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Evaluation of Nonchromated Thin Organic Coatings for Corrosion Inhibition of Electrogalvanized Steel

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The toxicity of chromium that is used to impart corrosion resistance to galvanized steel created environmental and health-related concerns and generated a great deal of interest in developing chrome-free treatment coatings. In the present work, organic-inorganic composite coatings were used to coat electrogalvanized steel (EG) sheets for corrosion protection without degrading its weldability property. The new coatings composed of specially modified polyurethane dispersion hybridized with silicate and unique inorganic-organic inhibitors were developed during this work. It was found that about 1 µm thickness of coating layer is secure enough in corrosion resistance of flat and formed part even after alkaline degreasing. Overall chemical resistances including fingerprint resistance and paint adhesion property were satisfied with the test specification of Sony technical standard of SS-00260-2002. Therefore, it is concluded that the newly developed chrome-free product can replace the conventional chromated product.

Keywords *: nonchromated, corrosion inhibition, electrogalvanized steel, thin organic coatings, salt spray, welding*

1. Introduction

Galvanized steel utilizes the principle of sacrificial zinc corrosion, which is a general method for preventing the corrosion of iron steel. However, the corrosion product generated when zinc corrodes in the atmosphere produces so-called white rust on the steel sheet, which leads to a deterioration in appearance and impairing paint adhesion to the plated steel sheet. These problems are generally solved by treating the sheet with chromates or by employing a phosphate conversion coating in conjunction with a chromate rinse.[1),2)] While such chromate treatments provide resistance to the formation of white rust and produce strongly paint-adherent chromate film, hexavalent chromium is highly toxic and environmentally undesirable. Research efforts have focused on developing nonchromate corrosion inhibiting system that provides same level of performance.[3)-7)] It has been challenging specifically with regard to thin organic coatings with limited barrier functionality, such as coil and aircraft coatings.[8),9)] Finding nonchromate inhibitors that are broadly effective on multi-substrates has been also a challenge as well. The state of art of thin organic coating involves polyurethane and ethylene-acryl copolymer dispersions as main binders for basic type treatment and epoxy dispersion for acidic treatment. There are still strong needs of improvement of corrosion performance especially after alkaline degreasing and of decreasing peak metal temperature.

The purpose of this investigation is to develop non-chrome surface treatment agent providing improved corrosion resistance and improved adhesion characteristics to electrogalvanized steel (EG) substrates. Basic type of aqueous organic/inorganic hybrid solution was developed and overall physical and chemical characteristics of the coated EG steel were investigated.

2. Experimental procedure

The corrosion resistance, electrical conductivity, spot-weldability, fingerprint resistance, formability and other physical/chemical properties were evaluated by the following methods using commercially available electrogalvanized steel sheets. Nonchromated treatment liquids were typically prepared by mixing stepwise ingredients given in Table 1. The anticorrosive coating solution obtained was coated by bar coater No. 3 or No. 4 onto a degreased electrogalvanized steel sheet with a deposited film amount of about 1000 mg/m^2 and dried at a peak metal temperature (PMT) of 150 ℃ for several seconds to prepare test

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specimens for the following evaluations.

2.1 Corrosion resistance

The test pieces were subjected to 7 mm extrusion work by an Erichsen tester and followed by salt spray tests (ASTM B-117 and Sony cycle test (spray 8 h + dry 16 h)[10]). White rust resistance was evaluated in terms of the area percentage of white rust on the flat area and the domed area. Other test pieces were degreased with alkaline solution (CL-N364S and FC-L4460 from Nihon Parkerizing Co.) and then subjected to a salt spray test. The anticorrosion performance after alkaline degreasing was evaluated.

