KAWASAKI STEEL TECHNICAL REPORT
No.46 (JUNE 2002)
"Environment-friendly Steel Products" and
"Environment Preservation Technology"

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In the field of electrical appliances, a material used for the chassis needs a good electric-conductivity to accomplish a stable ground property in addition to good white rust resistance. On the other hand, in reply to the social requirement of eliminating hexavalent chromium, which is one of the environmentally un-friendly materials, chromate-free treated electrogalvanized steel sheet has been developed. "RIVER ZINC FC-X" has been developed to meet those requirements. "RIVER ZINC FC-X" shows good white rust resistance, high electro-conductivity and anti-fingerprinting property. Furthermore, "RIVER ZINC FC-E" accomplishes a good frictional property in addition to the performance of "RIVER ZINC FC-X" by applying lubricant wax. The performance of those new products has been found to be good enough for practical uses in comparison with the conventional electrogalvanized steel sheets having a chromate layer.

The body can be viewed from the next page.

Properties of Chromate-Free Coated Electrogalvanized Steel Sheets for Electrical Appliances*


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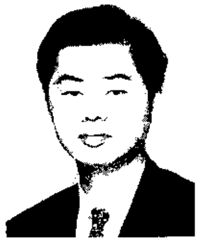
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Synopsis:

In the field of electrical appliances, a material used for the chassis needs a good electric-conductivity to accomplish a stable ground property in addition to good white rust resistance. On the other hand, in reply to the social requirement of eliminating hexavalent chromium, which is one of the environmentally un-friendly materials, chromate-free treated electrogalvanized steel sheet has been developed. "RIVER ZINC FC-X" has been developed to meet those requirements. "RIVER ZINC FC-X" shows good white rust resistance, high electro-conductivity and anti-fingerprinting property. Furthermore, "RIVER ZINC FC-E" accomplishes a good frictional property in addition to the performance of "RIVER ZINC FC-X" by applying lubricant wax. The performance of those new products has been found to be good enough for practical uses in comparison with the conventional electrogalvanized steel sheets having a chromate layer.

1 Introduction

Recently, stricter standards have been applied to household electrical appliances, including peripheral devices for personal computers, telecommunication devices, and copying machines, to prevent damage due to leakage of electromagnetic wave from the chassis at the recommendation of CISPR (International Special Committee on Radio Interference) through voluntary self-regulation under VCCI (Voluntary Control Council for Information Technology Equipment)[1]. Therefore, material used for the chassis needs good electric-conductivity to ensure a stable grounding property, in addition to good white rust resistance. To meet these requirement, the highly corrosion resistant chromate coated steel sheet RIVER ZINC FX[2] (hereinafter called FX), which has surface conductivity equal to that of ordinary electrogalvanized steel, was developed and is now being manufactured. The self-lubricating steel sheet RIVER ZINC FE[3] (hereinafter called FE), which has surface conductivity of the same level as conventional sheets, was also developed.

Chromate films applied to the surface of electrogalvanized steels have an inhibiting effect of hexavalent chromium contained in the film which acts as a barrier against corrosion. Even defective or scratched thin films retain their protective property as a result of the self-healing effect of slow leaching hexavalent chromium compounds when in contact with humid conditions. However, it is necessary to minimize the possibility of environmental pollution because the chromate treatment solution and chromate treated products contain environmentally unfriendly hexavalent chromium compounds. In recent years, the concern about environmental protection is increasing on a worldwide level. The European Union environment ministers have reached a first-reading agreement on directives to introduce producer responsibility for managing waste electrical and electronic equipment (WEEE) and restricting hazardous substances in product manufacture. Under an agreement for restricting hazardous substances in product manufacture, industry will have until January 2007 to find substitutes for lead, mercury, cadmium, hexavalent chromium, and the brominated flame retardants PBB and PBDE, in products. In response to those trends, Kawasaki Steel began to develop a new chromate-free treatment for electrogalvanized steel sheet.

