Chromium-free Coated Steel Sheet “GEO-FRONTIER COAT” and Chromium-free Prepainted Steel Sheet “GEO-FRONTIER EXCEL COAT” for Electrical Appliances

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The centerpieces of NKK’s new series of environmentally friendly steel sheets, a new chromium-free coated steel sheet “GEO-FRONTIER COAT” and a new chromium-free prepainted steel sheet “GEO-FRONTIER EXCEL COAT”, have been developed. The major advantage of “GEO-FRONTIER COAT” is that it has excellent corrosion resistance comparable to conventional chromate coated steel sheets even after alkaline degreasing. This property is due to a proprietary organic composite coating. It is a new product with a good balance of corrosion resistance, electrical grounding properties, and is easy to weld. While developing “GEO-FRONTIER EXCEL COAT”, a new type of primer coating was designed in order to achieve excellent corrosion resistance comparable to that provided by the conventional chromate-based prepainted steel sheet.

1. Introduction

Chromate coating of galvanized steel sheets is effective at suppressing the formation of white rust on the zinc coating layer. This technique is widely applied as an economical method of corrosion prevention. In line with advances in corrosion prevention technology and the increasing demand for high-quality materials, various coated steel sheets and prepainted steel sheets with excellent properties are increasingly being used for producing electrical appliances[1),2)].

The chemical liquid used in chromate coating contains hexavalent chromium (Cr^{+6}). Various environmental measures have been taken during the production process and while applying the product. The Japanese environmental standard for Cr^{+6} is less than 0.05 mg/l. The water quality survey carried out in 1998 by the Environment Agency of Japan indicated that there were no sites in Japan that had water quality measurements exceeding this standard. This confirmed the fact that the environmental measures had been firmly established for preventing the release of Cr^{+6} from sites where it was in use[3)]. However, society’s increasing environmental awareness in recent years has promoted the move toward reducing the use of environmentally harmful substances. The EC Commission’s Proposal on Waste Electrical and Electronic Equipment[4),5)] includes a stipulation concerning restricting or prohibiting the use of substances such as Pb, Cr^{+6}, Cd, and Hg. Progress on this proposal is drawing attention.

In response to society’s need for new, environmentally compatible products, NKK has endeavored to develop coated steel sheets that are environmentally friendly. As a result, a unique chromium-free coated steel sheet, “GEO-FRONTIER COAT” (GF) with excellent properties has been successfully developed[6)-8)]. In addition, a chromium-free coated steel sheet, “GEO-FRONTIER COAT Type-L” (GF-L) that has surface lubricity, has also been developed. A chromium-free prepainted steel sheet for electrical appliances, “GEO-FRONTIER EXCEL COAT” (GF-E) has been developed by applying a new unique form of primer design.

2. Developing the chromium-free coated steel sheet “GEO-FRONTIER COAT”

2.1 Problems with conventional chromium-free coated steel sheet

A number of studies have been carried out in the past on technologies that could replace chromate coating with some other methods that did not use chromium. Methods

reported include: (1) molybdate coating[9], which was expected to have a passivation effect comparable to Cr; (2) tannic acid coating[10], which was expected to have a chelate effect with zinc through the OH radical; (3) silicate[11] and electrolytic phosphate coatings[12], which were expected to exhibit barrier effects using inorganic polymer compounds, and (4) organic coating[13] such as polyolefin and acrylic resin. However, the level of corrosion resistance achievable with these technologies is generally inferior to that of chromate coating. In order to secure sufficient levels of corrosion resistance, it is necessary to apply a thick coating of more than 3 μm, which inevitably degrades the electrical grounding properties and weldability[13]. To date these shortcomings have hindered the wide use of these chromium-free technologies.

2.2 Developing “GEO-FRONTIER COAT”

2.2.1 Coating design concept

Generally, corrosion resistance increases with increasing thickness of the organic composite coating, as a result the electrical grounding properties and weldability suffer. In order to secure good electrical grounding properties, the coating thickness needs to be less than 1 to 2 μm. Conventional chromium-free technologies apply a thick coating of more than 3 μm to ensure corrosion resistance.