Table 1. Standard recipe for making Cr-free coating solution

Ingredients	Amount	Remark
Polymer dispersions	40 - 70	Pre - crosslinked or Hybrid type
Crosslinker	2 - 15	Melamine - Formaldehyde, etc
Silica sol	10 - 30	Alkaline type
Inorganic inhibitors	0.2 - 5.0	Silicate or phosphate
Oragnic inhibitors	0.1 - 2.0	Hetero atom containing
Silane	0.1 - 2.0	Glycidyl type
Transition metal compounds	0.5 - 5.0	Group IVB ~ VIIB
Lubricants	0.5 - 3.0	PTFE, PE wax
Defoamer	0.1	-
Wetting agent	0.2	-
Solvent	1 - 10	Water miscible
pH adjusting agent	0.1 - 0.5	Amine or ammonia

2.2 Conductivity and spot-weldability

Surface electrical resistance was measured by the 4-point probe method using Loresta EP of Mitsubishi Chemical Co. Specimens were welded as shown in Fig. 1. The electrode shape was a DR type with 6 mm tip diameter and welding force was 2.5 kN. A spot welding of 1000 spots was carried out and a percentage of good weld spots relative to all the weld spots was determined and used as criteria of weldability. Generation of expulsion and surface flash at all the weld spots was visually evaluated.

2.3 Coefficient of dynamic friction and scratch resistance

Friction property was evaluated by estimating the dynamic friction coefficient using Draw bead tester. The test specimen was fixed between flat dies with a holding

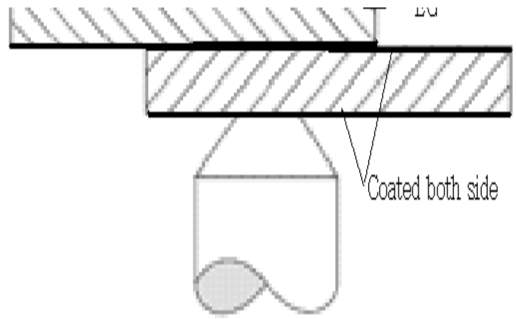


Fig. 1. Schematic set-up for a resistance spot-welding

pressure of 10 MPa and subjected to sliding in the direction D at 20 mm/s. The coefficient is calculated by F/2P where F is sliding force and P the pressure between die. Scratch resistance was evaluated by making a stainless ball slide on the surface of test panels under loads.

2.4 Other properties

Chemical resistance: The change in color of the tested sheet was measured before and after rubbing 10 times with solvent-soaked clothes. Methanol, methyl ethyl ketone, methylene chloride, gasoline and acetone were used as the solvents to be tested.

Fingerprint resistance: A finger was pressed onto the surface of the treated sheet followed by evaluation by visual inspection of the status of the residual fingerprint trace. Colorimeter was also used to measure color difference (ΔE) after applying a white petroleum jelly to the specimens to evaluate fingerprint resistance.

Condensation resistance: Visually evaluate the appearance of the tested pieces after recovering from the humidity chamber at 65 ℃, 95% relative humidity for 192 hours.

Resistance to artificial sweat solution: Drop 0.05 cc of artificial sweat on the test specimens at 5 places and then put them in a chamber at 65 ℃ 95% RH for 48 hours. Evaluate visually if there left any apparent damaged marks. The artificial sweat solution were made with 8 g of sodium phosphate, 8 g of sodium chloride, 5 g of acetic acid in 1 liter of distilled water and its pH was adjusted to 4.5 with sodium hydroxide.

Paint adhesion: A paint of polyester-melamine type (from KCC) was applied to the test pieces and baked to form a film of 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. Same test protocol was repeated with the test pieces after drawn to 7 mm depth by Erichsen tester.

