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Development of Highly-functional Conversion Treated Steel Sheets with Highly-dense Barrier Layer[†]

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Abstract:

The ideal structure of coating film, with both high corrosion resistance and high conductivity, was examined by scanning electron microscope (SEM) analysis of conventional chromate-free coated steel sheets such as phosphoric acid composite coating. JFE Steel found that it is effective to inhibit dissolution of zinc plating against high conductivity and it is also possible to improve corrosion resistance by forming highly-dense barrier layer at the molecular level. Based on the results, the "eNano^{TM} coat" was developed. Furthermore, highly-functional conversion treated steel sheets, "Eco Frontier^{TM} coat JX", were commercialized by blending lubricants which have excellent lubricity under hard press condition without lubricant oil. They have high corrosion resistance, high conductivity and excellent lubricity.

1. Introduction

Chromate conversion treated steel sheets were developed beginning in the 1980s in order to improve the corrosion resistance of Zn-coated steel sheets. Since chromate coatings have a high barrier component and a self-healing component, chromate conversion treatment provides excellent corrosion resistance even with a thin conversion treatment film, and also secures good conductivity. The chromate film has a high barrier property because polymerization is achieved by either hydroxy (Cr−OH−) or oxo (Cr−O−) cross-linking of chromium oxide hydrate. The self-healing property is also a distinctive feature of this type of coating, as the oxidation reaction of hexavalent chromium forms a passivation film if the film is damaged[1)].

Chromate conversion treated steel sheets were widely adopted until the 1990s, taking advantage of their excellent corrosion resistance and conductivity, as well as economy and other features. However, active development of chromate-free conversion treated steel sheets has been underway since the 2000s, occasioned by strict new environmental regulations on chromium, etc. in Europe[2)]. To date, many types of chromate-free conversion treated steel sheets have been developed and commercialized. As a common feature, these products share the basic concept of improvement of corrosion resistance shown in **Table 1**, namely, (1) formation of a barrier layer against corrosion factors (oxygen, water) corresponding to the cross-linked chromate oxide hydrate film, and (2) achievement of a self-healing property corresponding to the reduction reaction of hexavalent chromate in parts where film defects occur. Where (1) is

Table 1 Concept of anticorrosion in chromate coating and chromate-free coating

	Chromate coating	Chromate-free coating
Barrier component	Cross-linked chromate oxide hydrate	Passive layer formed by reaction of acid and zinc
Self-healing component	Oxidation reaction by hexavalent chromate	Inorganic inhibitor

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concerned, a dense barrier layer is generally obtained by reaction products of acid components such as phosphoric acid, etc. and the zinc (Zn) coating[3]. For (2), the use of inorganic corrosion inhibitors is the main practice, and transition metal elements, rare earth elements, metal chelates, and other substances have been investigated in this connection[4]. Many chromate-free conversion treated steel sheets realize moderate levels of corrosion resistance and conductivity by forming a high corrosion resistance film using a hybrid approach of (1) and (2) while controlling the film thickness to no more than 1 μm (**Fig. 1**).

On the other hand, accompanying the progress of digitalization, adoption of high speed central processing units (CPUs), etc. in electrical appliances in recent years, these products are now equipped with shield boxes to prevent leakage of electromagnetic waves in the housing. However, due to the inadequate conductivity of the conversion treated steel sheets used in the shield box, connections are made via nickel gaskets and other conductive materials. In products in which high corrosion resistance is required, such as freezer showcases, etc. it is possible to secure corrosion resistance by adopting a thick conversion treatment film or using a powder coating. However, a post-painting process is necessary, as these methods reduce electrical conductivity, thereby causing problems in spot weldability and grounding.

Furthermore, with hard-to-form parts such as deep-drawing parts, etc., galling and cracks will occur if pressing is performed without a lubricant. For this reason, press forming is performed under lubrication during pressing, followed by degreasing.

As outlined above, conventional chromate-free steel sheets use a combination of conductive materials, powder paint, press oil, etc., and are applied to various types of materials by using special grades of conversion treated steel sheets.

In this paper, the element technologies for corrosion resistance, conductivity, and formability were constructed in order to develop next-generation conversion-treated steel sheets which satisfy these performance requirements at a higher order. First, the ideal film structure for satisfying both corrosion resistance and conductivity at a high order was verified, and it was found that preventing dissolution of Zn coating crystals is effective for imparting high conductivity. To impart high corrosion resistance, JFE Steel developed "eNano™ coat," which enables formation of a dense barrier layer at the molecular level in the thin film portion in the convex parts of the Zn coating crystals. Next, a search for a high lubricity wax with an excellent sliding property under severe sliding conditions without a lubricant was conducted. As a result, a high-functionality conversion treated steel sheet, "Eco Frontier™ coat JX," which satisfies corrosion resistance, conductivity, and formability at a high order was commercialized by combining this "eNano™ coat" with a high lubricity wax.

