Technical Report

UDC 669 . 14 - 408 . 2 : 669 . 586 . 5 : 669 . 715 ' 5

Chromate-free Prepainted Steel Sheets for Building Exterior Materials

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Abstract

Steel sheets coated with a 55% Al-Zn alloy and paint are widely used for building exterior materials. This paper overviews the elimination of chromate from the coating of these sheets, and explains the properties of the chromate-free sheets thus developed, which proved to be practically the same as those of the conventional sheets containing chromate. In addition, an example of actual use of the developed chromate-free prepainted sheets, through which their good corrosion resistance and durability have been confirmed, is presented herein.

1. Introduction

Prepainted steel sheets for roofs and walls of plant buildings and housings mostly contained chromate in the layers of chemical treatment and primer paint for the sake of good corrosion resistance. The latest trend is, however, that prepainted sheets used for the bodies of home appliances are required to be free of chromate, and accordingly, environment-friendly materials are used in preference.

In view of this, the present paper discusses the current technology and future prospects of chromate-free prepainted sheets for building exterior materials using steel sheets hot-dip coated with a 55% Al-Zn alloy, GALVALUME®, as the base metal.

2. Outlines of Chromate-free Prepainted Steel Sheets

The coating structure of chromate-free prepainted steel sheets using GALVALUME® sheets as the base metal is illustrated in **Fig. 1**.[1] The front side coating on the GALVALUME® sheet surface comprises three layers: a chemical treatment film, a primer paint layer and a top paint layer. These layers exert the following functions: the chemical treatment film secures the adhesion of the primer paint and is resistant to corrosion; the primer paint is mainly responsible for resistance to corrosion; and the top paint provides good appearance with its color and gloss, and where required, protection against smears and wear. The rear coating usually comprises three layers as on the front side, but sometimes the same grade of appearance is not required for the rear, and the primer coating may be omitted.

The corrosion resistance of prepainted sheets used to be obtained using a protective agent containing chromate for the chemical treatment and mixing protective pigment containing hexavalent chromium in the paint for the primer coating. Recently, however, it became necessary to replace these chromate-containing protective agent and pigment with those free of such chromium compounds, and yet secure a prescribed level of corrosion resistance. In this situation, steelmakers and paint manufacturers are exercising their expertise to develop new products that meet the requirement.

3. Measures to Eliminate Chromate

Two regulatory laws were implemented in Europe in 2006: the Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment, known as the RoHS Directive; and the Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on End-of-life Vehicles, known as the ELV Directive. Accordingly, upper limit figures were set forth for the amount of hexavalent chromium that electric appli-

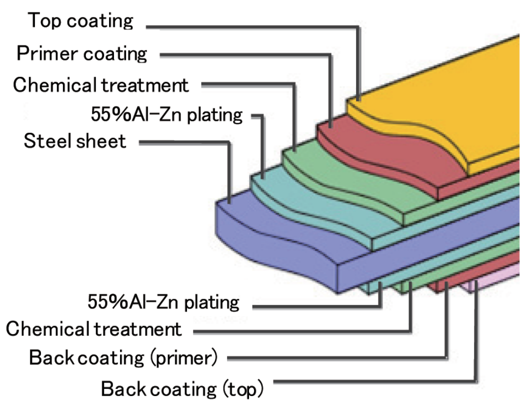

Fig. 1 Schematic illustration of prepainted steel sheet [1]

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ances and automobiles marketed in the territory should contain. At this, the Japanese makers of consumer electronics introduced self-imposed regulations not to use either tri- or hexavalent chromium, and the Japanese automobile builders prohibited the use of hexavalent chromium.

In the Japanese construction market, on the other hand, hexavalent chromium and lead in the paint for post-painting came under public regulation by the Law on Promoting Green Purchasing enacted in 2002 to encourage use of environment-conscious materials for public construction projects. In view of this, paint makers and steelmakers, on their own initiative, are aiming at stop using hexavalent chromium and lead for the paints for prepainting, following the case of those for post-painting.[2)]

Regarding the materials used for public construction projects, the Standard Specifications for Public Building Construction set forth by the Ministry of Land, Infrastructure, Transport, and Tourism are revised every three years. The Specifications, which are originally meant for public building construction projects, are often also applied to private buildings, and thus have wide influence over the entire construction industry in Japan.

