

# Properties of Chromium-free Coated Steel Sheet “GEO-FRONTIER-COAT”

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*A new chromium-free coated steel sheet “GEO-FRONTIER COAT” was developed for electrical appliances as the centerpiece of NKK’s new series of environment-friendly steel sheets. A major advantage of the new product is that it has the excellent corrosion resistance, even after alkaline degreasing. It is due to a proprietary organic composite coating on galvanized steel sheet. GEO-FRONTIER COAT is a new product with a good balance of corrosion resistance, anti-fingerprint property, conductivity and paint adhesion. Another new chromium-free organic composite coated product, “GEO-FRONTIER COAT type-L” was developed that has excellent lubrication property.*

## 1. Introduction

Chromate treatment is widely used as an inexpensive method to control white rust from zinc on galvanized steel sheets. As corrosion prevention technology advances and the demand for higher performance has increased, the chromate treatment process has been increasingly employed for coated steel sheets for household electrical appliances<sup>1)</sup>.

Chromate treatment uses a solution containing hexavalent chromium. Completely closed systems for treating waste water from manufacturing processes have been implemented as measures for environmental conservation, along with the development of dry-in-place chromate coating technologies that do not require water washing<sup>1,2)</sup>. Some researches for making dry-in-place chromate coatings even less soluble have been carried out<sup>4)</sup>. In addition, organic composite coated steel sheets have been developed that consist

of chromate coating and thin organic composite coating. The thin organic coating prevents elution of the trace hexavalent chromium contained in the chromate coating<sup>3)</sup>.

Recently, however, the concept of environmental conservation has gone beyond mere pollution control as represented by such terms as air pollution control or water pollution control. The concept of environmental control being accepted today is elimination or containment to the extent possible of potential dangers or environmental risks that could emerge in one way or another in the future<sup>5)</sup>. This new concept of environmental control finds expression in the PRTR (Pollutant Release and Transfer Register) system and in the practice of green procurement that is increasingly adopted by the household appliance manufacturing industry.

Under these circumstances and in anticipation of the growing need for environment-friendly products,

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NKK has developed chromium-free coated steel sheets to completely free of to completely conform to the requirements of global environmental conservation. As a result of this endeavor, NKK successfully commercialized its proprietary, high-performance, chromium-free coated steel sheet, or “GEO-FRONTIER COAT” (GF). Along with GF, NKK also commercialized “GEO-FRONTIER COAT type-L” (GFL), a chromium-free coated steel sheet with excellent lubricating properties. This paper reports development of these two products.

## 2. Problems with conventional chromium-free coated steel sheets

Various aspects of chromium-free coated steel sheet have been studied. Among the reported studies are (1) the formation of a passivation film of molybdenum, which falls in the same group as chromium on the periodic table<sup>6)</sup>, (2) formation of a barrier coating of a biphosphate salt<sup>7)</sup> and (3) chelating effect as tannic acid<sup>8)</sup>. These are, however, inferior to the chromate coating in its barrier effect and self-healing effect, and inferior to that in its corrosion resistance. So these have not been commercialized as a substitute for chromate treated galvanized steel sheets. Recently, a molybdic acid/phosphoric acid-based passivation coating<sup>9)</sup> and the application of a 3  $\mu$  m or thicker coating consisting of a water-borne resin and a phosphate-based corrosion inhibitor<sup>10)</sup> have been proposed. These technologies have not yet been developed sufficiently to excel and replace chromate coating in corrosion resistance or in cost.

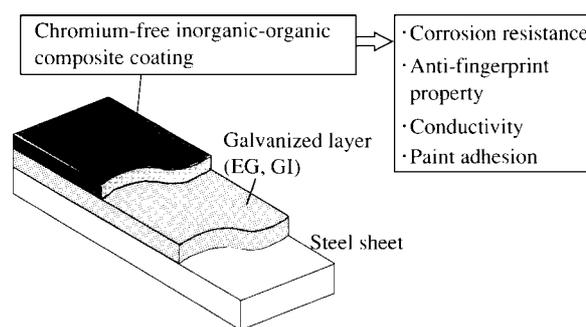
## 3. Development concept and target of GEO-FRONTIER-COAT

GF was designed to achieve comparable performance to usual organic composite coated steel sheets (chromate coating and thin organic coating of 1 to 2 microns)<sup>3, 11–13)</sup>, which are rapidly finding expanding uses notably in OA equipment, in such quality items as corrosion resistance, anti-fingerprint property, electrical conductivity (or grounding conductivity and spot weldability), and paint adhesion.

