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Technical Report

Development of Chromate-free Pre-painted Steel Sheets, Edge-red-rust-resistant VIEWKOTE™

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Abstract

A new type of pre-painted steel sheet product, resistant to red rust forming at cut edges rapidly in wet seasons in regions free of airborne salt, has been developed. The developed product, named edge-red-rust-resistant VIEWKOTE™, has proved to be as good as conventional chromate-free VIEWKOTE™ in terms of long-term resistance to paint blistering. The special paint coating on the back side of the new product exhibits excellent workability, making it fully suitable for heavy forming applications.

1. Introduction

Steel sheets coated with paint ex-works are called pre-painted sheets. Nippon Steel & Sumitomo Metal Corporation manufactures and markets pre-painted sheets under the trade name of VIEWKOTE™. The users of these products do not have to keep the equipment and personnel for the painting work, and in appreciation of the additional advantages of being free from having to handle volatile organic compounds and able to effectively use the plant space otherwise required for the paint work, many manufacturers of electrical appliances, construction materials, etc., prefer to use pre-painted sheets.

Figure 1 shows a typical coating structure of a pre-painted sheet. To secure good corrosion resistance, hot-dip or electrolytic galvanized steel sheets (GI or EG, respectively, for short) are commonly used as the base metal. Before the paint layers are applied, the base metal is chemically treated for the purpose of securing good paint adhesion. Usually, two paint layers are provided on the front side: the primer paint is responsible mainly for securing good adhesion to the base metal and corrosion resistance, and the top paint is responsible for surface properties such as good appearance, adequate hardness, workability, and protection against smears. Polyester resin paint excellent in workability, smear resistance, hardness, etc., in a well-balanced manner is widely used for the primer and top coats, and melamine or isocyanate compounds as the hardening agent.

On the other hand, the back side is usually coated with one layer of polyester paint, because in most cases pre-painted sheets are used such that the back side is hidden from sight, and no special functions are required for this side. When certain properties are required of the back side or high corrosion resistance of cut edges is essential, however, two coats are provided.

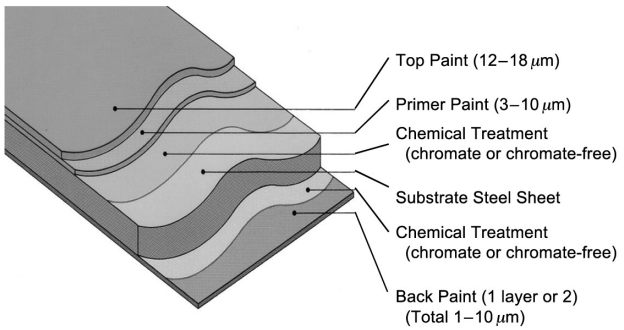

Fig. 1 Cross section of prepainted steel sheet

The use of pre-painted sheets expanded rapidly in the 1970s, and ever since, chromate, which is excellent in paint adhesion and corrosion resistance, was used widely for the chemical treatment, and it was a common practice to mix highly corrosion-resistant chromate pigment in the primer paint. After 2000, however, in consideration of the regulations such as the RoHS (Directive 2002/95/EC of the European Parliament and of the Council of January 27, 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment, enforced in 2006) on substances containing hexavalent chromium, measures have been actively taken to reduce or ban the use of environmentally hazardous substances for industrial products.

In response, the authors developed a chemical treatment agent, not containing chromate, having as good adhesion as the chromate treatment and highly corrosion-resistant, and chromate-free primer paint, and using them, launched chromate-free pre-painted steel sheets (trade name: chromate-free VIEWKOTE™) to the market. After that, the

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Table 1 Paint film compositions of samples used in this study

Type of VIEWKOTE™		Edge-red-rust-resistant VK	Chromate-free VK	Chromate VK
Substrate		0.6 mm thick galvanized steel sheet (Zn: 40 g/m^2 per side)		
Chemical treatment		Chromate-free		Chromate
Front side	Primer paint (5 μm)	Polyester resin with chromate-free pigment		Polyester resin with chromate pigment
	Top paint (15 μm)	Polyester resin (standard top-coat paint)		
Back side	Primer paint (5 μm)	Polyester resin with special pigment	Polyester resin with chromate-free pigment	Polyester resin with chromate pigment
	Top paint (5 μm)	Polyester resin with special pigment	Polyester resin (standard back paint)	

use of chromate-free pre-painted steel sheets expanded rapidly. At that time, Ueda et al. reported the excellent properties of the developed product equal to those of the conventional products containing chromate: including workability at bending, deep drawing, stamping, etc., and the corrosion resistance at cut edges, coating scratches as well as at deep-drawn or bent portions under outdoor conditions.[1)]