When using conventional chromate-free treatments such as organic composite films, corrosion resistance can be improved by increasing the thickness of the chromate-free film, but thicker chromate-free films have the disadvantage of higher electric resistance. Kawasaki

* Originally published in *Kawasaki Steel Giho*, 33(2001)2, 82-87

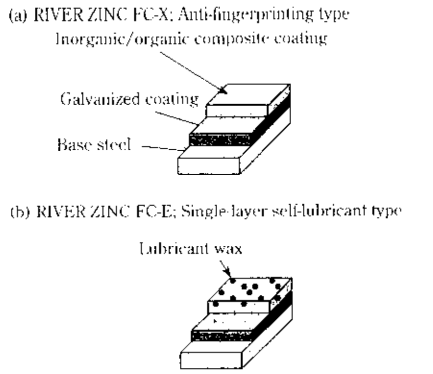

Fig. 1 Cross sectional view of single-layer type chromate-free coating

Steel therefore developed a new chromate-free electrogalvanized steel sheet RIVER ZINC FC-X (see **Fig. 1** (a); hereinafter called FC-X) with excellent corrosion resistance and electrical conductivity by adopting an inorganic/organic composite treatment without any chromium compounds. The self-lubricating chromate-free steel sheet RIVER ZINC FC-E (Fig. 1 (b); hereinafter called FC-E), which has corrosion resistance and surface conductivity on the same level as FC-X, was also developed.

2 Experimental Procedure

The corrosion resistance, electric conductivity, and anti-fingerprint property, and other properties of the newly developed chromate-free electrogalvanized sheets were examined by the methods described below.

2.1 Test Specimens

Table 1 summarizes the test specimens used in this study. The developed chromate-free films were coated on the surface of electrogalvanized sheets (20 g/m^2 Zn coating weight per side). For comparison, FX and FE as dry-in-place chromate treated sheets were used. Organic coated anti-fingerprint sheet RIVER ZINC F (F), and an organic composite coated steel without chromate treatment (G) were also prepared.

Table 1 Test pieces used in this study

Symbol	Type	Coating
FC-X	Chromate-free	Inorganic/organic composite coating (0.8 μm)
FC-E	Chromate-free	Single-layer self-lubricant type coating (0.8 μm)
FX	Chromate	Dry-in-place chromate coating (Cr; 40 mg/m^2)
FE	Chromate	Dry-in-place chromate coating containing polyethylene wax (Cr; 40 mg/m^2)
F	Chromate	Chromate coating (Cr; 30 mg/m^2) + Organic composite coating (1 μm)
G	Chromate-free	Organic composite coating (0.8 μm, 2 μm)

2.2 Corrosion Resistance of Flat and Worked Portions

The specimens were cut into 50 × 100 mm test pieces. The edges and reverse surfaces were sealed with polyester tape. Some of the test pieces were drawn to a 7 mm depth by Erichsen tester. A salt spray test at 35°C was then performed as specified in the Japanese Industrial Standards (JIS) Z-2371. The area covered with white rust on the flat pieces and Erichsen drawn test pieces was visually inspected.

2.3 Electric Conductivity

Measurement of surface electric resistance: The specimen was sheared to a 300 mm × 200 mm size. The average surface resistance was evaluated with a 4-head probe surface resistance meter ("Loresta AP" manufactured by Mitsubishi Chemical Corp.).

Measurement of interlamination insulation resistance: An electro-resistivity measuring device as specified in JIS C2550 (Takei Electric Industries Co., Ltd.) was used for the evaluation. Measurement conditions were pressure force of 1.96 MPa and applied voltage of 0.5 V.

2.4 Fingerprint Resistance

The change in color (L value, a value, b value) of the specimens was measured before and after dipping in an artificial sweat solution (urea NH_2CONH_2: 1 g/ℓ, L-lactic acid: 1 g/ℓ, sodium chloride: 7 g/ℓ, methanol: 500 mℓ/ℓ), using a spectral differential color meter ("SQ2000" manufactured by Nippon Denshoku Industries Co., Ltd.). Evaluations were based on ΔE in Eq. (1). Conventionally, chromate-treated sheets having a anti-fingerprint property show ΔE value of less than 2.

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \cdots\cdots (1)$$

ΔL shows the difference of psychrometric lightness, L.
Δa shows the difference of color tone, a.
Δb shows the difference of color tone, b.