**Fig. 1** schematically shows the structure of the GF coat. GF has a thin layer of a specially developed organic composite coating that is developed on the galvanized surface of either electro-galvanized or hot-dip galvanized steel sheet. This special layer of organic composite coating is endowed with excellent corrosion

resistance consisting of excellent barrier and self-healing effects, coupled with superior anti-fingerprint and paint adhesion.

Some users of steel sheets use alkaline degreasing to remove oil and grease from the surface after press processing of steel sheets. Alkaline decreasing can damage the surface coat of conventional chromium-free steel sheets, thereby seriously decreasing the corrosion resistance. One of the development objectives of GF was to form a coating that could retain good corrosion resistance after alkaline degreasing.



**Fig. 1** Cross-sectional view of GF

## 4. Experimental method

A GF (coated on electro-galvanized steel sheet with 20 g/m<sup>2</sup> zinc) was prepared to have properties equal to a conventional organic composite coated steel sheet. Another sheet (GF) was also prepared with a thinner layer of the special organic composite coating to provide a good balance of corrosion resistance and good electrical conductivity.

Electro-galvanized sheets with the following three different coats were prepared as controls: (A) an organic composite coating (20 mg/m<sup>2</sup> coated chromium + 1  $\mu$  m organic composite resin coating), (B) a dispersed-silica-containing dry-in-place chromate (30mg/m<sup>2</sup> coated chromium), and (C) a reacted-in-place chromate coat (20 mg/m<sup>2</sup> coated chromium). In addition, (D) an electro-galvanized sheet coated with the same organic composite as that on (A), but with a thickness of about 2  $\mu$  m and without the chromate coating, was prepared as an example of sheet not containing hexavalent chromium.

**Table 1** shows test specimens.

### (1) Corrosion resistance

The edges and backs of the specimens were covered with a sealing tape. The specimens were then subjected to the (JIS Z2371) salt spray test, and the condition of white rust generated after 72 hours was observed. Also, a salt spray test was done after alka-

**Table 1 Test specimens**

GF	
Thinner coating	Thinner inorganic-organic composite coating
A	Chromate coating(Cr 20mg/m <sup>2</sup> ) +organic composite coating(1 μ m)
B	Dry-in-place chromate coating(Cr 30mg/m <sup>2</sup> )
C	Conventional chromate coating(Cr 20mg/m <sup>2</sup> )
D	Chromate-free organic composite coating(2 μ m)

line degreasing (10 g/liter, 60 °C, 2 min. spraying) using CL-N364S by NIHON PARKERIZING CO., LTD.

(2) Anti-fingerprint property

The specimens were immersed in an artificial sweat solution, dried and compared for color difference, E, before and after the treatment.

(3) Electrical conductivity

The JIS C2550 method was used to measure the inter-layer resistance of the coating. A four-pin-probe Lolesta AP (Mitsubishi Chemical Co., Ltd.) with ASP probe measuring terminals was used to measure the surface resistance.

(4) Spot weldability

Determination of the optimum range of welding current was done using Cu-Cr electrodes under a welding force of 300 kgf, and continuous spot welding tests were done on 1.2 mm thick sheets. The results of continuous spot welding tests were evaluated in terms of the weld nugget diameters.

(5) Paint adhesion

After alkaline degreasing using CL-N364S of NIHON PARKERIZING CO., LTD. (60 °C, 2 min. spraying), the specimens were painted with thermo-

setting paint consisting of a melamine alkyd resin, Delicon #700 of Dai Nippon Toryo Co., Ltd. to a film thickness of 30 μ m. The specimens were tested for paint and wet adhesion, the latter after immersion in boiling water for two hours. The paint adhesion performance was evaluated by the Erichsen method. In this method a cross cut portion was tested first for the degree of peeling of the paint when a pressed tape was detached; and second by the degree of paint peeling by pulling a pressed tape after the cross cut area had been extruded to a length of 5 mm.

