NIPPON STEEL TECHNICAL REPORT No. 87 JANUARY 2003

UDC 669 . 586 / . 587 : 669 . 14 - 416

Electro- and Hot-dip Galvanized Steel Sheets with Chromate-free Treatment Layer on the Surface, "ZINKOTE 21" and "SILVERZINC 21"

Atsushi MORISHITA*[1] Akira TAKAHASHI*[1]
Makoto NAKAZAWA*[1] Kimitaka HAYASHI*[1]
Teruaki IZAKI*[2] Hiroshi KANAI*[1]

Abstract

"ZINKOTE 21" and "SILVERZINC 21" have been developed, which have an equivalent or superior corrosion resistance, electro-conductivity, lubrication, scratch resistance, anti-finger print, dew spot resistance, and paint adhesion compared with conventional chromate treated products. They have good corrosion resistance even at formed parts, and keep good corrosion resistance after degreasing by alkali degreasing agents or solvents. The new environment-conscious products can be used as substitutes of conventional chromate treated steel sheets.

1. Introduction

Environment-consciousness is becoming important all over the world, and the rapidly growing trend among steel users is to turn to materials causing less environmental loads. Many home appliance and office automation device manufacturers have set forth policies to switch to steel products that do not contain 6-valent chromium and lead, and are requesting steelmakers to supply more environment-friendly products. Foreseeing such a move, Nippon Steel Corporation has aggressively promoted development of environment-conscious steel products, and preemptively launched new products such as a plated steel sheet, "ECOTRIO,"[1)] which is suitable for lead-free soldering and excellent in anti-whisker property, an electro-galvanized steel sheet, "ZINKOTE 21" (hereinafter ZC21), and a hot dip galvanized steel sheet, "SILVERZINC 21" (hereinafter GI21), the latter two having chromate-free treatment coating films and the same level of corrosion resistance as that of conventional chromate-treated galvanized steel sheets[2,3)]. This paper describes the performance of these two new products in comparison with conventional chromate-treated galvanized sheet products.

2. Structure of ZINKOTE 21 and SILVERZINC 21

SC21 and GI21 are, respectively, electro-galvanized and hot dip galvanized steel sheets having special chromate-free coating films formed on the outer surfaces, and the special coating films have a barrier function against corrosive elements and a self-recovery function. While a chromate coating film has both these functions by itself, the chromate-free coating film of the new products is so designed as to realize these functions through combination of more than one technology. The new products comprise two types: QF type wherein priority is given to corrosion resistance and QS type wherein priority is given to electric conductivity with thinner coating films to reduce surface insulation resistance. **Fig. 1** shows the structure of the developed products.

3. Test methods

The authors examined the performance of the new products through tests using test pieces of the following products: three products in which electro-galvanized steel sheets (coating weight 20 g/m^2) were used as base plates, namely ZC21 (QF and QS), E-treatment sheets with conventional corrosion resistant chromate treat-

*1 Technical Development Bureau

*2 Yawata Works

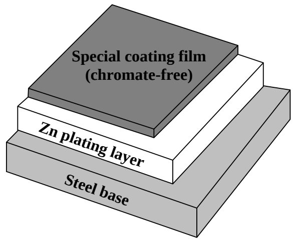

Fig. 1 Structure of ZINKOTE 21 and SILVERZINC 21

ment called E-treatment (Cr weight 50 mg/m^2) and anti-finger print sheets (hereinafter UF) with an organic composite film 1 μm in thickness formed on an dry-in-place type chromate treatment film (Cr weight 20 mg/m^2); and two products using hot dip galvanized steel sheets (coating weight symbol Z18) as base plates, namely GI21 (QF) and E-treatment sheets (Cr coating weight 50 mg/m^2). **Table 1** shows the specifications of these products. The objects and methods of the tests are described in the following sections.

3.1 Corrosion resistance

Test pieces were subjected to 7-mm extrusion work by an Erichsen tester and then a salt spray test (JIS Z 2371), and white rust resistance was evaluated in terms of the area percentage of white rust on the flat portions and the Erichsen-worked portions. Cut edges of all the test pieces were sealed. Other test pieces were degreased with an alkali solution or a solvent and then, subjected to a salt spray test, and the corrosion resistance of the flat portions after the degreasing was compared with that without degreasing. The alkali degreasing was done by heating a 20-g/l solution of Fine Cleaner FCL-4460 of Nihon Parkerizing Co., Ltd. with 12 g/l of an auxiliary to 60°C and immersing the test pieces in the solution for 2 min. The solvent degreasing was done by washing the test pieces in a methylene chloride bath at the room temperature for 2 min. in an ultrasonic washer.