2.5 Chemical Resistance

The change in color (L value, a value, b value) of the specimens was measured before and after dipping in methylene chloride, benzine, alkaline degreasing solution, distilled water, and acetone for 168 h using a spectral differential color meter ("SQ2000"). Evaluations were based on ΔE in Eq. (1).

2.6 Formability

Figure 2 summarizes the 90° bending test method used in this study. Three 1.0 mm thick specimens were bent continuously under conditions of dice clearance 1.0 mm, and drawing speed, 60 mm/s. The appearance of drawn parts after drawing without lubricant oil powdering on the die were evaluated.

The friction property was evaluated by estimating the

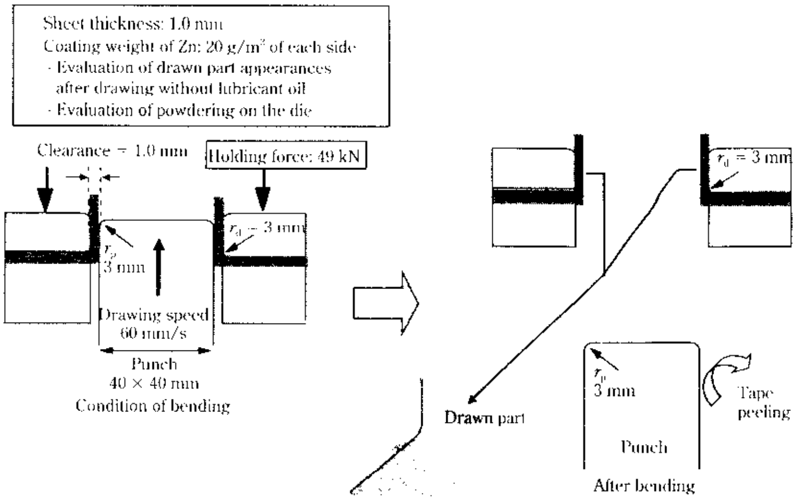

Fig. 2 Appearance of formed part and powdering resistance after 90° bending test

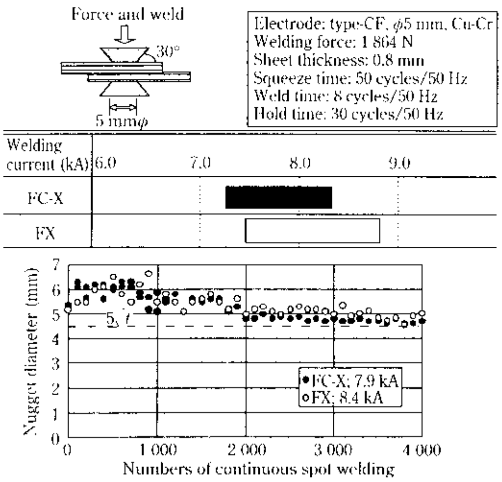

Fig. 3 Spot weldability of FC-X and chromate coated sheet

dynamic friction coefficient μ without lubricant oil. The test specimen was fixed between flat dice with a holding pressure of 9.8 MPa and subjected to sliding in direction D at 20 mm/s. The dynamic friction coefficient, μ was calculated by $\mu = D/2P$, where D is the sliding force and P is the pressure between the dice.

2.7 Adhesion of Finishing Coating (Primary Adhesion)

As specified by JIS K-5400, a melamine-alkyd resin ("Orgaselect 120 white" manufactured by Nippon Paint Co., Ltd.) was bar-coated on the specimens to a coating thickness of 20 μm, followed by baking at 135°C for 15 min and subsequent hardening. Thereafter, 100 cuts of 1 mm × 1 mm (10 × 10 cuts) were made, which penetrated through the coated layer on the specimen and reached the substrate steel, and adhesive tape was placed on the cuts. After peeling from the specimen, the tape was visually inspected to determine the tape surface area to which the coated layer had attached.