Then, as the use of chromate-free VIEWKOTE™ expanded for outdoor applications, a new problem arose: red rust formed at the cut edges of the sheets after actual use in outdoor environments in a short period of several weeks. It became clear through examination of these cases that the problem occurred only with those appliances installed in the June–July rainy season at places away from the sea and free of airborne salt. The positions of the red rust were mainly those where rain water was likely to get into and remain, such as the engaged joints between the top and the side boards of outdoor units of air conditioners. In contrast, the red rust did not form on units that were installed before or after the rainy season.

From these findings, the red rust was suspected to have resulted from cut edges of VIEWKOTE™ kept wet for a long period with water containing little electrolyte. It was presumed that in such a condition, corrosion cells of zinc and iron did not form because the conductivity of rain water was low and the sacrificial protection effect of zinc did not show. In the case of outdoor units installed after the rainy season, on the other hand, it was suspected that the cut edges of the sheets got wet and dry at short cycles as it rains only occasionally, zinc oxides and protective pigments were eluted little by little from the metal coating and paint layers and stuck to the steel edges to form protective films, which effectively prevented red rust from forming. The chromate-free VIEWKOTE™ is sufficiently resistant to the growth of paint blisters from cut edges in regions of airborne salt, but when it is used in regions of little airborne salt, red rust is likely to form within a short period.

In view of the above, the authors have developed a new type of VIEWKOTE™ resistant to the formation of red rust in regions of little airborne salt under high-temperature and high-humidity conditions. The essence of the developed product is that a special corrosion resistant agent is mixed to the paint for the back coating so that it is eluted from the coating layer when a cut edge gets wet with water, sticks to the base metal, and forms a protective film to prevent red rust formation. This paper reports the results of comparative tests using the developed type of VIEWKOTE™ resistant to edge red rust (hereinafter referred to as the edge-red-rust-resistant VK) and the conventional chromate-free VIEWKOTE™ for outdoor applications (hereinafter referred to as the chromate-free VK). Note that, for some test items, VIEWKOTE™ for outdoor applications containing chromate (hereinafter referred to as the chromate VK) was also used as additional comparative samples.

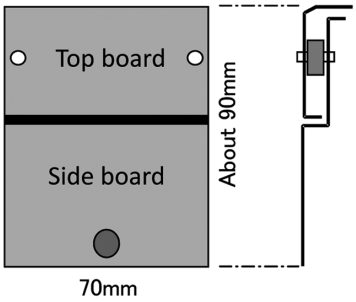

Fig. 2 Test piece simulating engaged joint of air conditioner outdoor unit

2. Tests

2.1 Specimens

Hot-dip galvanized steel sheets with a coating weight of 40 g/m^2 per side (all units herein are metric) were used as the base metal of the specimens of the edge-red-rust-resistant VK, the chromate-free VK, and the chromate VK for the present tests. For the chemical treatment of the edge-red-rust-resistant VK and the chromate-free VK, a chromate-free solution was used and no chromate-containing pigments were used for the paint layers either on the front or the back side. Note that the special rust-preventive agent mixed to the back-side paint of the edge-red-rust-resistant VK does not fall into the category of substances banned under the RoHS or the pollutant release and transfer register regulations. For the chromate VK specimens, on the other hand, chromate was used for the chemical treatment, and paints containing chromate protective pigment were used for the primer coating on both sides. The coating structures of the specimens are given in **Table 1**.

2.2 Evaluation methods

2.2.1 Resistance to red rust at cut edges

(1) Exposure test at location free of airborne salt

Exposure test was conducted at Weathering Site Kimitsu, located among hills and away from sea shore in Chiba Prefecture, a place free of salt attack, where the sacrificial protection effect of zinc is unlikely to show. The test duration was a three-month period from the time when the Meteorological Agency forecasted the beginning of the early-summer rainy season. The specimen sheets were formed into test pieces simulating the engaged joint between the top and side boards of the outdoor unit of an air conditioner such that the distance between the cut edge of the top board and the L bend of the side board was 0.5 mm (see **Fig. 2**); this gap was defined through previous studies as that with which rain water went easily into it and remained there.