3. Design concept of cr-free coating compositions

Generally, corrosion resistance increases with increasing thickness of the organic composite coating while electrical conductivity and welding characteristics suffer. In order to secure good welding characteristics, the coating thickness needs to be less than 1 to 2 µm. Because the level of corrosion resistance achievable with nonchromated coatings is generally inferior to that of chromated coatings, it is necessary to apply a thick coating of more than 3 µm, which inevitably degrades the electroconductivity and weldability. To overcome such problem, nonchromated organic coatings should be designed to have most effective barrier functionality and highly effective corrosion inhibiting capacity possibly together with self-healing effect (Fig. 2). The following factors were taken into consideration for this investigation;

- good storage stability of colloidal coatings,
- fast film-formation of the coatings,
- crosslinked polymer network under lower PMT baking condition,
- organic-inorganic composite coatings,
- combination of nontoxic inorganic corrosion inhibitors and organic corrosion inhibitors,
- incorporation of transition metal compounds and silane coupling agents, and
- combination of waxes

4. Quality performance of developed cr-free coated electrogalvanized steel

4.1 Corrosion resistance

Fig. 3A shows corrosion resistance of the developed steel sheets after 7 mm drawn by Erichsen tester and after alkaline degreasing treatment. Without any physical and

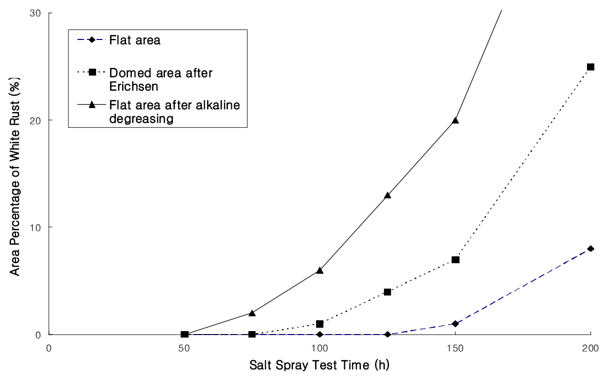


Fig. 3A. Corrosion resistance of the developed EG steel sheet

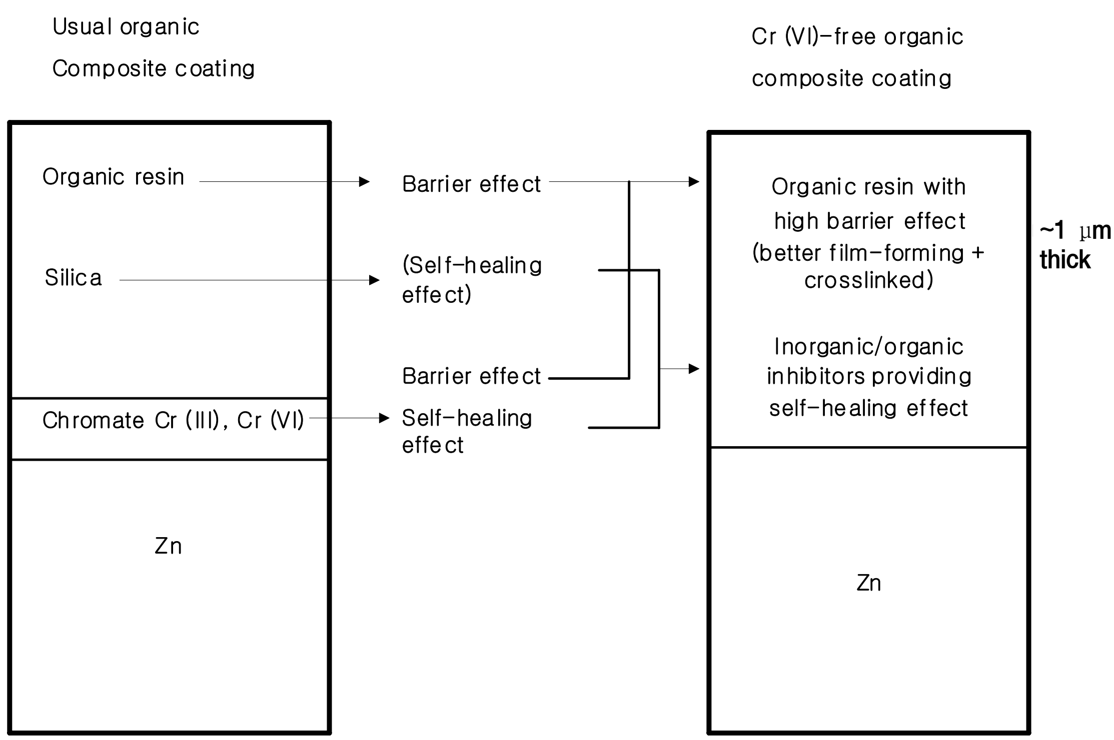


Fig. 2. Basic design concept of developing chrome-free thin organic composite coatings