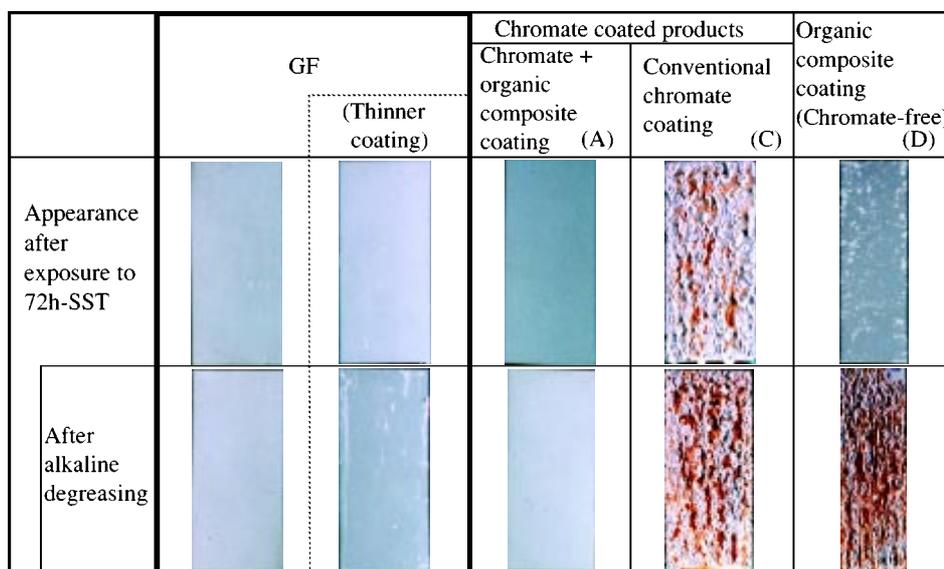
(6) Coefficient of friction

Coefficient of dynamic friction was measured by using a bead, which was made of SKD11 and measured 1 mm by 12 mm on the flat portion of the tip, under a pressure of 80 N/mm<sup>2</sup> at a drawing speed of 500 mm/min.

**5. Characteristics of GEO-FRONTIER-COAT**

**5.1 Corrosion resistance, corrosion resistance after alkaline degreasing**

**Photo 1** shows the appearance of specimens after the salt spray test. One specimen was subjected to the salt spray test only, while the other was subjected to alkali degreasing before the salt spray test. The evaluation was based on conditions after a 72 hour salt spray. GF exhibited excellent corrosion resistance without growing white rust on its flat portion, as was the case for the organic composite coated sheet (A). GF showed virtually no decline in corrosion resistance, even after alkali degreasing. Specimen (D), a sheet coated with an organic resin without a chromate coating, exhibited



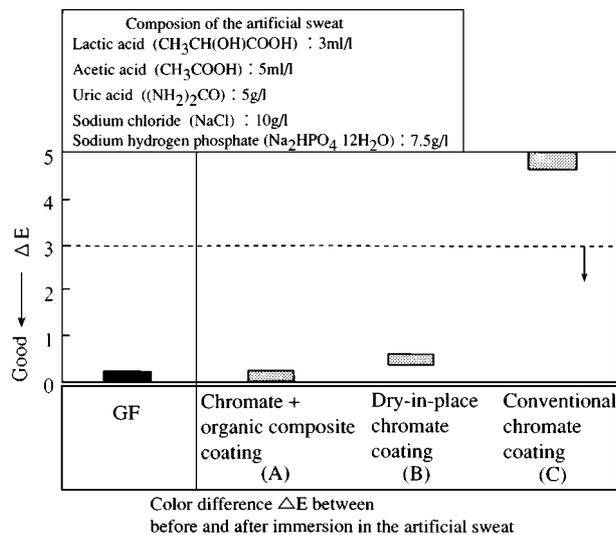
**Photo 1 Corrosion resistance of various coated steel sheets**

white rust. The organic resin coat peeled after alkaline degreasing, and the sheet grew red rust in the corrosion test. These results indicate that the special organic composite coating makes GF particularly resistant to corrosion.

GF (thinner coating) did not grow white rust when tested without alkaline degreasing, which is indicative of its excellent corrosion resistance.