The chromate-free treatment of galvanized steel sheets was first included in the Specifications as an alternative to the chromic acid treatment in the section of chemical treatment processes in the 2007 revision, which meant that the chromate-free treatment was officially allowed for public construction projects. This stipulation remained unchanged in the 2010 and the 2013 versions.

In the study for the revision on the 2013 version, however, in consideration of the general increase in environment consciousness, the Ministry sounded the views of the Japan Iron and Steel Federation about possible unification to chromate-free treatment, prohibiting hexavalent chromium or chromate. At the hearing for the members' views by the Federation, the number of people who agreed to the elimination of the hexavalent chromium/chromate was nearly the same as the number of those who disagreed. With this result, the Federation responded to the Ministry that it was difficult to change the treatment entirely to chromate-free treatment by the consensus of the members, and in the absence of a standard for the chromate-free treatment of painted galvanized steel sheets, requested the Ministry to first include chromate-free treatment in the JIS system to encourage galvanized sheet suppliers to take adequate measures, and after the inclusion of the treatment in JIS, revise the said Specifications accordingly.

In this circumstance, the manufacturers of construction materials and paint are now endeavoring to eliminate the use of chromate for prepainted steel sheets for construction use.

4. Properties of Chromate-free Prepainted Sheets

Some outstanding property items of the chromate-free prepainted galvanized sheets for building exterior applications that Nippon Steel & Sumitomo Metal is developing are described in this section together with the mechanisms of corrosion.[3)]

4.1 Corrosion resistance

4.1.1 Paint blistering

When painted GALVALUME® sheets are used for building exterior materials, paint blisters form as a result of the accumulation of corrosion products under the paint coating. The evaluation results of the blisters that formed at cut ends, cross scratches, and bends of specimen sheets at outdoor exposure test are presented below.

Table 1 describes the coating structures of the prepainted sheet specimens used for the test: GALVALUME® sheets AZ150, 0.35 mm in steel thickness, and 20 μm in coating thickness per side (all units herein are metric), were used as the base metal, and after the chromate-free chemical treatment, a primer paint layer with protective pigment not containing hexavalent chromium and a top paint layer were formed on the front side (No. 1 of Table 1). For comparative specimens (No. 2 of Table 1), a chemical treatment film containing chromate, a primer paint layer with protective pigment containing hexavalent chromium and the same top paint layer as that of no. 1 were applied on the front side of the same GALVALUME® sheets. The exposure test was conducted on racks slanted by 45° to the south at a site about 1 km from the sea in Funabashi, Chiba (about 20 km to the east from the center of Tokyo), for a period of three years.

Figure 2 shows the maximum widths of blisters that formed at the cross scratches and the cut edges of the specimens. With either the chromate-free or chromate-containing samples, the blister width from the scratches was 0.5 mm; there was no difference between the two. On the other hand, the blister width from cut edges having burrs turned towards the front side (front burrs, for short) was 1 mm in the two types, larger than that at the cross scratches; however, there was no difference between the two either.

Figure 3 shows the evaluation of the paint blistering at the 2T-bend portions of the specimens in five-grade evaluation: mark 5 being the best (no blisters) and mark 1 the poorest (blisters in all the bent area). The chromate-free and the chromate-containing test pieces got mark 3; while the blister occurrence was not at all good, there was no difference between the two.

As stated above, there was no difference between the chromate-free and the chromate-containing test pieces in terms of paint blistering at cut edges, cross scratches, and bent portions.

4.1.2 White rust

Next, the results of the combined-cycle corrosion test (CCT) on the occurrence or otherwise of white rust are explained below.

The specimens had coating layers, as shown in **Table 2**: the coating structure was basically the same as that given in Table 1, except that the primer and top coats on the front side were 3- and 15-μm thick, respectively, and two paint layers were present on the rear.

Before the CCT, the test pieces formed two different shapes. Some of them underwent 4T or 6T bending, and the occurrence of white rust after 60 to 180 cycles of the CCT was assessed by five-grade evaluation. Others, 50 × 100 mm in size, were bent into an L shape (90°) along the 100-mm-long centerline such that the front side faced out-

Table 1 Coating structure of outdoor exposure specimens

No.	Base metal	Chemical treatment	Front primer	Front top	Back side
1	GALVALUME® Steel Sheet (AZ150) 0.35 mm thick	Chromate- free	Epoxy resin, with chromate-free pigment 4 μm thick	Polyester, (blue) 10 μm thick	Polyester, no pigment 5 μm thick
2		Chromate	Epoxy resin, with chromate pigment 4 μm thick		