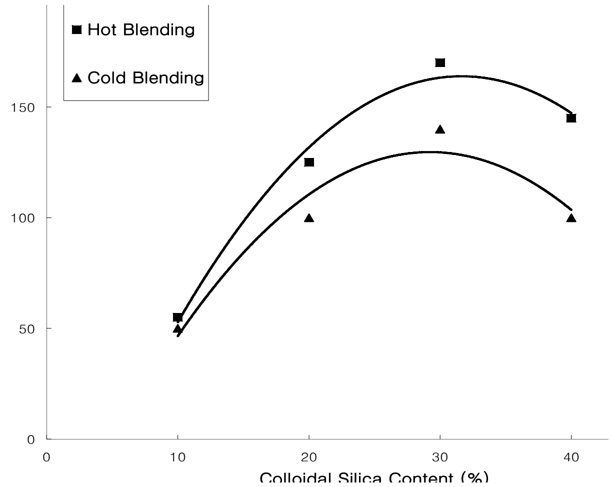


Fig. 3B. Effect of colloidal silica on corrosion resistance

chemical degradations, the coated EG steel did not generate any white rust until 125 hours and demonstrated high corrosion resistance comparable to conventional chromate coated EG steel. Effect of incorporation of silica sol on the anti-corrosion performance was shown in Fig. 3B, where it was found that incorporation of around 30 % of silica provided best anti-corrosion performance and hot blending together with silane coupling agent resulted better anti-corrosion performance compared to cold blending. It was believed that chemical couplings between polymer particles and silica particles would help to form more compact film under very short drying condition which is the case in this work. As shown in Fig. 3C, the corrosion resistance after degreasing is depending on the type of organic binders and better result was found with polyurethane dispersion where polymer chains were in-situ pre-

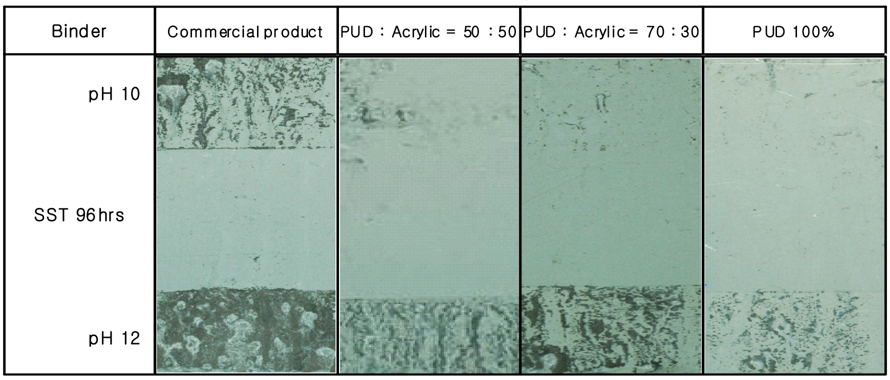


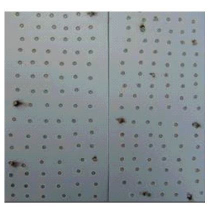
Fig. 3C. Alkali degreasing resistance of Cr-free EG sheet (Effect of binder type)

Weldability

Welding Condition	Welding machine	Electrode	Force (kN)	Welding time (Cycle)			
				Squeeze	Up-slope	Weld	Hold
	Welding Simulator	Al_2O_3 dispersed Cu (DR type) 6mmΦ	2.5	20	3	13	5

Result	Steel substrate				Lower limit	Upper limit	Current range	Life of electrode
	EG	DDQ	0.75t	20/20	5.7	8.3	1.6	1,009

Welded substrate



Front

Rear

Welding Tip

Fig. 4. Weldability of Cr-free EG sheet

crosslinked during their preparation. The finding of corrosion resistance being improved when acrylic polymer was incorporated during polyurethane particle formation supported the importance of proper film formation to have high barrier functionality.