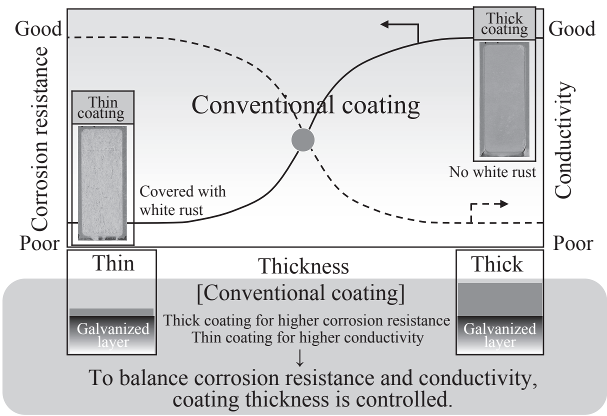


Fig. 1 Relationship between corrosion resistance and conductivity of conventional chromate-free coating

2. Film Structure and Performance of Conventional Chromate-free Technology

In conventional chromate-free coatings, a barrier property corresponding to a cross-linked film of chromium oxide hydrate is realized by reaction of the acid component in the conversion treatment solution and the Zn coating, and formation of a reaction layer of insoluble metal salts. In particular, with a composite layer of a water-based organic resin and phosphoric acid, it is known that a reaction layer consisting of phosphoric acid and Zn is formed at the interface with the Zn coating, and this improves corrosion resistance[3]. Therefore, an investigation was carried out by surface observation of the structures of water-based organic resin single component coatings and composite coatings of water-based organic resins and phosphoric acid by scanning

	Coating component		Sub-stance	Corrosion resistance (SST: 96 h)	SEM Image	Conductivity* (Conduction ratio)
	Resin	Phosphoric acid				
Single component coating	Contained	Not contained	Neutral	Poor (Covered with White rust)	Conductive points: Exist; Conductive points; 1 μm	Good (100%)
Composite coating	Contained	Contained	Acidic	Good (No white rust)	Conductive points: Disappeared; 1 μm	Poor (30%)

SST: Salt spray test
SEM: Scanning electron microscope
*The surface resistance of the test piece above was measured using an ASP probe of Loresta GP manufactured by Mitsubishi Chemical Analytech Co., Ltd. The surface resistance was measured while a load on the probe was 300 g. The conductivity was evaluated by determining the conduction ratio that achieved a surface resistance of $10^{-4}\,\Omega$ or less.

Fig. 2 Influential factor of corrosion resistance and conductivity of conventional chromate-free coating electron microscopy (SEM), and the relationship between the coating structure and performance was verified.

Figure 2 shows the corrosion resistance, conductivity, and surface SEM images of a single component coating of a water-based resin and a composite coating of a water-based organic resin and phosphoric acid. The composite coating displayed satisfactory corrosion resistance, as no white rust occurred even after 96 hours of the salt spray test (SST: conducted in accordance with JIS Z 2371 (JIS: Japanese Industrial Standard)). However, with the single component coating, white rust occurred over the entire surface. On the other hand, the conduction ratio (conductivity) of the composite coating was 30%, which was inferior to that of the single component coating. Thus, the composite coating could not satisfy both corrosion and conductivity. Comparing the respective coating structures and their performance, in the surface SEM image of the composite coating, virtually no convex parts of Zn crystals were observed. Based on this, it is considered that conductivity was reduced by the loss of conduction points, while corrosion resistance was improved by insoluble metal salts of dissolved Zn and phosphoric acid. Convex parts of the Zn coating crystals were observed in the SEM image of the single component coating. Therefore, while this coating showed satisfactory conductivity, it is thought that its corrosion resistance was reduced because a reaction layer was not formed, and as a result, the barrier property was inadequate.

3. Development of "eNano™ coat" with High Corrosion Resistance and High Conductivity

3.1 Coating Design Satisfying High Corrosion Resistance and High Conductivity

From the results of the analysis of the water-based organic resin/phosphoric acid composite film, in order to satisfy both corrosion resistance and conductivity at a high order, it appears promising to form a barrier layer corresponding to a chromium oxide hydrate cross-linked film or insoluble metal salts, while maintaining the convex shape of the Zn coating crystals of the galvanized sheet. In other words, (1) the convex shape of the electrogalvanized Zn crystals which form conduction points should be maintained, and (2) the coating should have a high barrier property even with a thin film. To realize these features, the authors conducted a search for (1) a new barrier layer structure replacing the insoluble metal salts of the acid/zinc coating type and (2) a film component that enables high density 3-dimensional cross-linking.