2.8 Weldability

Specimens were welded as shown in **Fig. 3**. The electrode shape was a CF (cone flat) type (diameter: ϕ5 mm), the welding force was 1.86 kN, and the welding pattern was such that holding time of 50 cycles, welding time of 8 cycles, cooling time of 30 cycles. After welding, the possible welding current range was estimated by measuring the nugget diameter. The lower limit of the welding current was defined as the point satisfying 5 times the square root of the sheet thickness. The upper limit of the welding current range was defined as the point at which sputter or sticking was observed.

3 Characteristics of "RIVER ZINC FC-X"

3.1 Corrosion Resistance

Figure 4 shows corrosion resistance of FC-X, which has a film thickness of 0.8 μm, compared with FX, which is a dry-in-place chromate coated electrogalvanized sheet with a 40 mg/m² chromate coating weight as Cr. White rust formation was observed after around

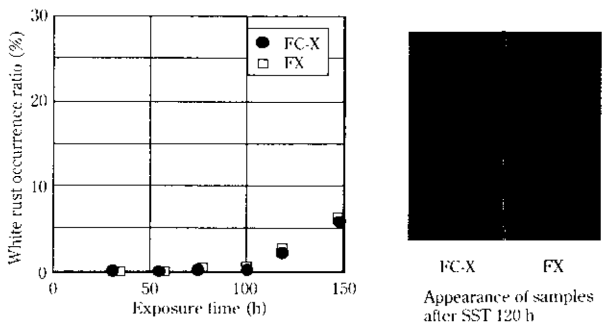

Fig. 4 Corrosion resistance of FC-X and dry-in-place chromate coated steel sheet

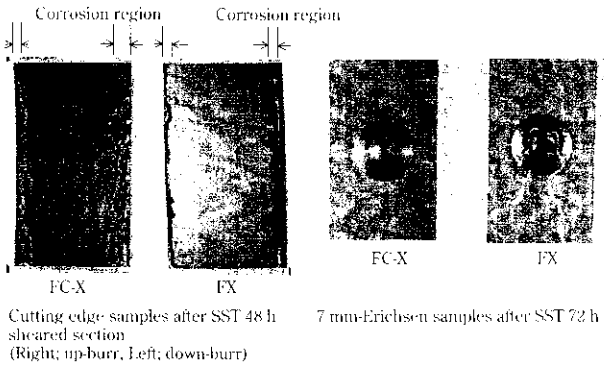

Photo 1 Appearances of cutting edge samples and Erichsen samples after SST

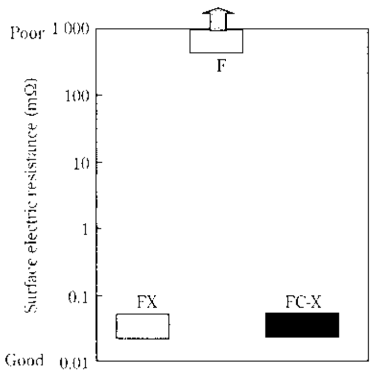

Fig. 5 Surface electric resistance of FC-X and chromate coated steels measured by the 4-head method

100 h in the salt spay test. White rust formation on FC-X was 3% at SST 120 h and 5% at SST 144 h. The anti-white rust property of FC-X was similar to that of the dry-in-place chromate coated electrogalvanized sheet, FX. **Photo1** shows the appearance of cutting edge samples and Erichsen samples after the SST. The anti-white rust property of FC-X at the cut edge region was equal to that of FX. In an evaluation of white rust formation at the drawing part in the Erichsen-draw test, FC-X showed corrosion resistance superior to FX.

3.2 Electric Conductivity

Electric conductivity was estimated by measuring the surface electric resistance and interlamination insulation resistance. Surface electric resistance was measured by the 4-head method as specified in JIS-K9174. An ASP type probe was used as the electrode. The measurement condition was 210 g per head of applied pressure. **Figure 5** shows the surface electric resistance of FC-X and chromate coated steels measured by the the 4-head method. The surface electric resistance of FC-X was extremely low compared with that of the organic coated anti-fingerprint sheet F. FC-X also showed surface electric resistance equal to that of FX (less than 0.1 mΩ).

Measurement of surface electric resistance by the 4-head method makes it possible to eliminate the influence of contact resistance by separating the applied current probe and applied voltage prove[4,5]. FC-X had surface conductivity equal to that of FX.