While developing GF, the following two unique new technologies were developed: (1) an organic coating that has an excellent barrier effect, and (2) inorganic corrosion inhibiting additives that have a self-healing effect on the organic coating. By combining these unique technologies, a highly corrosion resistant organic composite coating was achieved without sacrificing the electrical grounding properties (**Fig.1**)[6].

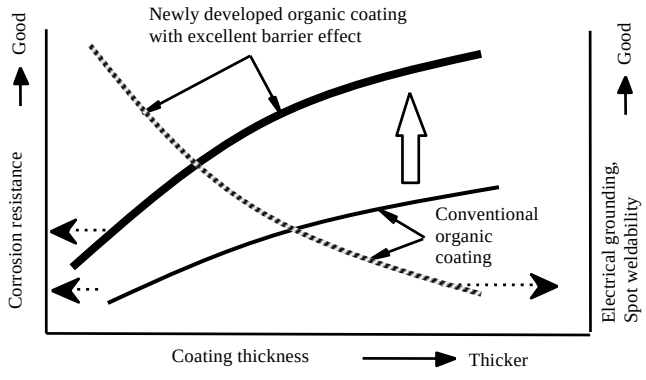


Fig.1 Basic concept of new chromium-free organic composite coating[6]

(1) Developing a new organic coating with excellent barrier properties

The relationship between the oxygen permeability coefficient and corrosion resistance was investigated for various types of organic coatings. It was found that an organic coating that has a lower oxygen permeability coefficient, and hence a higher barrier effect, exhibits higher corrosion resistance. Modified epoxy resin was found to have a particularly low oxygen permeability coefficient, and hence a higher corrosion resistance (**Fig.2**)[14]. Based on this finding, a specially modified epoxy resin was developed.

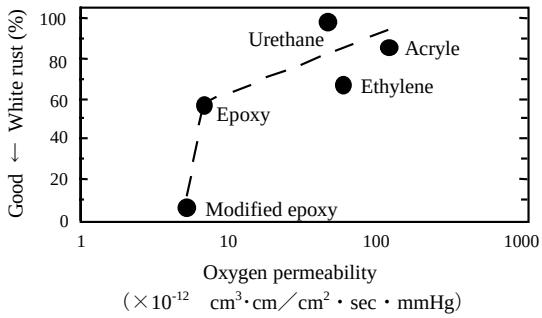


Fig.2 Relationship between O_2 permeability coefficient and corrosion resistance of various organic coatings[14]

(2) Developing inorganic corrosion inhibiting additives exhibiting a self-healing effect

Various corrosion inhibitors were added to the newly developed epoxy resin, and their self-healing effects were investigated. As a result, unique silica-based corrosion-inhibiting additives were identified.

2.2.2 Quality performance of “GEO-FRONTIER COAT”

(1) Corrosion resistance before and after alkaline degreasing

Corrosion resistance properties of various types of coated steel sheets were evaluated by 72 hours of SST (Salt Spray Testing) before and after alkaline degreasing. The results are shown in **Fig.3**. GF did not generate any white rust, and demonstrated high corrosion resistance comparable to chromate coated steel sheets. After press forming, some users apply alkaline degreasing to remove oil and other contaminants from the steel surface. The surface coatings of conventional chromium-free coated steel sheets are easily degraded by alkaline degreasing, and their corrosion resistance significantly lowered. GF’s corrosion resistance was not significantly affected by alkaline degreasing, and excellent properties were maintained.