### 5.2 Anti-fingerprint property

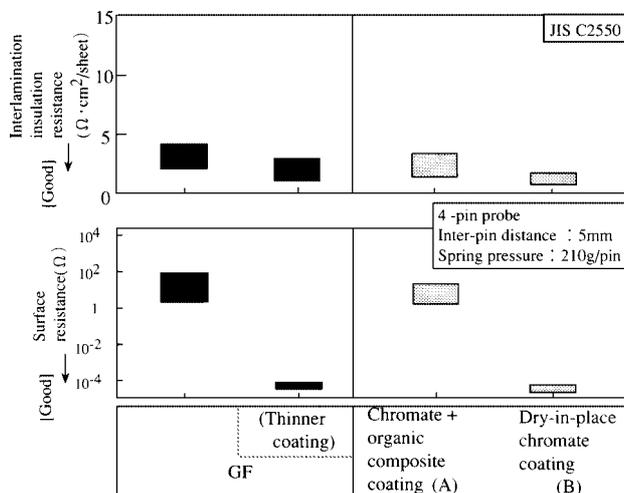
GF, like organic composite coated steel sheet (A), exhibited  $E < 1$  ( $E$  of less than 1) after immersion in artificial liquid sweat. This result is indicative of excellent anti-fingerprint property. (Refer to **Fig. 2**.)



**Fig. 2 Anti-fingerprint property of various coated steel sheets**

### 5.3 Electrical conductivity

**Fig. 3** shows the inter-layer and surface resistance. GF showed values of inter-layer resistance and surface resistance that are comparable to those of the organic

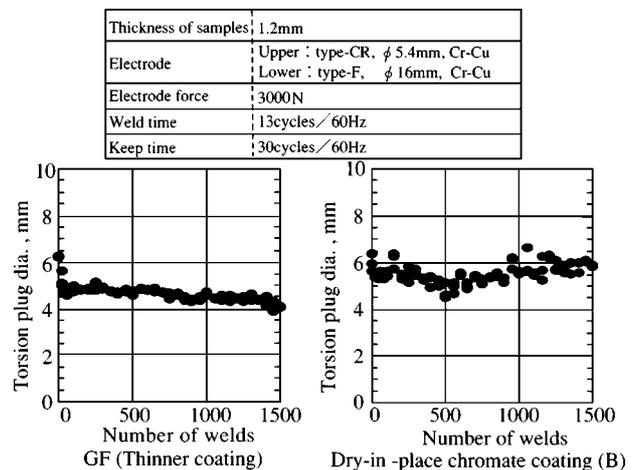


**Fig. 3 Electric resistance of various coated steel sheets**

composite coated sheet (A). GF (thinner coating) demonstrated superior inter-layer resistance and surface resistance. It may be noted from **Photo 1** and **Fig. 3** that the special organic composite coating of the thinner film GF is effective for uses that require a balance of good corrosion resistance and excellent electric conductivity.

### 5.4 Spot weldability

**Fig. 4** shows the results of a continuous spot weldability test on GF (thinner coating) and dry-in-place chromate sheet (B), as an example of weldability. GF (thinner coating) exhibited good continuous spot weldability that is comparable to dry-in-plate chromate sheet (B). As is the case above, the organic composite coat of the thinner film GF is suited to applications that require a balance of good corrosion resistance and excellent weldability.



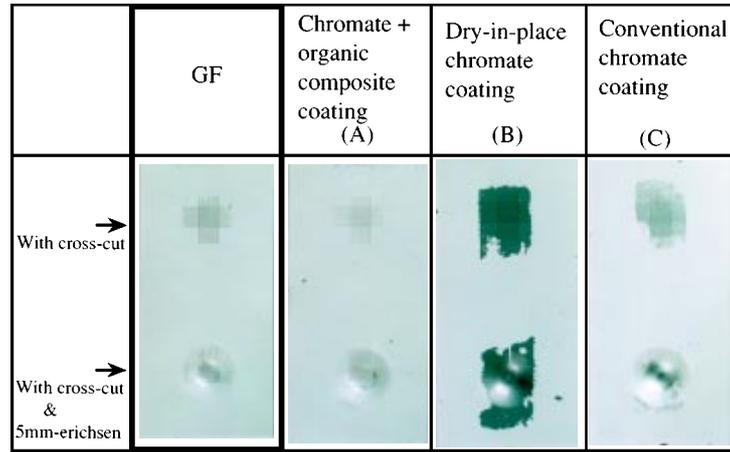
**Fig. 4 Weldability of GF and chromate coated steel sheet**

### 5.5 Paint adhesion

GF showed good paint adhesion and wet adhesion after immersion in boiling water that is comparable to those of organic composite coated steel sheet (A). (See **Photo 2**.)

