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Development of Chromate-free Pre-painted Steel Sheet Having High Corrosion Resistance

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Abstract

Pre-painted steel sheet goes through forming processes after painting. Therefore, the paint adhesion at deformed parts and the corrosion from the edges are serious problems. To avoid these problems, the conventional pre-painted steel sheet is treated including the six-valent chrome. However, the demands for the chromate free pre-painted steel sheet are increasing recently because of environmental issues. Therefore, a chromate free pre-painted steel sheet exhibiting high corrosion resistance was developed. This product has good paint adhesion in the various forming ways such as bending, drawing and press forming. Furthermore, it has high corrosion resistance in the outdoor exposure test. It is concluded that the newly developed product can replace the conventional product.

1. Introduction

A pre-painted (or pre-coated) steel sheet is a steel sheet having paint layers as in **Fig. 1** applied before shipment. Its use frees users from painting of the sheet and brings to them various advantages such as solution of the problems related to volatile organic compounds and utilization of plant areas of the painting work for other purposes. For this reason, the demands for the pre-coated steel sheet have increased, resulting in its being widely used among the manufacturers of home appliances, building materials and so forth[1]. In most cases, the pre-coated steel sheet is cut and worked in the as painted state and consequently, paint film adhesion at worked portions and corrosion resistance at cut edges, where the substrate is exposed to air, are important properties for the product.

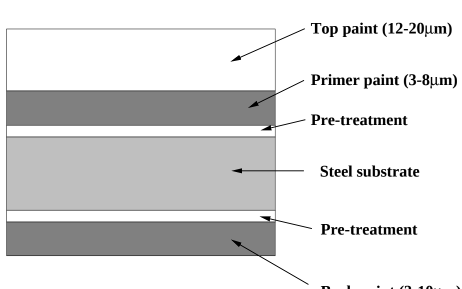

Fig. 1 Typical structure of pre-coated steel sheet

To satisfy these requirements, it is a general practice to apply a pre-treatment for creating excellent paint adhesion and corrosion resistance to the substrate before a painting process. Chromate treatment and zinc phosphate treatment are known to be effective as the pre-treatment[2], and owing to the ease of treatment bath control, and the simplicity of the process, chromate treatment using 6-valent chromium is widely applied for conventional pre-coated steel sheet products. In addition to the pre-treatment, a corrosion resistant pigment containing 6-valent chromium are used in the primer paint film of conventional pre-coated steel sheets for the purpose of enhancing corrosion resistance at cut edges. However, because of the latest trend to eliminate environmentally hazardous materials from industrial products, the automobile, home appliance and other industries are eliminating the 6-valent chromium from their products.

In consideration of the trend at an early stage, Nippon Steel Corporation began development of surface-treated steel sheets not con-

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taining 6-valent chromium and as a result, launched a chromate-free electro-galvanized steel sheet "Zincoat 21", a chromate-free hot dip galvanized steel sheet "Silverzinc 21" and a chromate-free pre-coated steel sheet for indoor applications using an electro-galvanized steel sheet as stock sheet[3]. This paper reports on the result of comparative studies of the performance of a newly developed chromate-free pre-coated steel sheet (hereinafter chromate-free PCM) excellent in corrosion resistance and applicable to outdoor uses with that of conventional pre-coated steel sheets containing chromate (hereinafter chromate PCM).

2. Experimental

2.1 Samples

Both the developed chromate-free PCM and the conventional chromate PCM were tested. Test pieces were prepared by applying a pre-treatment to both the surfaces of hot dip galvanized steel sheets (coating weight 60 mg/m^2 per side), then, two coats, a primer paint (film thickness 5 µm) and a top paint (15 µm), on the top side and one coat of a back paint (5 µm) on the back side. Here, for the test pieces of chromate-free PCM, a special pre-treatment material and a special primer paint (a polyester paint) newly developed and free from 6-valent chromium were used. For the test pieces of chromate PCM, on the other hand, conventional chromate pre-treatment and a currently used primer paint (a polyester paint) containing the corrosion resistant chromate pigment for outdoor applications (mainly for outdoor units of air conditioners) were used. All the test pieces were finish-painted with the same top paint and back paint (polyester paints) free from 6-valent chromium.

2.2 Experimental methods

2.2.1 Bending Tests

The following 180° T-bending tests were carried out in an atmosphere of 20°C and in the method according to JIS K 5400.8.1: 0T-bending test wherein test pieces were bent in 180° flat on itself; 1T-bending test wherein test pieces were bent in 180° with another steel sheet of the same thickness between the inner surface of a test piece; and 2T-bending test wherein test pieces were bent in 180° with two other steel sheets of the same thickness between the inner surface. After the bending tests, the damage to the paint films at the bent portion was observed, and the adhesion of the paint films at the bent portion was evaluated by peeling them off with an adhesive tape.

2.2.2 Deep Drawing Test

Cylindrical forming work was applied to test pieces under a blank holding force of 1 t without lubricant, using an Erichsen deep drawing tester, and the damage to the paint films at the drawn portion was observed after the forming. Here, the drawing ratio was 2.0 and the punch and the die had a shoulder radius of 3 mm.

2.2.3 Draw Bead Test

As is well known, draw bead test is a method for simulating the damage occurring to coating layers when a surface-treated steel sheet undergoes press forming work[4]. Thus, the draw bead test was employed for evaluating the damage to the paint films of the test pieces of PCMs at press forming work. The test was done under a pressure of 600 kgf and in an atmosphere of 25°C, and the appearance of the test pieces after the test was observed.

