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Electro- and Hot-dip Galvanized Steel Sheets Having Cr-free Treatment Layer on the Surface and Cr-free Prepainted Electrogalvanized Steel Sheets

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Abstract

Various types of coated steel sheets, which are among the major products of Nippon Steel's sheet and coil products, have a chromate layer on those surfaces to ensure good white rust resistance and finish-coat adhesion. However, hexa-valent chromium contained in the chromate layer is one of the environmentally un-friendly materials. In reply to our users' requirement of eliminating such materials, we have recently developed a Cr-free electrogalvanized steel sheet "ZINKOAT-21", a Cr-free hot-dip galvanized steel sheet "SILVERZINC-21", and a Cr-free prepainted electrogalvanized steel sheet "VIEWKOAT-21". The performance of those new products have been found to be enough for actual uses in comparison with the conventional coated steel sheets which contain chromium.

1. Introduction

Chromate coating is widely used for surface treatment of thin steel sheet products because of its excellent corrosion resistance performance with a barrier effect against corrosion factors and self-healing ability of film defects as well as its being a good pre-treatment material for finish-coating[1]. In many cases, however, the chromate treatment bath and the chromate-treated products contain environmentally unfriendly hexa-valent chromium and undesirable effects are expected from the preparation of the treatment bath, the chromate treatment process itself, and use and disposal of the chromate-treated products.

In the recent years demands are growing rapidly to cause environmentally unfriendly matters to be eliminated from industrial products, and a draft of the "Proposal for a Council Directive on End of Life Vehicles"[2] was presented to the European Parliament in July 1997 proposing to ban materials containing hexa-valent chromium, Hg, Cd and Pb by the year 2003. Preparations for meeting the requirements of the guideline are being made by European and American carmakers as well as by Japanese counterparts who sell their cars in the areas in question. Also, many of Japanese electric appliance makers on their own have introduced so-called "green procurement schemes"[3] for reducing the environmentally unfriendly matters in the procured parts and materials, and this movement is being successfully carried forward. It is further expected that there will arise a strong general movement to eliminate hexa-valent chromium from the industrial processes from the viewpoint of LCA (life cycle assessment)[4].

Nippon Steel has long been conscious of the above trend and has exercised efforts to developed chromium-free surface-treated sheet products and to commercially launch a Cr-free surface-treated electro-

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galvanized sheet product "ZINKOAT-21". They have also launched a Cr-free surface-treated hot dip galvanized sheet product "SILVERZINC-21". A Cr-free pre-painted electro-galvanized sheet product for indoor use "VIEWKOAT-21" not containing Cr both in the paint pre-treatment and in the anti-corrosion pigments in primer coating was also introduced. This paper reports performances of the developed Cr-free sheet products in comparison with the conventional Cr-containing galvanized products.

2. Galvanized Steel Sheets with Chromium-free Surface Treatment

A new Cr-free film material was developed which could give corrosion resistance (anti-white rust property), finish-coat adhesion and anti-fingerprint properties to the galvanized sheet products by forming a film on the surface of the sheets. The newly developed film has a strong adhesion to the galvanized surface thanks to the effect of a special additive and the corrosion resistance (anti-white rust property) is maintained without Cr due to combined effects of the film and the additive. Since most of the plated/coated steel sheet products are used after some forming work, it is essential that the surface treatment films/layers do not peel off during the work for ensuring the corrosion resistance performance in the actual use. For keeping the corrosion resistance for a long period it is also important to retain the films/layers even under humid conditions.

In consideration of the above, a technology was developed to ensure adhesion of the film without using the chromate treatment. Performance of the galvanized sheets with chromium-free surface treatment was investigated in comparison with those of the conventional chromate-treated galvanized sheets.

2.1 Test method

2.1.1 Specimens

The developed Cr-free films, 0.7 - 1.7 μm thick, were formed on the surface of electro-galvanized sheets (20 g/m^2 per side, hereinafter called EG) and zero-spangle hot dip galvanized sheets (60 g/m^2 per side, hereinafter called GI). For comparison, specimens of EG and GI with a chromate treatment by an applicator (chromium weight 50 mg/m^2) were also prepared.