Figure 6 shows the interlamination insulation resistance of FC-X and chromate coated steel. The interlamination insulation resistance of FC-X was from 0.5 to 1.0 Ω · cm^2/sheet.

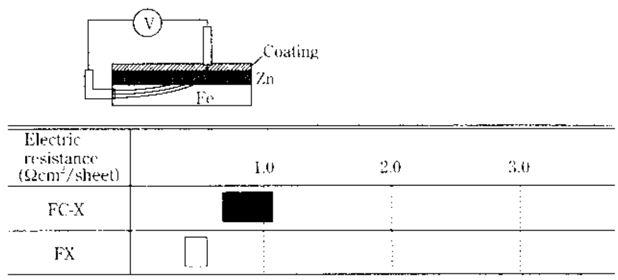

Fig. 6 Interlamination insulation resistance of FC-X and chromate coated steel

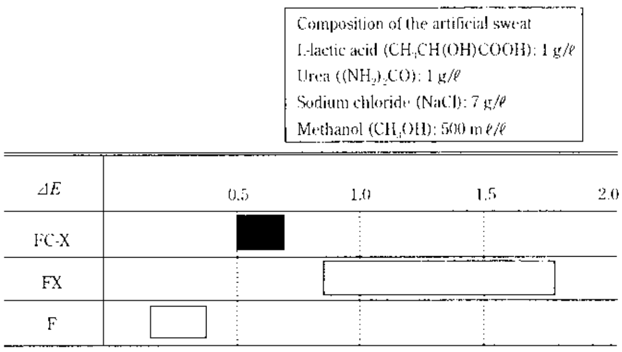

Fig. 7 Anti-fingerprinting property of FC-X and chromate coated steels

3.3 Fingerprint Resistance

Figure 7 shows the change in color, ΔE, before and after dipping of FC-X and chromate coated steels in the artificial sweat solution. The ΔE value of FC-X was less than 1. FC-X showed an anti-fingerprint property equal to that of the organic coated anti-fingerprint sheet F.

3.4 Chemical Resistance

Figure 8 shows the change in color, ΔE, before and after dipping for 168 h in various solvents. FC-X showed chemical resistance similar to that of the chromate coated sheet FX.

3.5 Formability

Figure 9 shows the dynamic friction coefficients μ of FC-X and chromate coated steels without lubricant oil. The μ value of FC-X was from 0.25 to 0.30. This means that FC-X has a frictional property superior to that of FX.

Photo 2 shows the appearances of formed parts and

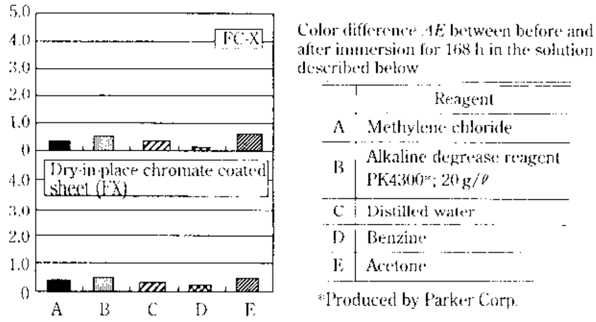

Fig. 8 Anti-chemical property of FC-X and chromate coated steel

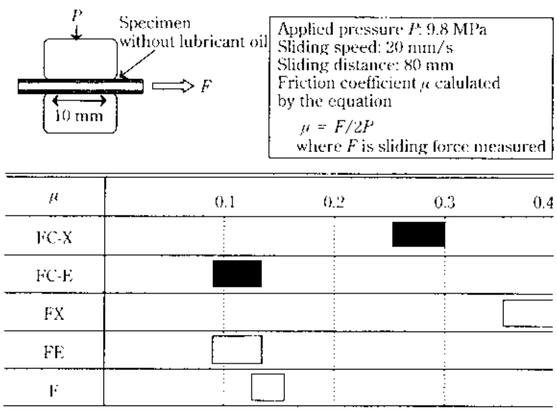

Fig. 9 Frictional coefficients of FC-X, FC-E and chromate coated steels

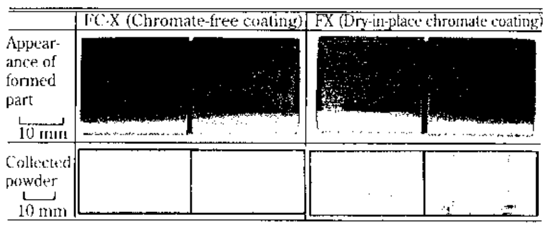

Photo 2 Appearance of formed part and powdering resistance after 90° bending test