Table 2 Condition of chemical conversion treatment

	No. 1	No. 2	No. 3	No. 4
Coating component	Inhibitor (Constant)			Composite coating
	A1	A2	A3	
Particle size	Small	Medium	Large	—
substance	Neutral	Neutral	Neutral	Acidic

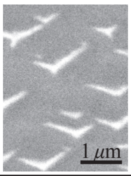
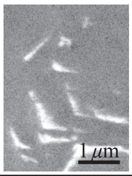
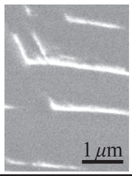
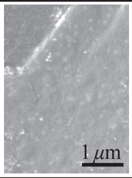
3.2 Specimen Preparation and Performance Evaluation

Silica barrier components A1 ("eNano™ coat"), A2, and A3 with different particle sizes were mixed in a conversion treatment solution containing a constant amount of inhibitor with the compositions shown in **Table 2**, and the solutions were adjusted to a neutral pH to prevent dissolution reaction of the Zn coating. For comparison purposes, a mixed solution of a water-based organic resin and a phosphoric acid (composite coating) was also prepared. Next, each of the conversion treatment solutions was coated on an electrogalvanized steel substrate so as to obtain a uniform coating weight, and the specimens were dried by induction heating (achieved sheet temperature: 140°C, heating time: 5 s). The corrosion resistance of the specimens was then evaluated by the SST. Conductivity was evaluated by measuring surface resistance using a LORESTA* GP manufactured by Mitsubishi Chemical Analytech Co., Ltd. and an ASP (4-probe series probe) terminal. Surface resistance was evaluated by performing measurements 10 times with a terminal load of 300 g, and considering the number of times which it was possible to achieve 10^{-4} Ω or less as the conduction ratio. In order to confirm the state of the Zn coating crystals, surface observation was performed using an SEM. To confirm the barrier effects of A1, A2, and A3, the anodic and cathodic polarization curves of the specimens were measured in a 5% NaCl aqueous solution (25°C) under a condition open to the atmosphere. Measurements of the polarization curves were performed by the potential sweep method at a sweep speed of 20 mV/min using a platinum counter electrode and an Ag/AgCl electrode as the reference electrode.

3.3 Results and Discussion

The corrosion resistance, conductivity, and surface SEM images of coatings containing the silica barrier components A1, A2, and A3 are shown in **Fig. 3**. The conduction ratios of all the coatings were 100%, showing satisfactory conductivity independent of the particle size of the barrier component. Because remaining convex parts of the Zn coating crystals could be confirmed

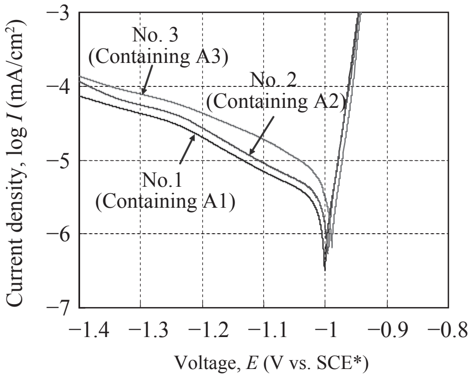
* "LORESTA/ロレスタ" is a registered trademark of Mitsubishi Chemical Corp. in Japan.

	No. 1	No. 2	No. 3	No. 4
Coating component		Inhibitor (Constant)		Composite coating
	A1	A2	A3	
Particle size	Small	Medium	Large	—
SST 96 h				
SEM Image				
Conductivity (Conduction ratio)	Good 100%	Good 100%	Good (100%)	Poor (30%)

eNano™ Coat (No. 1)

SST: Salt spray test
SEM: Scanning electron microscope

Fig. 3 Performance of “eNano™ coat” with high corrosion resistance and high conductivity



*Saturated calomel electrode

Fig. 4 Polarization curve for electrogalvanized steel sheets with coating Nos. 1, 2, and 3

in each of the SEM images, it is considered that the dissolution reaction of the Zn coating was suppressed by adjusting the pH of the conversion treatment solution to neutrality. The coating containing A1 showed satisfactory corrosion resistance, as no white rust occurred in a 96-h SST. However, white rust occurred with the coatings containing A2 and A3, and corrosion resistance tended to decrease with larger particle sizes. Therefore, polarization measurements were performed to verify the barrier effects of A1, A2, and A3. The results are shown in **Fig. 4**. As the particle size of the barrier component decreased, the cathodic reaction was suppressed, and the barrier property against oxygen increased. Accordingly, it is considered that A1, which had the smallest particle size, suppressed the oxygen reduction reaction by forming a denser barrier layer, and therefore displayed higher corrosion resistance than A2 and A3.