2.1.2 Evaluation items

a) Corrosion resistance of flat portions and worked portions

The specimens were cut into 70 × 150 mm test pieces. The edges and the reverse surface were sealed with polyester tapes. Some of the test pieces were drawn to 7 mm depth by an Erichsen tester and then they underwent a salt spray test (SST, as specified under JIS Z 2371). The area covered with white rust was visually inspected after 72 hrs of the salt spray in the case of the Erichsen-drawn test pieces and 168 hrs in the case of the flat pieces.

b) Adhesion

(1) Adhesion of the Cr-free film

EG and GI with the Cr-free film were drawn to 8 mm depth by the Erichsen tester and the film at the worked area was peeled with adhesive tapes. After this, the test pieces were immersed in an acetone solution of methyl violet for staining the film and the film peeling was visually evaluated.

(2) Adhesion of finish-coating (primary and secondary adhesion)

A white melamine alkyd paint (Amilack #1000 of Kansai Paint) was applied by a bar coater on the test pieces to form a 20μm thick (when dried) film. Some test pieces were dried in a laboratory dryer for evaluating primary adhesion, and others were dried in the same manner, then immersed in boiling water for 30 minutes. They were left in the room atmosphere for 24 hrs for evaluating secondary adhesion. The coating layer thus prepared was then cross hatched with a sharp knife into 100 checkered squares at 1 mm interval, peeled off with adhesive tapes, and the remaining coating was visually evaluated. Yet other test pieces were drawn to 7 mm depth by the Erichsen tester after the paint drying, the coating layer in the worked area was peeled off with adhesive tapes and the remaining paint was visually evaluated.

The evaluation ratings for both (1) and (2) were as follows: ◎ no peeling off; ○ 0 < peeling < 10%; △ 10% ≦ peeling < 30%.

c) Anti-fingerprint property

Fingers were actually placed on the film surface and the markings were visually evaluated. The ratings were: ◎ fingerprint invisible; ○ little seen if any; △ seen but unclear; × clearly seen.

d) Electrical conductivity

An electro-resistivity measuring device in accordance with JIS C 2550 (made by Tori Kogyo) was used for the evaluation. The lower the measured electro-resistivity the better the conductivity.

2.2 Test results

At visual inspection, the appearance of the chromium-free surface-treated EG and GI was good and uniform.

Fig. 1 shows the relationship between corrosion resistance and film thickness of the flat test pieces and **Fig. 2** the same of the Erichsen-drawn test pieces. **Fig. 3** shows photographs of the Erichsen-drawn test pieces of EG and GI with 1.5 - 1.7 μm thick film after a 72 hr salt spray test along with those of the conventional chromate-treated test pieces. The thicker the Cr-free film the better corrosion resistance became. This was considered because the barrier effect of

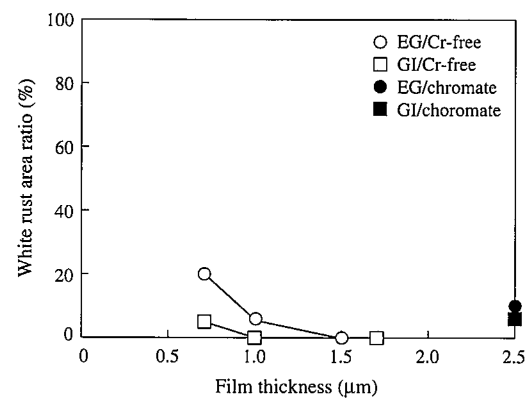

Fig. 1 Relationship between film thickness and white rust formation at flat portion after 168 hrs of salt spray test

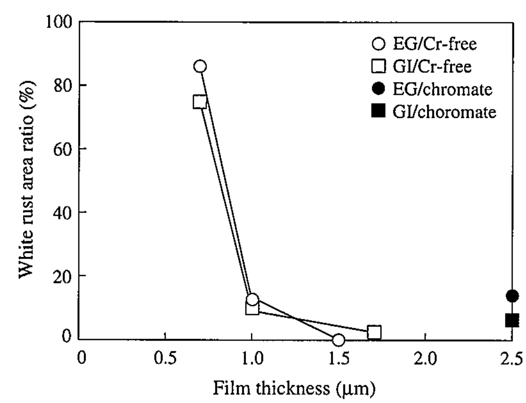

Fig. 2 Relationship between film thickness and white rust formation at Erichsen-drawn portion after 72 hrs of salt spray test