## 6. Development of “GEO-FRONTIER COAT type-L”

There is an increasing demand for steel sheets with excellent lubrication that do not require lubricating oil for severe processing that stems from the desire to eliminate the degreasing process and improve the environmental impact of the sheet-processing industries. The chromium-free, coated steel sheets have to meet the same requirements. GEO-FRONTIER COAT type-L (GFL) was developed by combining the corrosion-

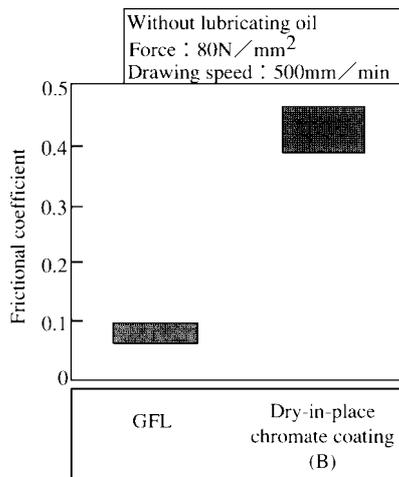


(Paint) melamine-alkyd resin painting  
 (Paint condition) thickness : 30  $\mu$ m, curing : 130°C  $\times$  30min  
 (Paint adhesion test) after immersion in boiling water for 2 h

**Photo 2** Appearance of various coated steel sheets after paint adhesion test

resistant coating technology of GEO-FRONTIER COAT with technology for preparing coating with excellent lubrication and corrosion resistance.

**Fig. 5** shows the results of measurements of the coefficient of friction of GFL. The measured coefficients of friction were 0.1 or lower, indicating good lubricat-



**Fig. 5** Frictional coefficient of GFL and chromate coated steel sheet

ing property. In addition, GFL has excellent corrosion resistance, anti-fingerprint property, electrical conductivity and weldability.

## 7. Summary of quality performance

**Table 2** summarizes the properties of these developed products. GF exhibits corrosion resistance, anti-fingerprint property, electrical conductivity and paint adhesion that is comparable to the present organic composite coated steel sheets. Therefore, GF is suited to applications such as the chassis of OA and AV devices, which require all of these properties. For applications that require a good balance of good corrosion resistance and excellent electrical conductance (good grounding property and good weldability), the thin coating GF with its thin film of special organic composite coating is a good selection. GFL is best suited for processing for deep drawing without using lubrication oil, because of its excellent lubricating property, corrosion resistance and electrical conductivity.

**Table 2** Properties of GF and GFL

	Corrosion resistance	Anti-fingerprint	Conductivity	Paint adhesion	Lubricity
GF	◎	◎	○	◎	○
(Thinner coating)	○	◎	◎	◎	○
GFL	◎	◎	○	○	◎
Chromate +organic composite coating	◎	◎	○	◎	○
Dry-in-place chromate coating	○	○	◎	△	○

◎ : Excellent, ○ : Good, △ : Fair

## 8. Conclusion

The increasing tendency toward green procurement in the household electrical appliance industry prompted the development of the high-performance, chromium-free coated steel sheet, "GEO-FRONTIER-COAT." The GEO-FRONTIER-COAT has achieved a high level of corrosion resistance that was conventional unachievable with conventional chromium-free products, by virtue of its proprietary special organic composite coating. Actually, GEO-FRONTIER-COAT is endowed with excellent qualities such as corrosion resistance, anti-fingerprint property, electrical conductivity and paint adhesion that are equal to those of cur-

rent organic composite coated steel sheet. Steel sheets with a thinner film of the special organic composite coating can meet those demands that require good corrosion resistance and high electrical conductivity. In addition, "GEO-FRONTIER-COAT type-L" with excellent lubrication was developed for applications that include difficult forming. These chromium-free, coated steel sheets, which were developed from NKK's proprietary technologies, are innovative products that can reduce hazardous emissions that were previously difficult to reduce using any conceivable substitute. These products have attracted much attention both at home and abroad.

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