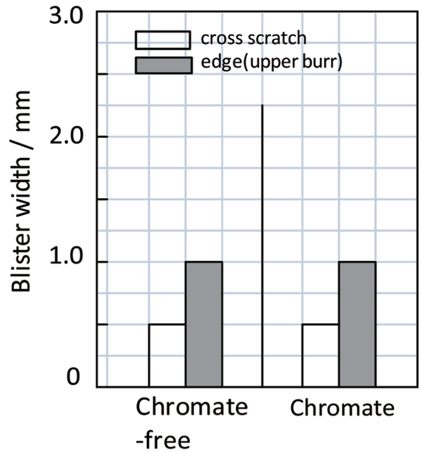

Fig. 2 Maximum blister widths of chromate-free prepainted steel sheet specimens [cross scratch, upper burr] (Funabashi, south 45°, 3years)

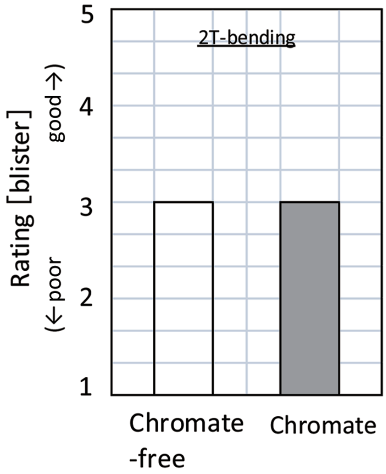

Fig. 3 Blister ratings of chromate-free prepainted steel sheet specimens [2T bending] (Funabashi, south 45°, 3years)

Table 2 Coating structure of CCT specimens

No.	Base metal	Chemical treatment	Front primer	Front top	Back side primer	Back side top
1	GALVALUME® Steel Sheet (AZ150) 0.35 mm thick	Chromate- free	Epoxy resin, with chromate-free pigment 3 μm thick	Polyester, (blue) 15 μm thick	Epoxy resin, with chromate- free pigment 1.5 μm thick	Polyester, no pigment 5 μm thick
2		Chromate	Epoxy resin, with chromate pigment 3 μm thick		Epoxy resin, with chromate pigment 1.5 μm thick	

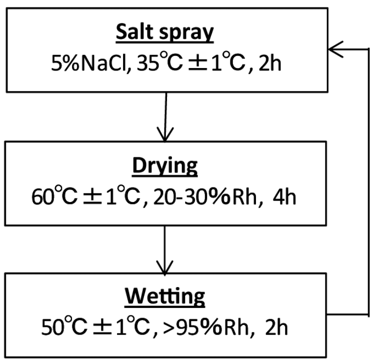

Fig. 4 CCT cycle

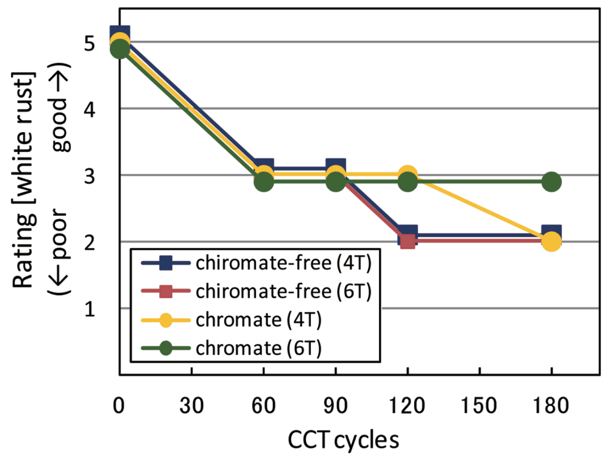

Fig. 5 Relation between white rust rating and CCT cycles [4T, 6T bending]

ward and the bending radius (R) at the rear gradually changed from 0 mm at one end to 5 mm at the other. During the test, the occurrence or otherwise of white rust was observed at prescribed intervals, and the bending curvature of the portion not covered with white rust at each observation timing was defined, in terms of the inner radius R (mm), as the limit bending curvature.

The CCT was conducted according to JASO M609, each 8-h cycle of the test being as given in **Fig. 4**: 2 h of salt spray, 4 h of drying, and 2 h of wetting.