powdering resistance after 90° bending test. The formed part of FC-X was free of damage and showed improved formability compared with that of FX. This was attributed to the fact that the FC-X coating layer consists of an inorganic/organic composite and has a better friction property.

3.6 Adhesion of Finishing Coating (Primary Adhesion)

Figure 10 shows the remaining paint ratio after tape peeling and appearance after the paint adhesion test. FC-X showed printability superior to that of FX.

3.7 Weldability

Figure 3 shows the appropriate current range for spot

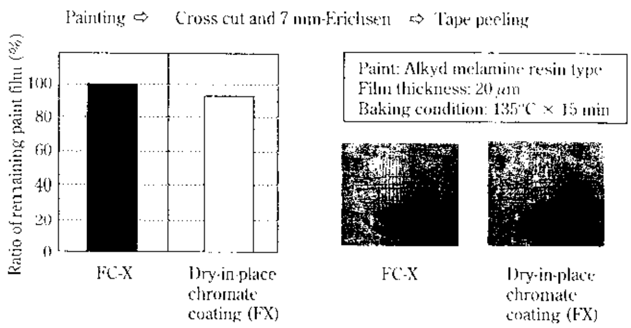

Fig. 10 Appearances of FC-X and chromate coated sheet after paint adhesion test

welding and continuous weldability. The appropriate current range of FC-X was over 1 kA, which was equal to that of FX. The welding current shifted to the lower side, which means that the welding resistance of FC-X is slightly high due to the characteristics of the inorganic/organic film itself and the film thickness of 0.8 μm. The continuous weldability of FC-X was almost as good as that of the chromate coated sheet FX until 4 000 welds.

4 Feature of "RIVER ZINC FC-E"

Single layer self-lubricant type chromate coated steel has been widely used. Because of the increased need for chromate-free coated sheets with lubrication and electric conductivity, "RIVER ZINC FC-E" was developed.

Figure 9 shows the dynamic friction coefficients μ of FC-E and chromate coated steels without lubricant oil. The μ value of FC-E was less than 0.15. This means that FC-E has a frictional property equal to that of FE. FC-E has excellent corrosion resistance, anti-fingerprint property, electric conductivity and printability because the film composition of FC-E consisted of the film used with FC-X and a dispersed polyethylene wax.

5 Summary for Properties of FC-X and FC-E

Figure 11 summarizes the relationship between the electric conductivity measured by the 4-head method and corrosion resistance (time to 5% white rust) of various coated steels. The conventional organic composite coated steel without chromate treatment G showed improved corrosion resistance at a 2.0 μm thickness compared with at a 0.8 μm thickness. However, electric conductivity deteriorated as the thickness of the organic composite film increased. Organic composite coated steels with a chromate coating such as F show excellent corrosion resistance but higher electric resistance. Dry-in-place chromate coated steels, such as FX and FE, have extremely low electric resistance and good corrosion resistance in spite of thinner film thickness (less than 0.1 μm). Newly developed chromate-free steel sheets realize both an anti-white rust property and an

Table 2 Properties of FC-X, FC-E and chromate coated sheets

	Corrosion resistance (h)*1	Anti-fingerprint*2	Surface electric resistance (mΩ)*3	Paint adhesion (%)*4	Lubricity*5
FC-X	≧120	0.5~0.7	<0.1	100	0.25~0.3
FC-E	≧120	0.5~0.7	<0.1	100	<0.15
Dry-in-place chromate coating (FX)	≧120	0.8~1.7	<0.1	95	0.3~0.4
Chromate + Organic fingerprint-resistant coating (F)	≧216	0.2~0.4	~10^5	100	<0.2