(2) Accelerated corrosion test

To simulate the condition for red rust formation at cut edges in environments free of salt attack, an immersion test in distilled water and a humidity cabinet test (HCT) were conducted as accelerated

corrosion tests. In the former, five specimen sheets, each 10 × 40 mm in size, were piled, and four such piles (20 sheets in total) were immersed in 40 ml of distilled water in a petri dish 90 mm in inner diameter, and the growth of red rust at the cut edges over time was observed. The rusting or otherwise was evaluated in 5-point marks in terms of the ratio of the area covered with red rust to the total edge area: 5 for a pile without red rust; 4 for the area having several rust spots; 3 for the area in which the ratio of red-rusted area is less than 25%; 2 for the area in which the rusted area ratio is from 25% to less than 50%; and 1 for the area in which the rusted area ratio is 50% or more. In the latter test, on the other hand, test pieces 50 × 100 mm in size were hung in a rotating humidity camber controlled at 40°C and 98% relative humidity, and the growth of red rust on the cut edges over time was evaluated in terms of percentage area. Note that here, the test pieces were cut in such a way that one of the long cut edges (100 mm) had a burr turning to the front side (front burr, for short), and the other a burr turning to the back side (back burr, for short).

2.2.2 Long-term corrosion resistance

While the edge-red-rust-resistant VK and the conventional chromate-free VK had the same paint coating on the front side, their coating on the back side was different from each other, and for this reason, it was possible for the two to exhibit different growth rates of paint blisters from cut edges on the front side. In consideration of this, the two types of VIEWKOTE™ were subjected to two kinds of acceleration tests on long-term corrosion resistance: salt spray test (SST) for 500 h and cyclic corrosion test (CCT) according to JASO-M609 in 90 cycles. Three test pieces, each having a front burr and a back burr along each of the long edges and a cross cut at the flat part, of the two types were used for each of the two tests (12 in total).

2.2.3 Workability of back-side paint coating

Since the specifications for the front-side paint coating of the edge-red-rust-resistant VK are the same as those of the conventional chromate-free VK, the performance of the front-side paint coating of the two types is basically the same. On the other hand, a special corrosion resistant additive is mixed to the paint for the back side of the edge-red-rust-resistant VK, and therefore, the workability of the back-side paint of this type may be inferior to that of the other types. To verify this, bending workability test (T-bend test) and deep drawing test were conducted. In the former, 0T, 1T, and 2T bending were applied according to JIS K 5400 to the test pieces, and the paint adhesion at the outer face of the bend was evaluated by crack observation and peeling with adhesive tapes. In the latter test, blistering or peeling of the paint coating was evaluated after forming the test pieces into round cups using an Erichsen drawing tester such that the back side came to the outer face of the cup under the following conditions: drawing ratio 2.0; shoulder radius of the die and the punch 3 mm; and blank holding force (BHF) 1 t.

3. Test Results and Discussion

3.1 Resistance to red rust at cut edges at location free of air-borne salt

After the exposure at Weathering Site Kimitsu over the three-month period including the early summer rainy season, the specimen joints were disassembled, and the insides were photographed. **Figure 3** shows some examples. Whereas, in the specimens of the chromate-free VK, a considerable amount of red rust was observed at the cut edge of the top board, and the paint coating of the side board was stained with the rust, no such rusting was found in the specimens of the edge-red-rust-resistant VK or the chromate VK.

The results of the distilled water immersion test, which was meant as an acceleration test, are given in **Fig. 4**, and the test pieces after 240 h in the water are shown in **Fig. 5**. While the chromate-free VK began to have red rust after 48 h of immersion, and the amount of the rust gradually increased thereafter, no red rust whatsoever appeared on the edge-red-rust-resistant VK up to 648 h of immersion.