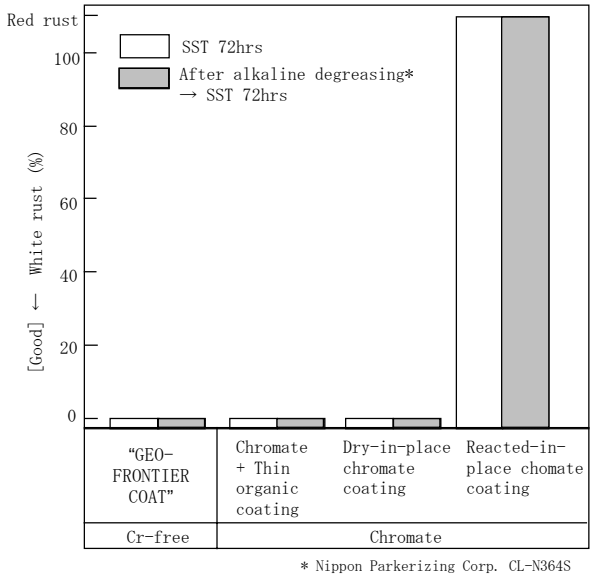


Fig.3 Corrosion resistance of various coated steel sheets

(2) Spot weldability

GF has a very thin surface coating, which assures excellent electrical grounding properties and weldability. Ricoh Company, LTD., a major Japanese copying machine manufacturer, evaluated spot weldability of chromium-free steel sheets produced by four major Japanese steel manufacturers. The result was reported in the magazine, Nikkei Mechanical. **Fig.4** is a quote from this magazine. GF was judged No.1 in terms of quality performance[15].

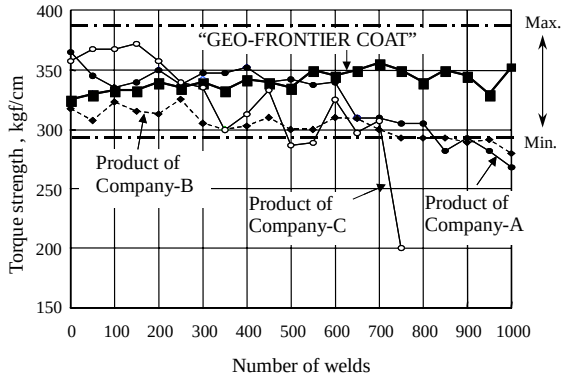


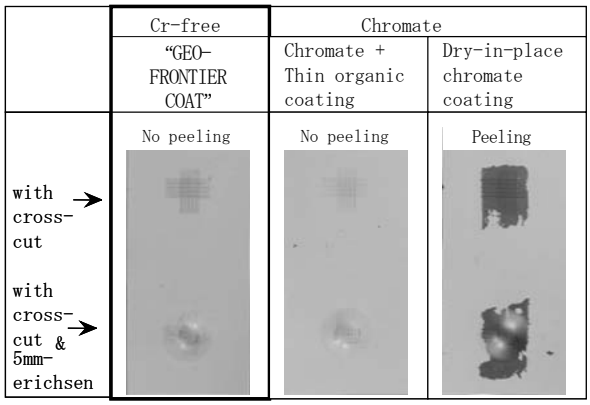
Fig.4 Weldability of various Cr-free coated steel sheets developed by major Japanese steel manufacturers[15]

(3) Anti-fingerprint properties

Due to the effect of the organic composite coating, GF has excellent anti-fingerprint properties, making fingerprints left on its surface less noticeable.

(4) Paint adhesion

Melamine-alkyd resin painting (Dai Nippon Toryo Co., Ltd.’s paint type Delicon #700) was applied on GF and chromate coated steel sheets, the sheets were then immersed in boiling water for two hours and subjected to tape peeling tests. **Photo 1** shows the appearance of the sheets after the tests[7]. Again, owing to the organic composite coating, GF exhibited excellent paint adhesion properties.



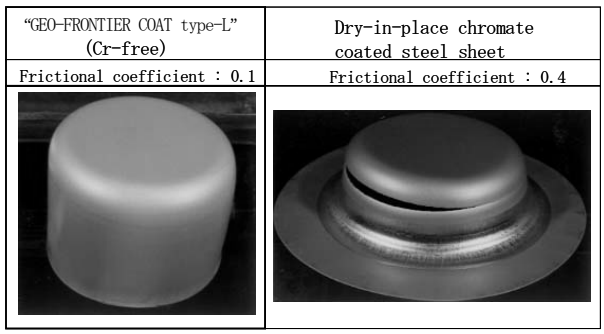
(Paint) Melamine-alkyd resin painting
(Paint condition) Thickness : 30 μm, Curing : 130℃×30min
(Paint adhesion test) After immersion in boiling water for 2 hours → Tape peel test

Photo 1 Appearance of various coated steel sheets after paint adhesion test[7]

2.3 Developing the lubricating “GEO-FRONTIER COAT Type-L”

In the light of environmental concerns and eliminating the degreasing process, customers’ demands are increasing for lubricating steel sheets that allow press forming of hard-to-form components without applying lubricating oil. In response to this demand, NKK developed GF-L[7].