4. Development of High Formability Technology

4.1 Concept of Improving Sliding Property in Deep Drawing

Figure 5 shows a schematic diagram of the deep drawing test. In case cracks occur during deep drawing, reduction of the sliding resistance between the blank holder and the steel sheet is effective[5]. Therefore, the authors conducted a search for a wax which displays excellent lubricity under severe environments without a lubricant under conditions simulating sliding, i.e., drawing between the blank holder and the steel sheet.

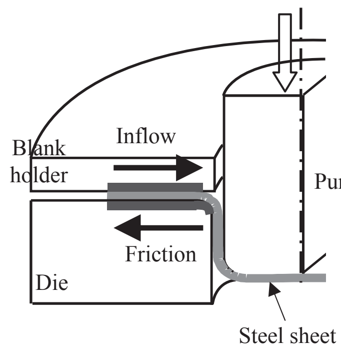


Fig. 5 Schematic diagram of deep drawing test

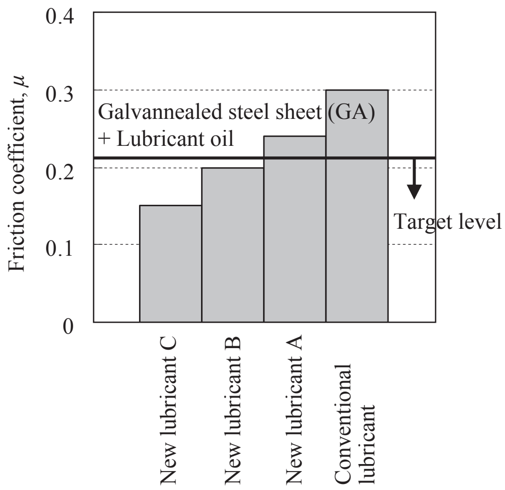


Fig. 6 Improvement of friction coefficient by adopting new lubricants; Lubricant oil was not used

4.2 Specimen Preparation and Performance Evaluation

Conversion treatment solutions were prepared by adding a conventional wax and various types of high lubricity wax to "eNano™ coat" (wax concentration in coating film: 5%). Next, each of the conversion treatment solutions was coated on an electrogalvanized steel sheet so as to obtain a uniform coating weight, and the specimens were dried by induction heating (achieved sheet temperature: 140°C, heating time: 5 s). Drawing was then performed with each specimen at a contact pressure of 7.8 MPa and drawing speed of 1.0 m/min without a lubricant, and the friction coefficient was calculated from the pulling load. A comparison specimen was also prepared by coating a fast-drying oil on a galvannealed steel sheet (GA), and the friction coefficient was calculated under the same conditions. Because this comparative material had been actually used to automotive press parts, it was used here as an index of cracking during press forming.

4.3 Results and Discussion

The results of the friction coefficients of each specimen are shown in **Fig. 6**. Compared to the comparison specimen, which displayed a friction coefficient of 0.22, adequate lubricity could not be obtained with the conventional wax, as its friction coefficient was 0.30. In contrast, the friction coefficients of the high lubricity waxes A and B were 0.24 and 0.20, respectively. Although this is considered to be sufficient for deep drawing, a high lubricity wax C with an even more favorable friction coefficient of 0.15 was found and adopted as the lubricant wax for the high-functionality conversion treated steel sheet JX.

5. Development of High-Functionality Conversion Treated Steel Sheet JX

A new high-functionality conversion treated steel sheet JX was developed, in which multiple functions that could not be achieved with the conventional conversion treated steel sheets were realized at a high order by combined use of a high lubricity wax, which provided excellent lubricity under severe sliding (drawing) conditions, and "eNano™ coat," which satisfied both corrosion resistance and conductivity requirements.