3.2 Conductivity and spot-weldability

Surface insulation resistance was measured according to the method specified in JIS C 2550, and contact resistance was measured by the 4-probing needle method using Loresta MP of Dia Instrument.

The optimum current range of spot welding was determined using Cu-Cr electrodes (CF type) 4.5 mm in tip radius and under the following condition: a steel sheet thickness of 0.8 mm, an electrode contact pressure of 200 N, a weld time of 10 cycles (50 Hz), and an electrode holding time of 10 cycles (50 Hz).

3.3 Coefficient of dynamic friction and scratch resistance

Coefficient of dynamic friction was measured as an index of press formability. A stainless steel ball 10 mm in diameter was made to slide on the surface of the test pieces under a load of 100 g at a speed of 150 mm/min., and the coefficient was calculated from the stress of the sliding.

Scratch resistance was evaluated by making a stainless steel ball 10 mm in diameter slide on the surface of the test pieces under loads of 200 and 1,000 g at a speed of 250 mm/min. in one direction and then in the opposite direction and visually judging scratches on the test piece surfaces. The evaluation was as follows: mark 4 for no scratches; mark 3 for slight scratches; mark 2 for clear scratches; and mark 1 for significant scratches.

3.4 Other properties

Finger print resistance: fingers were pressed onto the test piece surface and fingerprints were visually evaluated.

Condensation resistance: 1 ml of distilled water was dripped onto a test piece laid horizontally and, 24 h. thereafter, the mark of the water after it has dried was visually evaluated. This evaluation method is based on the fact that a clear mark is left on the surface if the coating film contains water-soluble components.

Paint adhesion: a paint of a melamine alkyd system (Amilac #1000 of Kansai Paint Co., Ltd.) was applied to the test pieces and baked to form a film 20 μm in thickness. The paint film was cross cut at an interval of 1 mm and then peeled off with an adhesive tape, and the paint adhesion was visually evaluated. Besides the above, after the painting and baking, the test pieces were immersed in boiling water for 30 min., and then the same tape peeling test was carried out without the cross cut.

4. Test Results

4.1 Corrosion resistance

Figs. 2 and 3 show the occurrence of white rust at the flat portions of ZC21 and GI21, respectively, after the salt spray test. With respect to corrosion resistance, the QF type ZC21 was better than the E-treatment sheet, and the QS type ZC21 was nearly equal to the E-treatment sheet. The QF type GI21 also showed better corrosion resistance than the E-treatment sheet did. The results show that the

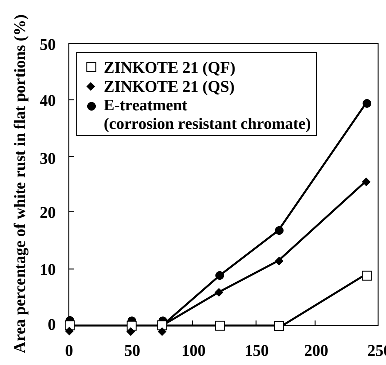

Fig. 2 Occurrence of white rust at flat portions of ZINKOTE 21 after salt spray test

Table 1 Specifications of tested steel sheet products

Base plate	Denomination		Treatment film	Remarks
Electro-galvanized steel sheet (ZINKOTE) (coating weight 20 g/m^2)	ZINKOTE 21 (ZC21)	QF	Chromate-free coating film	Corrosion resistance in priority
		QS	Chromate-free coating film	Conductivity in priority
	E-treatment sheet		Corrosion resistant chromate coating film	Conventional product
	UF		Chromate coating film + organic composite coating film (1 μm)	Conventional anti-finger print sheet
Hot dip galvanized steel sheet (SILVERZINC) (coating weight symbol Z18)	SILVERZINC 21 (GI21)	QF	Chromate-free coating film	Corrosion resistance in priority
	E-treatment sheet		Corrosion resistant chromate coating film	Conventional product

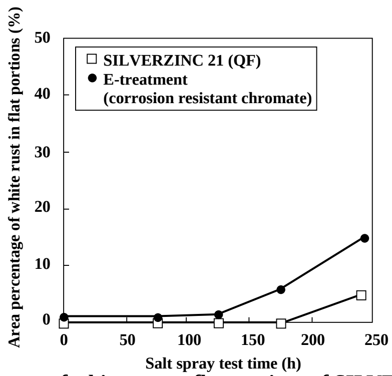

Fig. 3 Occurrence of white rust at flat portions of SILVERZINC 21 after salt spray test

chromate-free coating film realizes good corrosion resistance for a long period of time.