Figure 5 shows the CCT evaluation results of the specimens that underwent either 4T or 6T bending. The chromate-free specimens were rated at mark 3 after 60 cycles, and then, after 120 cycles, their rating fell to mark 2. The results of the specimens containing chromate were substantially the same: the rating after 120 cycles was mark 2 or 3, higher than that of chromate-free specimens by roughly 1 point.

Figure 6 shows the CCT results of the specimens that were longitudinally bent in right angles. The white rust increased with the number of cycles, but it took longer for white rust to expand to portions of larger bending radii R. Comparing the chromate-free and chromate-containing specimens, the former was a little more prone to white rust than the latter, whereas after 180 cycles, white rust expanded to the portions of the chromate-free specimens bent at a radius R of 2.4 mm or less; the limit bending curvature of the specimens containing chromate was 1.4 mm. This indicates comparatively poorer corrosion resistance of the chromate-free coating.

As explained above, in terms of the resistance to white rust, sheets containing chromate were better at the CCT than the chromate-free ones, but the difference was insignificant. From this and the results of the outdoor exposure test stated in section 4.1.1, it is reasonable to consider that chromate-free and chromate-containing prepainted steel sheets have practically the same corrosion resistance in ordinary outdoor conditions.

4.2 Corrosion mechanisms

The findings of the observation of the corroded portions of the chromate-free and the chromate-containing specimens after the outdoor exposure test are explained below.[4)]

Figure 7 shows sectional photomicrographs through a scanning electron microscope (SEM) and element mapping images taken at a corroded cut edge of a chromate-free specimen (part a) and the same of another containing chromate (part b), both exposed at the Funabashi test site for five years.

With coating containing chromate, corrosion product comprising mainly Al oxide was seen to form a comparatively tightly packed layer at the interface between the zinc alloy layer and the paint coating, checking the progress of corrosion. Although the specimen was observed only at a cut edge, the same corrosion suppression mechanism seemed to exist at the cross scratched portion.

With chromate-free coating, likewise, corrosion product comprising mainly Al oxide was found between the zinc coating and paint. This seems to indicate that with chromate-free coating, corrosion advances in the same manner as with that containing chromate, and corrosion product comprising mainly Al oxide forms to suppress the advance of corrosion.

Besides the above, there have been the following findings about the corrosion mechanisms of GALVALUME® sheets coated with paint containing chromate:[5, 6)]

(1) The corrosion at cut edges of prepainted GALVALUME® sheets starts at the open end and selectively advances in the Zn-rich layer in the Al-Zn eutectic phase.
(2) Na concentration is observed at the interface between the sound zinc alloy layer and the paint film in the inside of a corrosion front, but no marked concentration of Cl occurs at the corrosion front.
(3) The role of chromate in the primer paint is not to enhance the barrier function of the paint coating, but to stabilize the passivation film on the surface of the zinc alloy.

As seen with Fig. 7, the mode of corrosion and the corrosion suppression mechanism of chromate-free coating are very much similar to those of coating containing chromate, and therefore, the findings about the latter can be applied effectively to the study of the former.

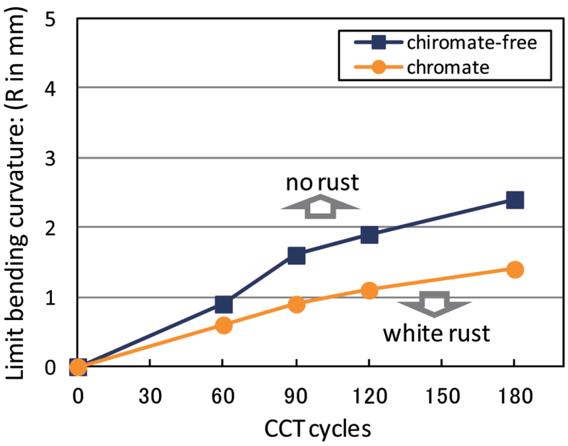

Fig. 6 Relation between white-rust-limit bending curvature and CCT cycles

5. Example of Actual Use of Chromate-free Prepainted Sheets

An example of building construction wherein chromate-free prepainted GALVALUME® sheets were used for external materials is presented in this section.