Next, **Fig. 6** shows the results of the HCT. Here again, the edge-

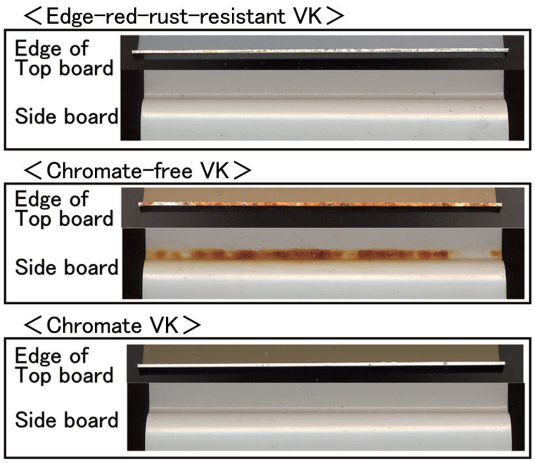

Fig. 3 Test pieces after 3 months exposure test in rainy season at inland area

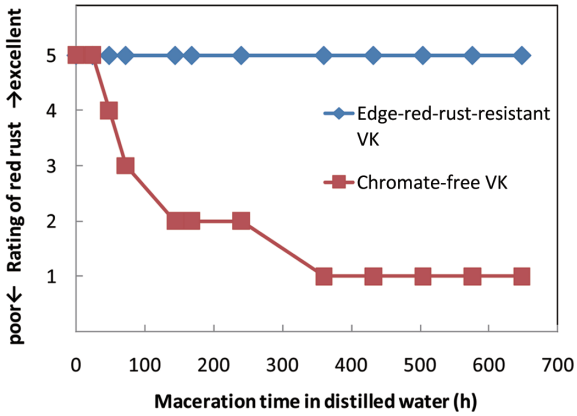

Fig. 4 Edge red rust development during immersion test in distilled water

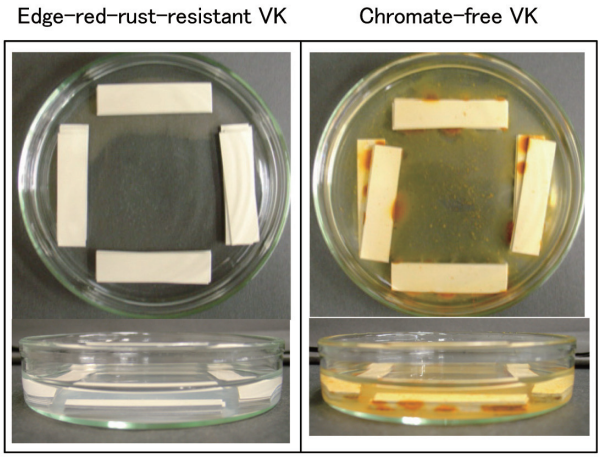

Fig. 5 Test pieces after 240 h maceration test in distilled water

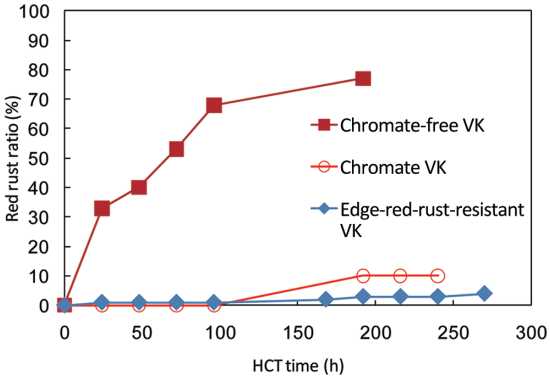

Fig. 6 Change in edge red rust ratio during HCT at 40°C

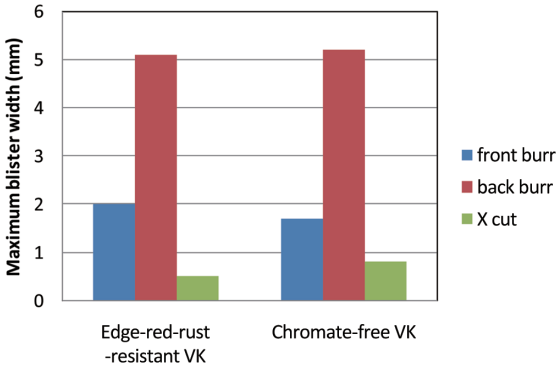

Fig. 7 Maximum blister width after SST for 500 h

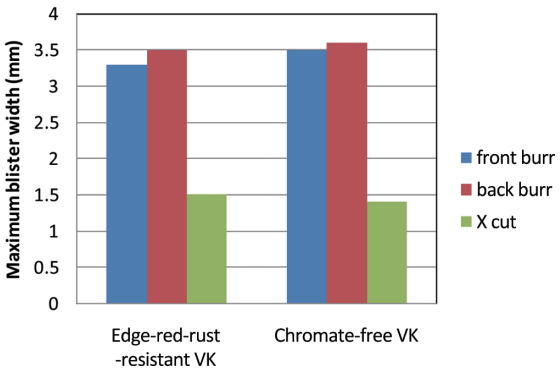

Fig. 8 Maximum blister width after 90 cycles of CCT (JASO-M609)

red-rust-resistant VK exhibited red rust ratios far lower than those of the chromate-free VK, and the result of the developed product was equal to or even better than that of the chromate VK. It has to be noted, however, that the red rust formation of the edge-red-rust-resistant VK at the HCT was not altogether nil. This is presumably because the test pieces were flat, the water could not remain at the cut edges, but fresh water continued to flow there, and it was impossible for the protective agent eluted from the back-side coating to stick there and work properly. This seems to indicate that the conditions of the HCT using flat test pieces were severer than those of the distilled water immersion test. The fact that the edge-red-rust-resistant VK exhibited considerable effect of preventing red rust at the severe HCT also indicates that the special corrosion-resistant additive mixed to the back-side paint is capable of quickly sticking to the surface of the base metal, which is mostly wet with fresh water, to form a protective film there effectively.

