Technical Report

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Development of SuperDyma™ with Chromate-free Treatment Layer

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Abstract

SuperDyma™ with two types of chromate-free treatment layer have been developed. The chromate-free SuperDyma™, type "QN", has the same corrosion resistance compared with conventional chromate treated products. The other type chromate-free SuperDyma™, type "QFK", has the same or better corrosion resistance and good formability. These new chromate-free products can be used as substitutes of conventional chromate treated SuperDyma™ and it will be obtained good performance compared with conventional chromate one according to the use.

1. Introduction

SuperDyma™ is a highly corrosion-resistant steel sheet plated with a hot-dip zinc alloy (Zn-11%Al-3%Mg-0.2%Si). Because of its excellent corrosion resistance, it has been used primarily in the field of building materials.[1] Formerly, after the plating, chromate treatment was generally applied to the steel sheet to improve its corrosion resistance. However, with the growing concern about environmental problems on a global basis in recent years, the movement to refrain from applying chromate treatment, started in the home appliances industry, is gaining momentum in the field of building materials too. Specifically, there is a strong possibility that guidelines on limiting the application of chromate treatment will be included in the Standard Specification for Public Building Works of the Ministry of Land, Infrastructure, Transport and Tourism in 2016. Under these conditions, Nippon Steel & Sumitomo Metal Corporation has been tackling the development of new environmentally friendly products, including several types of chromate-free film for SuperDyma™. In this technical report, the author shall describe the general performance of the newly developed chromate-free films as compared with the conventional chromate-containing products.

2. Structure of Chromate-Free Film

The chromate-free SuperDyma™ has a special film coated onto its hot-dip zinc alloy-plated surface. The structure of the chromate-free steel sheet is schematically shown in **Fig. 1**. The special film is composed of a material that permits imparting the barrier effect and self-repairing function of the conventional chromate-containing film to a chromate-free film. This is possible by mixing a corrosion inhibitor in a special film capable of shutting out the corrosive factors (**Fig. 2**).[2] This idea is the same as that applied to chromate-free zinc-coated steel sheets (ZINKOTE™, DURGRIP™).[3] Namely, the optimum film is designed according to plating type. In addition, by optimizing the inorganic/organic components and corrosion inhibitor composition according to the specific purpose, the company has developed two

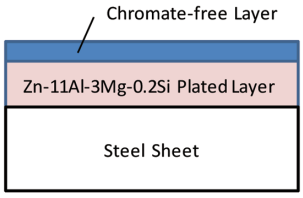

Fig. 1 Structure of chromate-free Zn-11Al-3Mg-0.2Si plated steel sheet

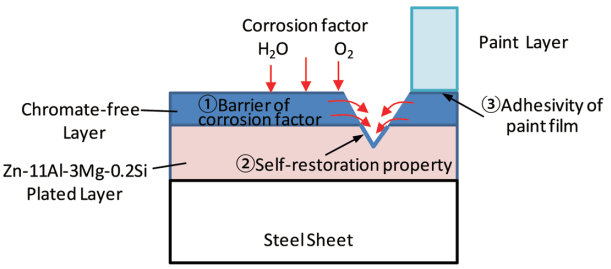

Fig. 2 Mechanism of corrosion resistant behavior of chromatefree treatment layer

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types of chromate-free films—"QN" consisting mainly of an inorganic compound and having corrosion resistance comparable to that of a conventional chromate film and "QFK" consisting mainly of an organic compound and having superior corrosion resistance and formability.

3. Test Methods

Specifications of the tested steel sheets are shown in **Table 1**. SuperDyma™ (coating weight: 90 g/m^2), used as the substrate, was subjected to two types of chromate-free treatment—QN and QFK. A conventional chromate-treated steel sheet (Y-treatment; Cr coating weight: 20 mg/m^2) was also tested as a reference.

3.1 Corrosion resistance

The flat surface of each test piece was subjected to a salt spray test (JIS Z 2371) to evaluate the resistance to white rust in terms of white rust area ratio. The test piece sides were kept sealed during the salt spray test.

In addition, the test pieces were subjected to an outdoor exposure test (at Miyakojima). With the sides and bottom of each test piece sealed, the test piece was exposed to the south at an inclination of 45°, and its white rust resistance was evaluated in terms of white rust area ratio.

3.2 Lubricating ability

As an indicator of press formability, the coefficient of dynamic friction of each test piece was measured using a HEIDON-14 (product of Shinto Scientific Co.). The slider used was a stainless steel ball 10 mm in diameter. It was slid over the test piece surface under a load of 1.0 N and at a sliding speed of 150 mm/min, and the dynamic friction coefficient of the test piece was obtained from the resulting stress.