Photo 2 shows the test result where GF-L was draw-formed into a cup without applying lubricating oil. GF-L has a frictional coefficient of less than 0.1 and has excellent lubricating properties. GF-L also has excellent corrosion resistance, anti-fingerprint and electrical grounding properties, and weldability.



Frictional coefficient condition	
Force on sample by bead	80N/mm²
Drawing speed	500mm/min

Cup drawing condition
Blank dia. : φ100mm
Punch dia. : φ50mm
Punch R : 7.5mmR
Die dia. : φ53.6mm
Steel sheet thickness : 1.0mm
Blank hold force : 10^4 N

Photo 2 Appearance of GF-L and chromate coated steel sheet after cup draw-forming

2.4 Features of “GEO-FRONTIER COAT”

GF has excellent corrosion resistance, electrical grounding and anti-fingerprint properties, and paint adhesion. These multi-functional properties make it most appropriate for use in applications such as OA and AV product chassis. GF-L is the most appropriate product for lubricant-free press forming or hard-to-form component forming. This is due to GF-L’s excellent lubricity, corrosion resistance and electrical grounding properties.

GF and GF-L were launched on to the market in 1998 and 1999 respectively and are being widely used for applications such as OA and OA chassis. Customers are very pleased with the results.

GF was given the Technology Award, 2002 by the Surface Finishing Society of Japan, an organization representing Japan in the field of surface finishing including metal coating, organic or inorganic coating, painting, and dry processes[8]. The Society recognized the product’s innovativeness and uniqueness in terms of “the development of an organic composite coating with a high barrier effect that achieves excellent corrosion resistance using a thin coating layer while securing other conflicting properties of excellent electrical grounding property and weldability” as well as the product’s commercial performance of “winning a high reputation among its customers including OA product manufacturers”. Nikkei Business magazine recently reported the commercial success of this new steel product[16].

3. Developing the chromium-free prepainted steel sheet “GEO-FRONTIER EXCEL COAT”

3.1 Conventional chromium-free prepainted steel sheet

Generally, a prepainted steel sheet is composed of a chemical treatment coating layer (formed by chromate or phosphate treatment), a primer coating layer, and a topcoat (paint layer) applied to the surface of the zinc coated steel sheet substrate. The primer coating layer generally contains chromate-type corrosion-inhibiting additives such as strontium chromate. The corrosion resistance of the chromate coated prepainted steel sheet is attributable to the self-healing effect of Cr^{+6} contained in the chemical treatment coating layer and the chromate-type corrosion-inhibiting additives.

Prepainted steel sheets make it possible to eliminate the painting process for the customer. Hence, they make a large contribution to environmental protection by reducing VOC emissions and energy consumption. However, it has been an issue to make them chromium-free, and prepainted steel sheets that contain no chromium have been actively developed since the latter half of the 1990’s. A chromium-free prepainted steel sheet is composed of a chromium-free chemical treatment coating layer, a primer coating layer that contains chromium-free corrosion-inhibiting additives, and a topcoat.

The chromium-free chemical treatment coating layers that have been developed to date do not exhibit as strong a corrosion resisting effect as that of chromate coating layers. Therefore, alkaline or acidic surface adjustment is performed prior to chemical treatment in order to increase coating adhesion, and hence corrosion resistance[17].

Chromium-free corrosion-inhibiting additives are also being developed for primer coating. New types of primer coatings have been reported; for example, the primer coating that uses phosphate and vanadium compounds in combination, and the one that contains ion-exchange pigment. However, these technologies have not been made public in any detail[18),19].

3.2 Chromium-free prepainted steel sheet for electrical appliances “GEO-FRONTIER EXCEL COAT”

NKK’s chromium-free prepainted steel sheet “GEO-FRONTIER EXCEL COAT” (GF-E) is produced by applying a chemical treatment coating layer and a primer coating layer, both chromium-free, on the surface of the hot-dip zinc coated steel sheet substrate, and then applying a topcoat. Since the topcoat does not contain any chromium even in conventional prepainted steel sheets, this new product is completely chromium-free (**Fig.5**).