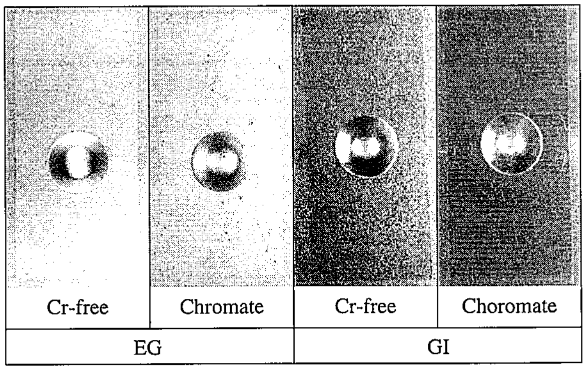

Fig. 3 Appearance of the hot dip galvanized steel sheets with chromium-free surface treatment after 72 hrs of salt spray test (Comparison with the conventional chromate-treated hot dip galvanized steel sheets)

the film against corrosion factors was increased with increasing thickness of the film. Corrosion resistance of the product was close to that of the chromate-treated sheets when the film thickness was 1.0 μm, and was the same or better when the thickness was 1.5 - 1.7 μm.

Table 1 shows evaluation results of the other items. Adhesion of the Cr-free film to the galvanized surface of EG and GI was good, and primary and secondary adhesion of the finish-coat was a little better than the chromate-treated sheets, regardless of the film thickness.

Anti-fingerprint property was also a little better than the chromate-treated sheets regardless of the film thickness or type of galvanization either.

Electrical conductivity proved to be largely dependent on the film thickness like corrosion resistance. The thinner the film, the better was the conductivity (low resistivity). The conductivity of the Cr-free film-treated sheets, either EG or GI, was equal to or better than the chromate-treated sheets when the film thickness was 0.7 μm, a little lower with 1.0 μm film, and considerably lower when the film thickness was 1.5 - 1.7 μm giving a corrosion resistance equivalent to or better than the chromate-treated sheets.

As was made clear in the above discussion, the newly developed Cr-free surface treated product with a film about 1.5 μm thick has a corrosion resistance equal to or better than the chromate-treated sheets (chromium weight 50 mg/m^2). Electrical conductivity of the Cr-free film with a film about 0.7 μm in thickness is nearly the same as or better than the chromate-treatment, when the conductivity is required the new product can be made to meet the requirement by adequately controlling the film thickness. Corrosion resistance and electrical conductivity of the product are a little off balance compared with the chromate-treated sheets, and when electrical conductivity is given priority (thin film is required), corrosion resistance becomes slightly inferior. Within the film thickness range of the tests the anti-fingerprint property and the finish-coat adhesion were superior to the chromate-treated sheets, which shows that the new product has a performance practically satisfactory as a substitute for the chromate-treated sheets. For this reason, the Cr-free film treated sheets have already been commercially used for some final products.

3. Development of Cr-free Pre-painted Electro-galvanized Sheet

Conventional pre-painted sheets are composed of the zinc plating layer on the base steel sheet, a chromate layer as pre-treatment for finish-coating, a primer layer with chrome anti-corrosion pigments and the colored paint finishing layer. The newly developed Cr-free pre-painted sheet product is manufactured based on electro-galvanized sheets, applying a Cr-free pre-treatment layer having good adhesion to the zinc plating layer, a primer combining a special resin and a Cr-free anti-corrosion pigment and, then, the same finishing paint that is used in the conventional product. The performances of the new and conventional products were compared as reported hereafter.