*1 Time to 5% white rust occurrence at salt spray test (JIS-Z2371)
*2 Color difference ΔE between before and after immersion in the artificial sweat
*3 Surface electric resistance measured by "Loresta AP" 4-head method
*4 Ratio of remaining paint film at cross cut and 7 mm Erichsen area after tape peeling
*5 Frictional coefficient without lubricant oil

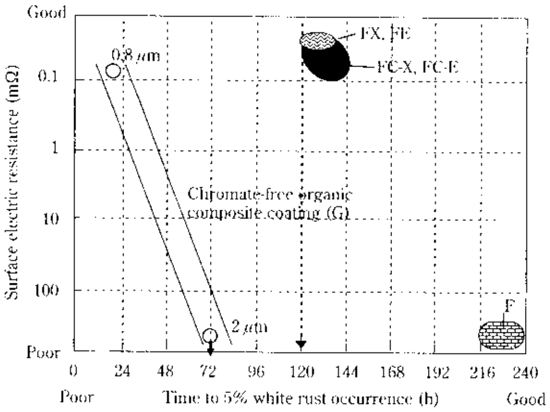

Fig. 11 Relationship between conductivity and corrosion resistance of various coated sheets

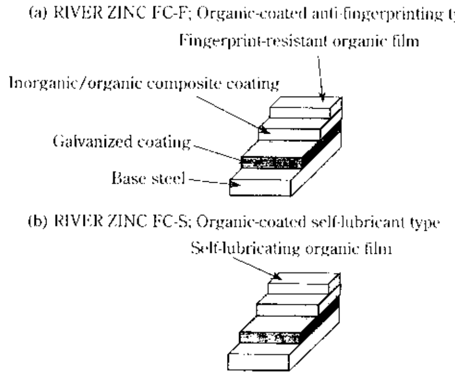

Fig. 12 Cross sectional view of double-layer type chromate-free coating

extremely low electric resistance, comparable to that of the chromate coated steels FX and FE, in spite of their 0.8 μm film thickness because a conductive film is applied.

Table 2 summarizes the properties of FC-X, FC-E, and the chromate coated sheets. FC-X has excellent corrosion resistance and electric conductivity. FC-E has not only an anti-white rust property and surface conductivity on the same level as FC-X, but also a self-lubricant property.

6 Conclusion

Many Japanese electric appliance and copying machine makers have voluntarily introduced so-called "green procurement schemes" for reducing environmentally-unfriendly substances in procured parts and materials. Kawasaki Steel has responded to this trend by developing the new chromate-free electrogalvanized steel sheet, "RIVER ZINC FC-X", which has excellent corrosion resistance and electric conductivity, by adopting inorganic/organic composite treatment without any chromium compounds, and the self-lubricating chromate-free steel sheet "RIVER ZINC FC-E", which has corrosion resistance and surface conductivity on the same level as FC-X.

The company has also developed the double-layer type chromate-free electrogalvanized steels shown in **Fig. 12**. "RIVER ZINC FC-F" is an organic-coated anti-fingerprint type chromate-free steel, which has superior corrosion resistance and an anti-abrading property equal to those of F. "RIVER ZINC FC-S" is an organic-coated self-lubricant type chromate-free steel, which has superior corrosion resistance and press formability without lubricant oil, equal to those of RIVER ZINC FS.

At present, the new chromate-free electrogalvanized steels in the RIVER ZINC FC series, with "RIVER ZINC FC-X" as the core product, are progressively being approved and used by Japanese electric appliance and copying machine makes.

References

1) Y. Hotta, and Y. Sato: "Fundamentals of Electromagnetic Wave Shielding", (1986), 155, [CMC]
2) N. Totsuka, T. Kurisu, T. Ichida, S. Tsugawa, and M. Kawai: *Kawasaki Steel Giho*, **23**(1991)4, 349–350
3) H. Ogata, M. Mabuchi, and Y. Naruse: *Kawasaki Steel Giho*, **27**(1995)3, 190–192
4) T. Nishii: "Monthly Display", (1996)9, 89–94
5) T. Nishii: "The Method for Resistivity of Coating Films", Text of Special Technical Lecture No. 3