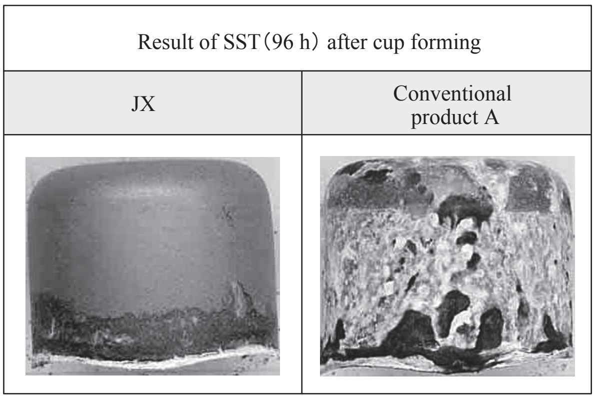
5.1 Quality Properties

The quality properties of the high-functionality conversion treated steel sheet JX and two conventional products are shown in **Table 3**. While maintaining the same conductivity as conventional product A, which had

Table 3 Performance of highly-functional conversion treated steel

	JX	Conventional product A	Conventional product B
Corrosion resistance	192 h	96 h	192 h
After degreasing	120 h	72 h	120 h
Conductivity	0.1 mΩ	0.1 mΩ	Not conductive
Scratch resistance	No scratch	Partially scratched	Entirely scratched
Lubricity	0.15	0.26	0.4
Paint adhesion	No peeling	No peeling	No peeling

Experimental procedure
· Corrosion resistance: Salt-spray test (SST) complying with JIS Z 2371
· Corrosion resistance after degreasing: Salt-spray test (SST) complying with JIS Z 2371
· Degreasing condition
(Degreaser) CL-N364S manufactured by Nihon Parkerizing Co.,Ltd.
(Condition) Spray, 60°C×2 min
· Conductivity: Complying with JIS K 7194.
(Instrument) Using an ASP probe of Loresta GP manufactured by Mitsubishi Chemical Analytech Co., Ltd.
· Anti scratching: Load=200, 300 kgf, Sliding speed=200 mm/min
Bead radius=0.5 mm, Sliding distance=110 mm.
· Lubricity: Contact pressure 7.8 MPa, Sliding speed=200 mm/min, Contact area=10 mm×50 mm
· Paint adhesion:
(Paint) Melamine alkyd paint, thickness 30 μm, baking condition 130°C×30 min.
(Condition) Immersing in boiled water for 2 hours
(Evaluation) Tape peel test was performed to evaluate the paint adhesion on the basis of the state of the remaining coating film.



SST: Salt spray test

Photo 1 Corrosion resistance after cup forming

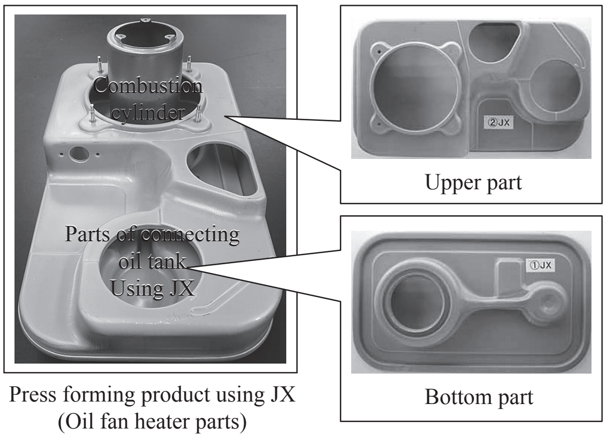


Photo 2 An example of application of highly-functional conversion treated steel sheets JX

good conductivity, corrosion resistance was improved by more than 2 times and achieved the same levels as conventional product B, which was a thick film, high corrosion resistance steel sheet. In comparison with the conventional products, lubricity and scratch resistance were also improved by blending the high lubricity wax, and as shown in **Photo 1**, corrosion resistance after cup forming was dramatically improved.

5.2 Example of Application

The high-functionality conversion treated steel sheet JX was applied to oil fan heater parts, which had been difficult to press form without a lubricant until then and required corrosion resistance after forming[6] (**Photo 2**).

6. Conclusion

"eNano™ coat," which is a chromate-free conversion treatment technology that simultaneously satisfies corrosion resistance and conductivity requirements, was developed based on a new concept different from that of conventional chromate-free technologies. Specifically, (1) the convex shape of the Zn coating crystals was maintained, securing conduction points, and (2) a barrier component which achieves a high barrier property with a thin film was discovered. A new high-functionality conversion treated steel sheet, "Eco Frontier™ coat JX," was also successfully commercialized by combining the "eNano™ coat" technology and a high lubricity wax lubricant. Expanded application to office automation and personal computer parts, which require high order conductivity, and to parts which require high corrosion resistance and high formability, such as freezer showcase and motor case parts, etc., is expected in the future.

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