3.2 Long-term corrosion resistance

Figures 7 and **8** show the results after 500 h of the SST and 90 cycles of the CCT according to JASO-M609, respectively. The bars of the graphs represent the average of the maximum paint blister widths in the three test pieces of each type of VIEWKOTE™. In either of the tests, there was no difference between the edge-red-rust-resistant VK and the conventional chromate-free VK in terms either of the blister width from the cross cut, the area around which is not covered by the effect of the protective agent in the back-side paint, or of the same from the cut edges.

3.3 Workability of back-side paint coating

Table 2 shows the results of the workability tests of the back-side paint coating. In either the T-bend test or the cup drawing test, all the test pieces demonstrated good workability, evidencing the excellent workability of the special paint for the edge-red-rust-resistant VK. As shown through these tests, the new type of VIEWKOTE™ can be safely used for applications where the materials undergo working as severe as that normally applied to the conventional chromate-free VK.

3.4 Future development

As has been explained above, the use of the newly developed edge-red-rust-resistant VK is expected to solve the problems of edge red rust that forms rapidly in the early-summer rainy season in regions free of airborne salt. It has to be noted, however, that, as stated in subsection 3.1, red rust actually formed, if slightly, from the edges of the edge-red-rust-resistant VK specimens at the HCT at 40°C, which was considered as a tough acceleration test. It will be possible to prevent this problem by using sheets coated with a Zn-11%Al-3%Mg-0.2%Si alloy, or SuperDyma™, as the base metal. Specimens of

Table 2 Workability of back-side paint

		Edge-red-rust-resistant VK	Chromate-free VK
T-bend and peeling	0T	No crack No peeling	No crack No peeling
	1T	No crack No peeling	No crack No peeling
	2T	No crack No peeling	No crack No peeling
Cup drawing		No peeling	No peeling

edge-red-rust-resistant VK and chromate-free VK and their respective modifications using SuperDyma™ as the substrates (four types in total) were subjected to HCT at 40°C. **Figure 9** shows the results; note here that, of the four specimen types, the base metal of the former two are referred to as GI, and that of the latter two as SD. It became clear that edge red rust could be prevented completely by using SuperDyma™ as the substrate and mixing the special corrosion-resistant agent to the back-side paint. It will be effective to use these different types of VIEWKOTE™ in consideration of the level of red-rust prevention required for the application.

4. Closing

A new type of pre-painted steel sheet, edge-red-rust-resistant VIEWKOTE™, has been developed as a product resistant to red rust that forms rapidly at cut edges especially in hot and rainy seasons and at places free of airborne salt. It has been confirmed through tests that the developed product has the following characteristics:

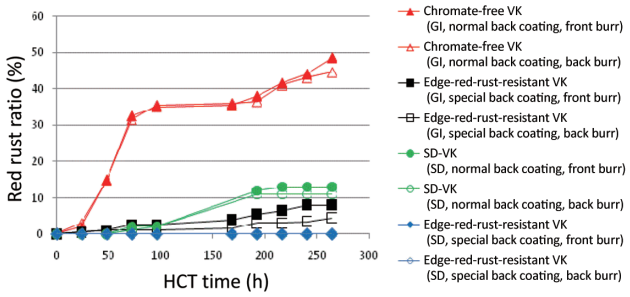

Fig. 9 Change in edge-red-rust ratio during HCT at 40°C

- In exposure test conducted at a location free of salt attack in the rainy season in early summer, the developed product exhibited excellent resistance to the formation of red rust at cut edges. This corrosion resistance is presumably due to the elution of a special protective agent from the back-side paint coating when the product sheets are wet with rain water, and covering the base metal surface exposed at the cut edge to bring about its effects.
- The long-term corrosion resistance (resistance to paint blistering) of the developed product was found to be as good as that of the conventional chromate-free VIEWKOTE™.
- The workability of the back-side paint of the product containing the special protective agent proved to be as good as that of the conventional chromate-free VIEWKOTE™.

Reference

1) Ueda, K. et al.: Shinnittetsu Giho. (377), 25 (2002)

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