The application in question is to the roof of the guest house in the

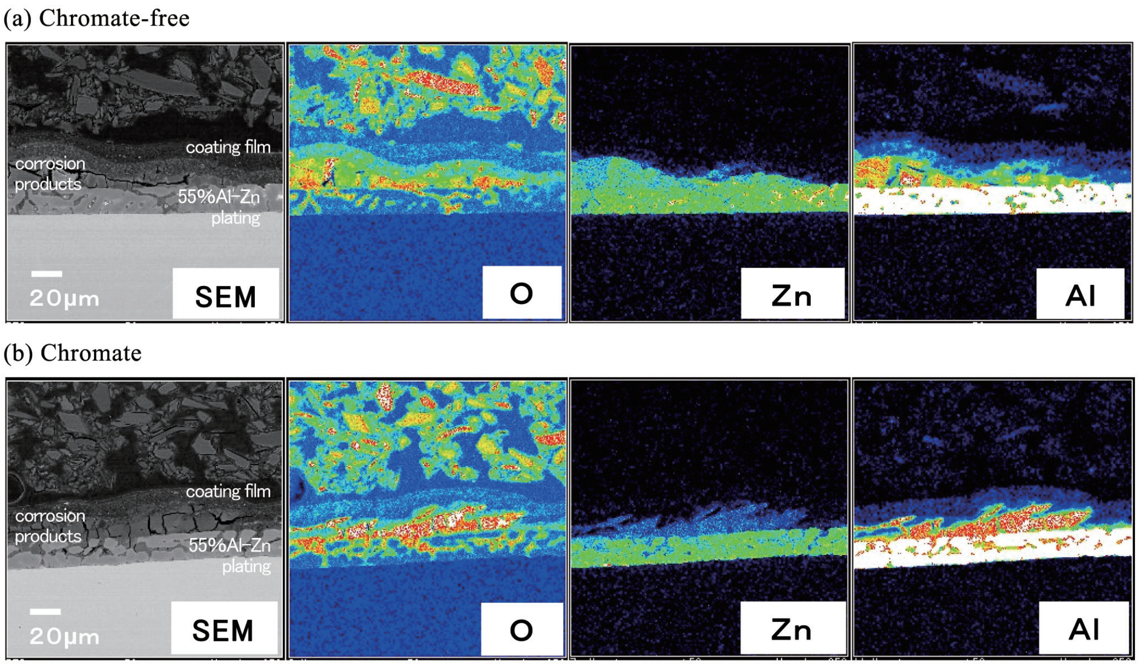

Fig. 7 SEM images and element mapping images of corrosion area in outdoor exposure specimens

Fig. 8 Example of chromate-free prepainted steel applied to roof materials (February 2009)

premises of the R&D Laboratories of Nippon Steel & Sumitomo Metal in Futtsu, Chiba, on the eastern side of the Bay of Tokyo. The roofing work with the prepainted sheets was completed in February 2009: the side of the roof seen in **Fig. 8** is covered with prepainted GALVALUME® sheets with chromate-free coats and the other side is covered with those having coats containing chromate, which is used as a comparative material.

After five years of installation, no problems have been found in the appearance of the roof. A close examination was conducted in May 2013 (four years and three months after the construction), yielding the following results:

(1) More white rust was found to form, though very slightly in absolute amount, at heavily bent portions of chromate-free sheets than on sheets containing chromate. No marked advance in corrosion from the previous examination two years earlier was observed.

(2) There was no problem of paint adhesion at tape peeling test of bent portions.

(3) There was little difference between the chromate-free and the chromate-containing prepainted sheets in the discoloration and gloss in the flat areas, although there usually were dark-red smudges on the surface.

From the above, chromate-free prepainted steel sheets using GALVALUME® as the base metal are considered, at the time of roughly five years of use, to have substantially the same corrosion resistance and durability as those containing chromate.

6. Closing

With prepainted, zinc-plated steel sheets for building exterior materials, the measures to eliminate chromate from the coating have been slower than with those for electric appliance use. A reason for this is presumably that the former is exposed to the environment; higher corrosion resistance is required for it and no other coating materials suitable for use have been made available.

This paper has outlined the actions for eliminating the use of chromate for the coating of the prepainted steel sheets for building exterior materials, explained the current corrosion protection performance of Nippon Steel & Sumitomo Metal Group's product, and presented an example of its actual application. While chromate-free sheets are slightly more prone to white rust at present than those containing chromate at tests, they are substantially equal to each other in terms of corrosion resistance in actual use, and their service life is practically the same.

As the demand for chromate-free prepainted galvanized sheets for construction use is expected to increase, Nippon Steel & Sumitomo Metal is determined to develop and offer products of enhanced performance.

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