2.2.4 Corrosion Test

Salt spray test is widely employed as a method of evaluating corrosion resistance of steel sheet products by accelerating their corrosion. However, whereas actual corrosion environment comprises repeated cycles of wetting and drying, the time of wetting is too long in the salt spray test and, for this reason, the method is known not to simulate the actual corrosion condition well[5]. In view of the above, the NCCT method was employed, because the method simulates the actual corrosion condition better. **Fig. 2** shows the cycle of the NCCT. The blister width of coating after 5 weeks of NCCT is viewed very similar to that after 3 years of exposure in Okinawa Prefecture[6], where corrosion condition is the toughest in Japan. Besides the NCCT, in order to confirm the corrosion resistance in actual outdoor conditions, an outdoor exposure test was carried out at a coastal location in Okinawa.

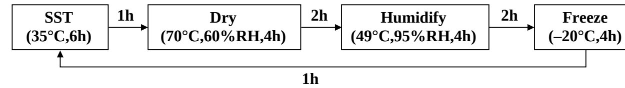

Fig. 2 Test cycle of NCCT

3. Test Results

3.1 Workability of Chromate-free PCM

Table 1 shows the results of the bending tests. The chromate-free PCM exhibited no cracks or exfoliation of coating films at the 0T-bending test, evidencing the same bending formability as conventional chromate PCM or better. **Fig. 3** shows photographs of the pre-coated sheets after deep drawing work. As is clear from the figure, the developed chromate-free PCM is excellent in deep drawability and no damage or peeling of paint coating occurs at the drawn portion. **Fig. 4** shows photographs of the pre-coated sheets after the draw bead test. The coating films of either the chromate-free PCM or the chromate PCM kept good appearance without being scratched by a die or peeling off.

3.2 Corrosion Resistance of Chromate-free PCM

Fig. 5 is a graph showing the maximum blister width at cut edges and scratched portions after the NCCT test for 5 weeks, and **Fig. 6** is

Table 1 Results of T-bending tests

	Chromate-free PCM	Chromate PCM
0T-bending	No cracks or exfoliation	No cracks or exfoliation
1T-bending	No cracks or exfoliation	No cracks or exfoliation
2T-bending	No cracks or exfoliation	No cracks or exfoliation

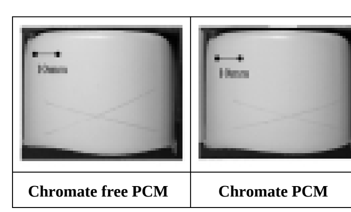

Fig. 3 Appearance of deep-drawn pre-coated sheets

Fig. 4 Appearance of pre-coated sheets after draw bead test

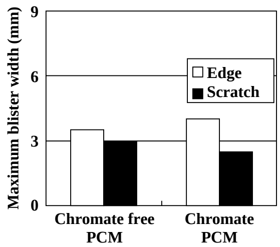

Fig. 5 Maximum blister width after 5-week NCCT

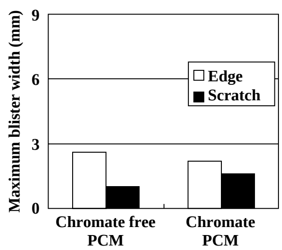

Fig. 6 Maximum blister width after 3-year outdoor exposure test in Okinawa

the same after the outdoor exposure test in Okinawa for 3 years. In either of the tests, the blister width of the chromate-free PCM was substantially the same as that of the chromate PCM. Thus, corrosion resistance of the developed chromate-free PCM was confirmed to be in the same level as that of the chromate PCM presently used for outdoor applications such as outdoor units of air conditioners. Photographs of the test pieces after the outdoor exposure test in Okinawa for 3 years are shown in **Fig. 7**. No substantial corrosion is observed at cut edges and scratched portions in either of the test pieces. Note

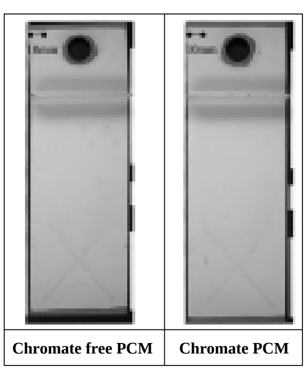

Fig. 7 Appearance of pre-coated sheets after 3-year outdoor exposure test in Okinawa

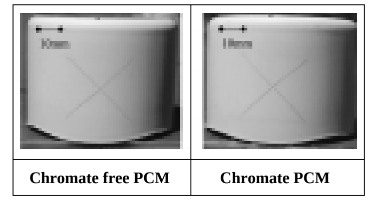

Fig. 8 Appearance of deep-drawn pre-coated sheets after 2-year outdoor exposure test in Okinawa

that the photos cover the portions bent at the 0T-bending test, and little corrosion is seen to start from the worked portions.

Fig. 8 shows the photographs of the samples of the new and conventional PCMs drawn into a cup shape and subjected to an outdoor exposure test in Okinawa for 2 years. Little corrosion at the drawn portion seen in the photos evidences the fact that the corrosion resistance of the developed chromate-free PCM is as good as that of the chromate PCM.

4. Conclusion

A newly developed chromate-free PCM excellent in corrosion resistance using a hot dip galvanized steel sheet as a substrate and a conventional chromate PCM for outdoor applications were comparatively evaluated with respect to workability and corrosion resistance. The results are as follows.

(1) No damage or exfoliation occurred to the coating films at worked portions of the developed chromate-free PCM during working such as bending, deep drawing and pressing and thus, the chromate-free PCM proved excellent in coating adhesion against working.

(2) The developed chromate-free PCM is excellent also in the corrosion resistance in outdoor applications; it exhibits the same corrosion resistance as conventional chromate PCM for outdoor use at any of cut edges and scratched, bent or drawn portion.

(3) As a consequence, it has been confirmed that the developed chromate-free PCM is applicable to outdoor exposed products of widely varied shapes.

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