In addition, to evaluate the slidableness of each test piece on a die press, the coefficient of dynamic friction for each test piece in a flat sheet pullout test was also measured. The flat sheet was held between plane dies (material SKD11, contact area: 30 × 25 mm) with a load of 0.5 kN. Its dynamic friction coefficient was obtained from the load required to pull out the test piece. The pullout speed used was 200 mm/min.

3.3 Conductivity

To determine the conductivity of each test piece, interlayer resistance and contact resistance (ground resistance) were measured. The interlayer resistance of each test piece was measured by a test voltage of 0.5 V and a test pressure of 2 N/mm^2 in accordance with JIS C 2550, and the contact resistance was measured by the four-point probe method (LORESTA GP of Mitsubishi Chemical Analytech Co.).

3.4 Paintability

First, a melamine-alkyd based paint (Amylac #1000 of Kansai Paint Co.) was applied and baked on the steel sheet surface so that the dry film thickness became 20 μm. Next, the film was given cross-cuts at intervals of 1 mm and covered with adhesive cellophane tape. Then, the tape was removed, and the condition of separation of the film was visually checked.

Table 1 Test pieces

Substrate	Kind of treatment		Note
Zn-11Al-3Mg-0.2Si hot-dip galvanized steel sheet (amount of plated layer: 90 g/m^2)	QN type	Chromate-free (inorganic type)	Conventional type
	QFK type	Chromate-free (organic type)	Corrosion resistance and formability
	Y treatment	Chromate	Conventional type

4. Test Results

4.1 Corrosion resistance

Figure 3 and **Photo 1** show the condition of occurrence of white rust on the surface of each test piece of the chromate-free SuperDyma™ in the salt spray test. It can be seen that the corrosion resistance of the QN type is comparable to that of the Y-treatment chromate-treated steel sheet and that the QFK type is superior in white rust resistance in comparison to the Y-treatment.

Figure 4 shows the results of a two year exposure test at Miyakojima. Under the test environment, the chromate-free SuperDyma™ showed corrosion resistance comparable with that of a conventional chromate-treated steel sheet.

4.2 Lubricating ability

Figures 5 and **6** show the results of measurement of dynamic friction coefficient in the stainless steel ball sliding test and flat sheet pullout test, respectively. In both tests, the QN type was nearly similar

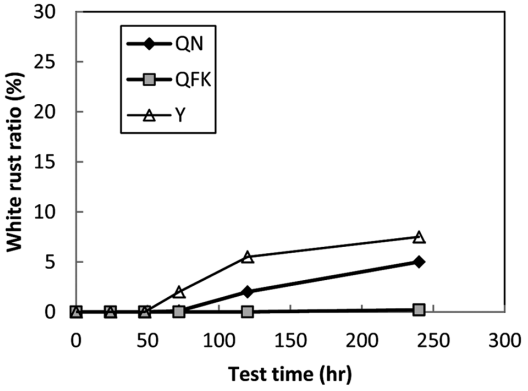

Fig. 3 Corrosion resistance of flat test pieces by salt spray test (SST)