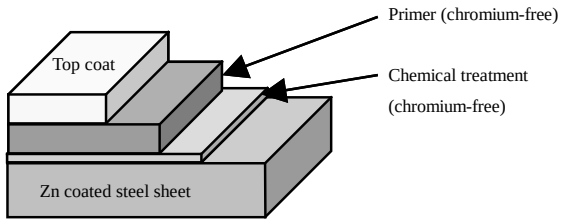


Fig.5 Composition of chromium-free prepainted steel sheet “GEO-FRONTIER EXCEL COAT”

The chromium-free chemical treatment coating layer has excellent adhesion properties. The newly designed primer coating layer, which uses developed resin and corrosion inhibiting additives, makes this steel sheet highly corrosion resistant and at the same time, highly formable. Different types of pigments, each having a different

corrosion-inhibiting effect, are used in combination to achieve high corrosion resistance. The resin used in the primer coating is highly ductile, and its degree of cross-linking is adjusted to obtain formability and corrosion resistance of the highest degree when applied in combination with corrosion-inhibiting additives. **Photo 3** shows the results of SST on prepainted steel sheets designed for use in electrical appliances. GF-E demonstrated a superior level of corrosion resistance to that of the conventional chromate coated steel sheet that was also designed for use in electrical appliances. Formability and other properties are equivalent to those of the conventional product (**Table 1**).

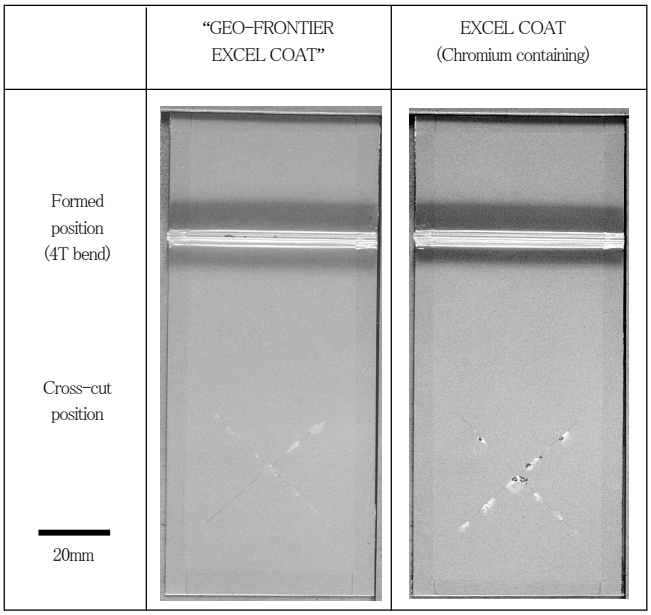


Photo 3 Corrosion resistance (SST, 240 hrs)

Table 1 Main properties of “GEO-FRONTIER EXCEL COAT”

	“GEO-FRONTIER EXCEL COAT”	EXCEL COAT (Chromium containing)
	General type	General type
Galvanizing	Hot dip galvanized steel sheet	Hot dip galvanized steel sheet
Pretreatment	Chromium-free	Chromate
Primer coat	Chromium-free primer (developed)	Chromate primer
Top coat	Oil-free polyester (balance type)	Oil-free polyester (balance type)
Back side	Oil-free polyester, 1 coat	Oil-free polyester, 1 coat
Acid resistance*	No change	No change
Alkaline resistance**	No change	No change
Adhesion after bending***	No peeling	No peeling

*5% acetic acid 24hr , **5% NaOH 24hr, *** 4T bend portion

4. Conclusions

The highly functional chromium-free coated steel sheet “GEO-FRONTIER COAT” was developed in response to expanding environmental needs. In developing this product, a specially modified epoxy resin with the highest barrier effect was combined with unique silica-based corrosion-inhibiting additives that exhibit a self-healing effect. As a result, excellent corrosion resistance was achieved using a thin coating layer while at the same time securing other conflicting properties of excellent electrical grounding properties and weldability. The Surface Finishing Society of Japan recognized the innovativeness, uniqueness, and commercial performance of this product and awarded it the Technology Award in 2002.

For use in electrical appliances, a highly corrosion-resistant primer coating was developed and the chromium-free prepainted steel sheet “GEO-FRONTIER EXCEL COAT” was developed and marketed.

These unique chromium-free coated steel sheets are gathering attention as world-leading products that contribute to the reduced use of environmentally harmful substances that were hitherto difficult to replace.

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