Figs. 4 and 5 show the occurrence of white rust at the Erichsen-worked portions of ZC21 and GI21, respectively, after the salt spray test. Like in the flat portions, with respect to the corrosion resistance of the worked portions, the QF type ZC21 was better than the E-treatment sheet, and the QS type ZC21 was nearly equal to the E-treatment sheet. From the fact that both ZC21 and GI21 exhibited the same level of corrosion resistance as chromate-treated steel sheets even when the treatment film was deformed by the working, the self-recovering function of the treatment film is considered to work as designed.

Fig. 6 shows the corrosion resistance after the alkaline and methylene chloride degreasing in comparison with that without the degreasing. In either case of degreasing, no apparent damage to the treatment film was seen. Either QF or QS showed little deterioration of corrosion resistance as a consequence to the degreasing at a 72-h. salt spray test. At a 120-h. salt spray test, the QS test pieces subjected to the alkali degreasing demonstrated some deterioration of corrosion resistance, but the extent of deterioration was small. As far as the above test was concerned, no adverse influence on corrosion resistance was confirmed regarding the solvent degreasing.

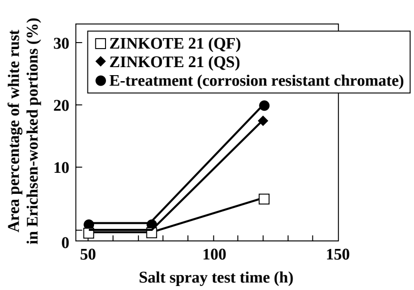

Fig. 4 Occurrence of white rust at Erichsen-worked portions of ZINKOTE 21 after salt spray test

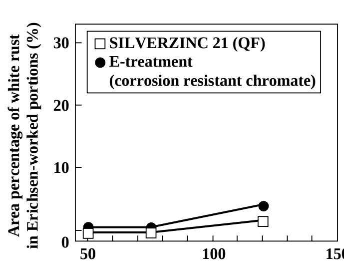

Fig. 5 Occurrence of white rust at Erichsen-worked portions of SILVERZINC 21 after salt spray test

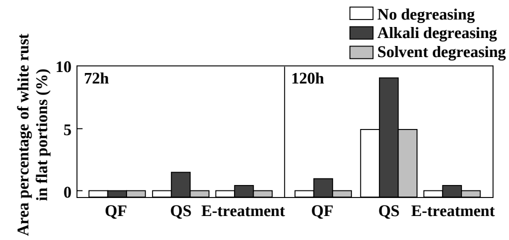

Fig. 6 Influence of degreasing treatment on corrosion resistance of ZINKOTE 21 (occurrence of white rust at flat portions after salt spray test for 72 and 120 h)

4.2 Conductivity and spot-weldability

Fig. 7 shows the surface insulation resistance of the test pieces and **Fig. 8** their contact resistance. The surface insulation resistance of the QF type ZC21 was substantially the same as that of the UF and a little higher (meaning less conductive) than the E-treatment sheet. The surface insulation resistance of the QS type ZC21, wherein priority is given to electric conductivity, was substantially the same as that of the E-treatment sheet.

In contrast, the contact resistance was little different depending on the kind of treatment films; any of the test pieces showed contact resistance values as low as 0.1 mΩ or less (meaning good conductivity). The value of conductivity varies depending on the method of measurement but, at the test of the authors, the QS type showed the same level of conductivity as the conventional E-treatment sheet did regardless of measurement methods.

The shaded portions in **Fig. 9** show the optimum ranges of current for spot welding. Whilst the optimum current ranges of ZC21 and GI21 are to the lower current side than that of the E-treatment sheet, the widths of the range are substantially the same as that of the E-treatment sheet, showing that the products are suitable for spot welding.

4.3 Coefficient of dynamic friction and scratch resistance

The measurement result of the coefficient of dynamic friction is shown in **Fig. 10**. The value of ZC21 was as low as 0.13, demonstrating its excellent surface lubrication compared with the E-treatment and UF sheets.