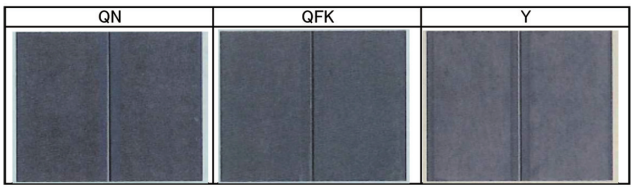

Photo 1 Appearance after 120 hours of SST

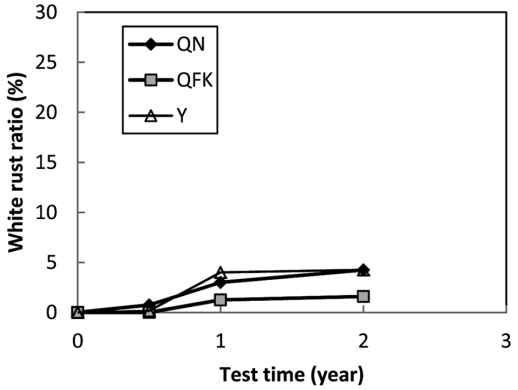

Fig. 4 Result of outdoor exposure test at Miyakojima

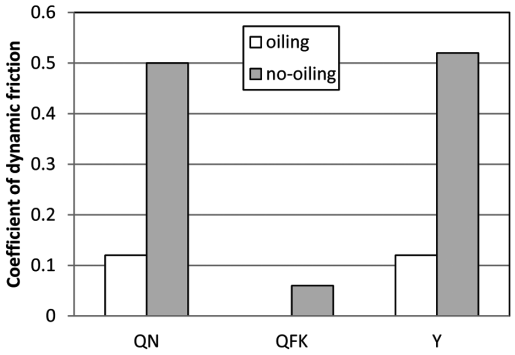

Fig. 5 Coefficient of dynamic friction by stainless steel ball sliding test

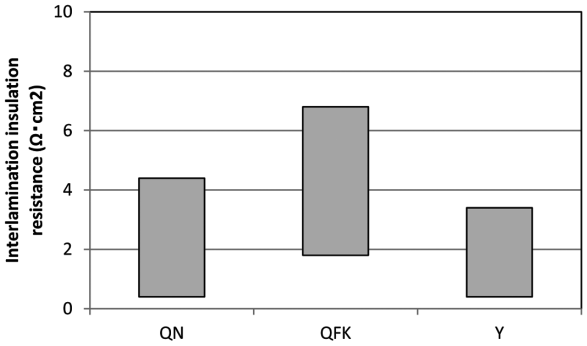

Fig. 7 Interlamination insulation resistance

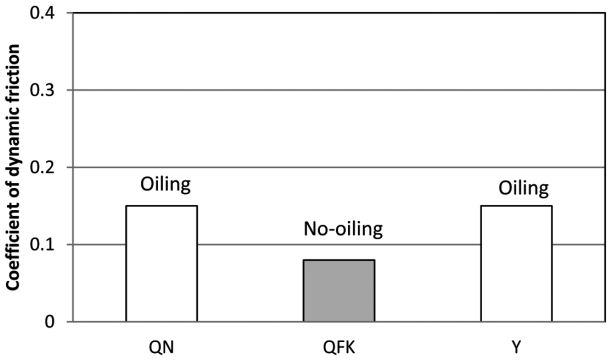

Fig. 6 Coefficient of dynamic friction by flat draw bead test

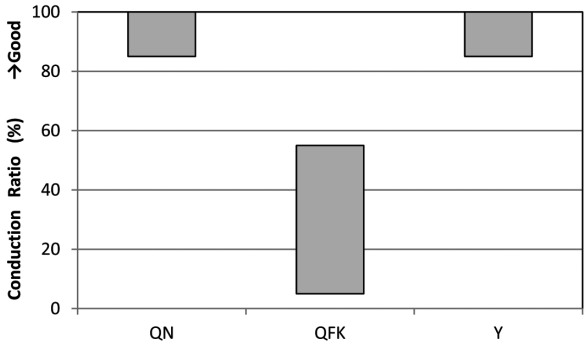

Fig. 8 Result of contact resistance: conduction ratio by LORESTA

in dynamic friction coefficient as the Y-treatment, whereas the QFK type showed a smaller dynamic friction coefficient even without lubrication.

4.3 Conductivity

Figures 7 and **8** show the interlayer and contact resistance of each test piece, respectively. The QN type is nearly similar in interlayer resistance as the Y-treatment, whereas the QFK type has an interlayer resistance slightly higher than that of the Y-treatment. This is because of the film design for QFK that attached importance to corrosion resistance.

4.4 Paintability

Table 2 shows the paintability of each test piece. Both QN and QFK are comparable in paintability to the Y-treatment.

Table 2 Results of finishing paint adhesion

Kind of treatment	Result
QN type	○
QFK type	○
Y treatment	○

○: Excellent, △ : Good, ×: Poor

5. Conclusion

As described above, the chromate-free SuperDyma™ is equal or superior in corrosion resistance, lubricating ability, conductivity, and paintability to conventional chromate-treated steel sheets, and hence it can be substituted for a chromate-treated steel sheet. In addition, obtaining better corrosion resistance and formability by selecting the optimum film type is possible. Moreover, selection of optimum chromium-free steel sheet according to a specific purpose is also possible. Under the growing movement to reduce the emissions of environmentally hazardous substances, it is expected that the chromate-free SuperDyma™ will find various applications in the future.

References

1) Morimoto, Y. et al.: Shinnittetsu Giho. (377), 22 (2002)
2) Kubo, Y. et al.: Shinnittetsu Giho. (391), 48 (2011)
3) Morishita, A. et al.: Shinnittetsu Giho. (377), 28 (2002)

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