3.1 Test method

3.1.1 Specimens

Specimens of the Cr-free pre-painted product were prepared through a pre-treatment with the newly developed Cr-free layer on the EG (20 g/m^2 per side), forming and baking a 5 μm thick layer (when dry) of the Cr-free primer thereafter, then finally forming and baking a 16 μm thick (dry) layer of conventional color paint (black) as the finish-coat. For comparison, other specimens were prepared through a chromate treatment by an applicator (chromium weight 50 mg/m^2) on the same EG material, forming and baking a 5 μm thick (dry) layer of primer with chrome anti-corrosion pigments, and then forming and baking a 16 μm thick (dry) layer of the same finishing paint that was used for the new product.

3.1.2 Evaluation items

Corrosion resistance was tested as follows: 70 × 150 mm test pieces were cut out and had the surface cross-cut with a sharp knife to the steel substrate, underwent 3 cycles of salt spray test, each cycle comprising 8 hrs of salt spray in accordance with JIS K 5400 and 16

Table 1 Performance of the galvanized steel sheets with chromium-free surface treatment

Products		Film thickness (μm)	Film adhesion	Finish-coat adhesion				Anti-finger print ability	Electric resistance (Ω·cm/sheet)
				Primary		Secondary			
Metal coating	Treat-ment			Cross hatch	Erichsen	Cross hatch	Erichsen		
EG	Cr-free	0.7	◎	◎	◎	◎	◎	◎	2.3
		1.0	◎	◎	◎	◎	◎	◎	3.3
		1.5	◎	◎	◎	◎	◎	◎	6.2
	Chromate			◎	◎	◎	△	△	2.3
GI	Cr-free	0.7	◎	◎	◎	◎	◎	◎	2.8
		1.0	◎	◎	◎	◎	◎	◎	3.8
		1.7	◎	◎	◎	◎	◎	◎	7.2
	Chromate			◎	◎	◎	△	△	3.4

hrs of operation stop, then washed with water. Maximum blistering width at the cross-cut (scribe) and the edges were measured. The reverse surface of the test pieces was sealed with polyester tapes.

Bendability and finish-coat adhesion at the worked portion were tested at 20°C in accordance with JIS K 5400. Test pieces were bent by 90° with 0 mm inside radius (0R bend), paint cracks at the bent portion was visually inspected under 10 times magnification, then peeling of the coating layer of the bent portion was visually observed after being peeled off with adhesive tapes. The evaluation ratings were: ◎ no crack or peeling off; ○ 0 < total area of crack and peeling < 10% ; △ 10% ≦ total area of crack and peeling < 30%; × 30% ≦ total area of crack and peeling.

Coin scratch resistance was tested with a 10 yen coin set at an angle of 45° and made to slide on the paint surface at 1 m/min under a load of 2 kgf. The ratings of visual inspection of the scratched paint surface were: ◎ damage only to the top coat; ○ 90% ≦ remaining primer; △ 60% ≦ remaining primer < 90%; × remaining primer < 60%.

3.2 Test results

Table 2 shows the results of the tests. Within the scope of the tests, corrosion resistance of the developed product was not different from the conventional product containing chromium and the new product is appropriate for indoor applications. The product showed good bendability and no crack or peeling was found of the paint at the 0R bend portion, which was the same as the conventional product. The coin scratch resistance was the same as the chromium-containing product.

As described above, the newly developed Cr-free pre-painted sheets are equivalent to the conventional pre-painted sheets with regards to formability and coating adhesion and they have enough corrosion resistance for indoor applications. The product, VIEWKOAT-21, has already been commercially applied for indoor uses.

Table 2 Performance of the chromium-free pre-painted electro-galvanized sheets

Products		Cyclic SST		0R-bend area		Coin Scratch resistance
Metal coating	Layer	Scribe	Edge	Crack	Adhesion	
EG	Cr-free	0.1	0.3	◎	◎	◎
	Cr containing	0	0.1	◎	◎	◎

4. Conclusions

In view of the fact that hexa-valent chromium is an environmentally unfriendly substance, galvanized sheets with chromium-free surface treatment and chromium-free pre-painted electro-galvanized sheets were developed and the new products were found to have sufficient level of performance. The authors will exercise further efforts for improving their performances for expanding their commercial applicability.

References

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