Fig. 11 shows scratch resistance of ZC21. The scratch resistance of ZC21, especially that of the QF type, is better than that of the

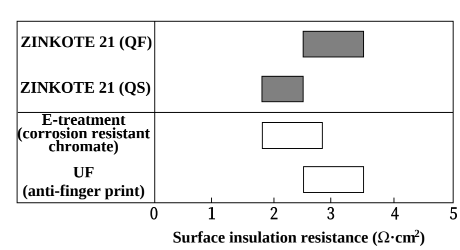

Fig. 7 Surface insulation resistance of ZINKOTE 21

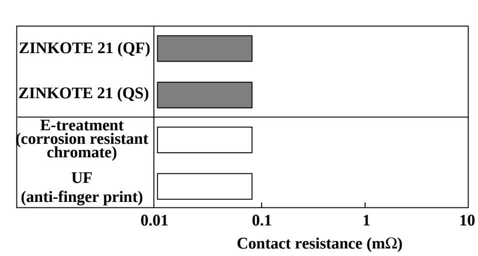

Fig. 8 Contact resistance of ZINKOTE 21

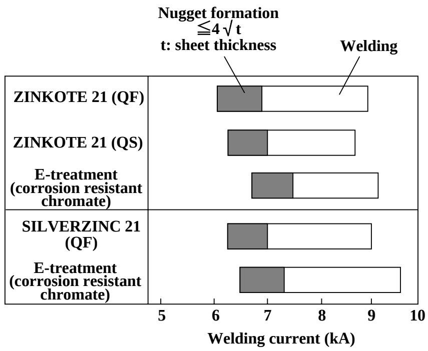

Fig. 9 Spot-weldability (optimum current range) of ZINKOTE 21 and SILVERZINC 21

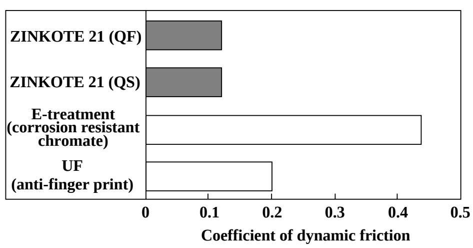

Fig. 10 Coefficient of dynamic friction of ZINKOTE 21

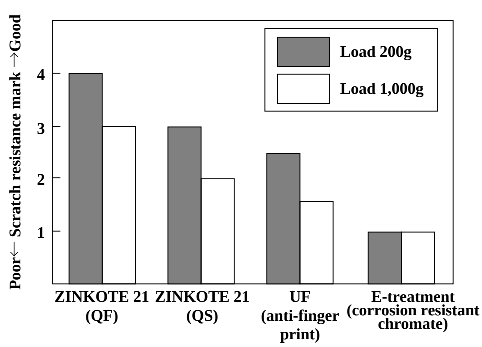

Fig. 11 Scratch resistance of ZINKOTE 21

conventional anti-finger print steel sheet, or UF.

4.4 Finger print resistance, condensation resistance and pant adhesion

Test results are summarized in **Table 2**. Either ZC21 or GI21 is better than the E-treatment sheet in finger print resistance, condensation resistance and paint adhesion.

4. Conclusion

As explained herein, the new chromate-free-treated galvanized steel sheets, ZC21 and GI21, have corrosion resistance, electric conductivity, surface lubrication, scratch resistance, finger print resistance, condensation resistance and paint adhesion equal to or better than those of conventional galvanized steel sheets with corrosion resistant chromate treatment and thus, they can be used as substitutes for the conventional products having E-treatment. The QS type new products have better conductivity than the QF type, but the latter is superior to the former in corrosion resistance and scratch resistance; thus either of them can be selected as substitutes of the conventional products depending on required performance. These environment-conscious products are gaining popularity in the market and their production is expected to surpass the 10,000-ton per month mark by the end of 2002. Nippon Steel will continue developing and offering new products having better utility and higher performance.

References

1) Nippon Steel: List of Environment-conscious Products Offered by Nippon Steel Corporation (Steel Sheets). 2000
2) Yamazaki, M. et al.: Shinnittetsu Giho. (371), 43 (1999)
3) Morishita, A. et al. : Proceedings of GALVATECH'01. 2001, p.229

Table 2 Finger print resistance, condensation resistance and paint adhesion of galvanized sheet products

Product			ZINKOTE 21		ZIN KOTE	SILVER ZINC 21	SILVER ZINC
Test items			QF	QS	E-treatment	QF	E-treatment
Finger print resistance			Little visible	Little visible	Visible marks	Little visible	Visible marks
Condensation resistance			No mark	No mark	Visible marks	No mark	Visible marks
Paint adhesion	Primary	Cross cut					
		Erichsen					
	Secondary	Cross cut					
		Erichsen					

◎ : excellent, ○ : good