sample	iii	iv	v	
Coating component	Base	Silicate + Metal salt	Silicate + Metal salt	Silicate + Metal salt
	Organic resin	-	Acryl	Urethane
Corrosion resistance (SST 96 hr)	Good	Good	Good	Good
Conductivity	Good	Good	Good	Good
Anti-fingerprint property (ΔE)	Poor (3.0)	Good (1.3)	Good (1.2)	Good (1.2)
Paint adhesion (peel ratio)	Good (0%)	Poor (20%)	Good (0%)	Good (0%)

Fig. 6 Performances of coatings with adding organic resins

Fig. 5. It is generally known that a sample possesses a good anti-fingerprint property if the color change (ΔE) before and after Vaseline wiping is less than 2.0. The ΔE of the acrylic resin, urethane resin and phenol resin all achieved values of less than 2.0, and those of the acrylic resin and urethane resin were particularly good, at 0.9 and 0.8, respectively. Moreover, in comparison with the phenol resin, the surface free energy of the acrylic resin and urethane resin showed low values. Since it is known that fingerprint painting is inhibited by reducing surface free energy⁸, the acrylic resin and urethane resin are assumed to have achieved a good anti-fingerprint property by preventing fingerprint painting.

Figure 6 shows the results when the acrylic resin and urethane resin, with which a satisfactory anti-fingerprint property was obtained, were added to coating iii. A satisfactory anti-fingerprint property was obtained by adding the acrylic resin and the urethane resin, as addition of these resins reduced ΔE from 3.0 to 1.3 and 1.2, respectively. Sample iv with the composite containing the acrylic resin showed a good anti-fingerprint property, but its paint adhesion property was poor. On

the other hand, sample v, the composite with the added urethane resin, realized a good anti-fingerprint property and good paint adhesion, while continuing to satisfy both high corrosion resistance and conductivity.

3.2 Improvement of Press Formability by Addition of Lubricants

3.2.1 Sample preparation and evaluation method

The lubricant was optimized in order to realize excellent press formability. Samples were prepared by adding high-lubricity materials A, B and C to the composite coating containing urethane resin (urethane-added coating iii).

The sample preparation conditions were the same as those in 3.3.1.

Press formability was evaluated by the friction coefficient in a sliding test. Sliding of the samples was performed under the conditions of a contact pressure of 7.8 MPa and sliding speed of 0.2 m/min without oil coating, and the friction coefficient was calculated from the pull-out load. A comparison sample was used as an index of press formability. This sample was prepared by coating a lubricant oil on GA (galvanized steel sheet), which is actually used in press-formed automotive parts. Galling during press forming was evaluated by the galling test shown in **Fig. 7**. The sample was inserted between the triangular bead and flat bead, and drawing was performed under conditions of a load of 2.9 kN and drawing speed of 0.2 m/min without oil coating. Galling resistance was evaluated by the appearance of the sample on the triangular bead side after the test.

3.2.2 Results and discussion

The results of the friction coefficient measurements are shown in **Fig. 8**. The friction coefficient of the comparison sample (GA + lubricant oil) was 0.22. The friction coefficients of the samples containing high-lubricity materials A and B were similar, at 0.23, but an excellent friction coefficient of 0.18 was obtained with

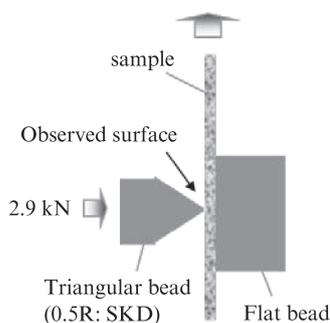


Fig 7. Schematic diagram of galling test

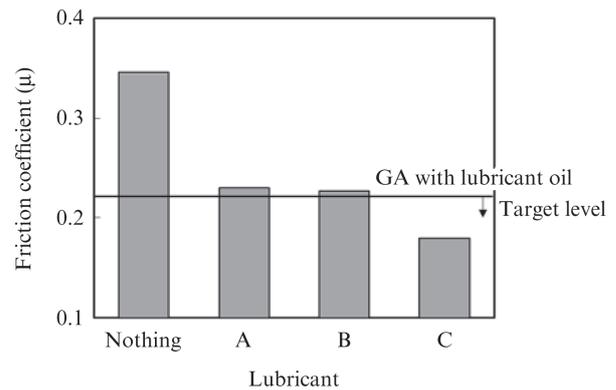


Fig. 8 Friction coefficients with different lubricant

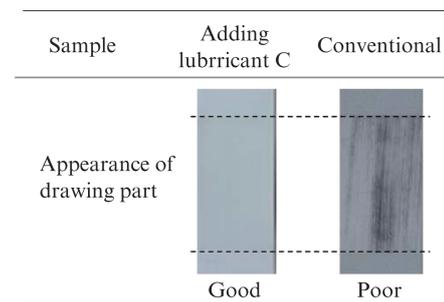


Fig. 9 Appearance of sample after galling test

the sample containing high-lubricity material C. The results of a galling test of a sample containing high-lubricity material C confirmed that this coating has good galling resistance (**Fig. 9**).

4. Development of Multi-Functional Conversion Coating

Utilizing the technology of “eNano coat,” which satisfies both high corrosion resistance and high conductivity requirements, a new multi-functional conversion coated steel sheet which realizes various functions at a high level was developed by adding the optimum organic resin and a high-lubricity material to the composite coating. The performance of the newly-developed product is shown in **Table 2**. In comparison with the general-purpose conventional product I, the developed product has high corrosion resistance and galling resistance while maintaining the same conductivity. In comparison with the heavy-coating conventional product II, the developed product can achieve high conductivity with the same high corrosion resistance. Thus, the newly-developed multi-functional conversion coated steel sheet successfully realizes high-level corrosion resistance and conductivity, while also providing a high anti-fingerprint property, paint adhesion, press formability and galling resistance combined.

Table 2 Performance of newly-developed chromate-free coating

(++) : Excellent, (+) : Good, (-) : Poor

Function	Newly developed	Conventional product I	Conventional product II
Corrosion resistance	++	+	++
Conductivity	+	+	-
Galling resistance	++	+	++
Anti-fingerprint property	+	+	+
Paint adhesion	+	+	+

Experimental procedure

- Corrosion resistance: Salt-spray test (SST) complying with JIS Z 2371
- Conductivity: Complying with JIS K 7194
- Galling resistance: Referring to chapter 3.2.1
- Anti-fingerprint property: Referring to chapter 3.1.1
- Paint adhesion: Referring to chapter 3.1.1

5. Conclusion

A new multi-functional conversion coated steel sheet was developed to respond to the diverse and more advanced performance demanded in electrogalvanized steel sheets (EG) for electrical appliances, and to allow users of EG to omit production processes. Concretely, compatibility of high-level corrosion resistance and electrical conductivity was realized by utilizing the technology of the inorganic polymer coating “eNano

coat,” in which conduction points are secured by using a neutral treatment solution to prevent dissolution of convex parts of Zn crystals, and a high barrier property is achieved with a thin coating by a coating composition consisting of a silicate binder and metal salt inhibitor. In addition, a new multi-functional conversion coated steel sheet with a combination of a high anti-fingerprint property, paint adhesion, press formability and galling resistance was commercialized by adding the optimum organic resin and lubricant to the composite coating.

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