4.2 Conductivity and weldability

The measured resistivity value of less than 0.2 mΩ indicated adequate grounding and EMI shielding performances of the developed steel sheets. Welding performance of the sheets having about 1 μm thick composite layer on both sides was shown in Fig. 4, demonstrating good continuous spot weldability with an appropriate welding current range.

4.3 Coefficient of dynamic friction and scratch resistance

The measurement result of the coefficient of friction is shown in Fig. 5. It was found that the types of lubricant and polymer dispersion and film thickness were most important factors to be controlled to achieve lower friction coefficient, better tribological performance, and better adhesion to subsequent layers.

4.4 Other properties

Typical properties of the coating solution developed and test results of the coated EG steel sheet are summarized in Table 2 and Table 3, respectively. Generally, it was reported that damaged marks are hardly visible if the measured color difference is less than three.[11] The color change values (ΔE) of the specimens after rubbing with various solvents were less than 2, that are comparable or better than those of the conventional chromate coated steels. The ΔE value of the specimens less than 1 after fingerprinting indicates good anti-fingerprint property. Condensation resistance and paint adhesion properties of the developed steel substrate were also good enough to be commercially used to replace conventional chromate coated one.

Table 2. Typical properties of the Cr-free coating solution

Appearance	Milky white liquid
Solids, %	13.0 ~ 20.0
pH	8.5 ~ 9.5
Viscosity, cps	< 20
Specific Gravity (25℃)	1.00 ~ 1.05
VOC	Less than 50 g/L
Chromium	Not contained

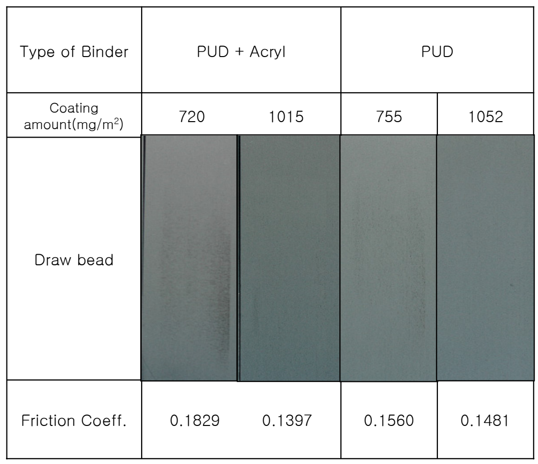


Fig. 5. Test result of formability of the Cr-free EG sheets

Table 3. Summary of overall performance of the developed Cr-free EG sheets

		Cr^{6+} type	Cr^{6+} free type	Method
Dried film build (mg/m^2)		1,000±200	1,000±200	Measure the dry film weight after delaminating with concentrated sulfuric acid
Salt spray resistance		◎	◎	Salt spray test (5%NaCl, 35 ℃) and 2 cycle pass with Sony test method
Condensation resistance		◎	◎	65 ℃ x 95% RH for 192 hrs
Alkali resistance	pH 10	◎	◎	Dip into alkaline solution at 60 ℃ for 2min
	pH 12	○	○	
Erichsen test		○	○	Salt spray test (5%NaCl, 35 ℃) after Erichsen test
Solvent resistance	MEK	◎	◎	10 times double rub with 1 Kg load
	Ethanol	◎	◎	
Paint adhesion		◎	◎	Reverse impact test with 1/16” cross hatch after painting polyester topcoat
Artificial sweat resistance		○	○	Visual evaluation of damaged marks by artificial sweat solution at 65 ℃ 95% RH for 48 hours

◎: Excellent (much better than required), ○: Good (better than required), △: Fair (just acceptable), X: Poor (not acceptable)

5. Summary

In this work, we evaluated the overall performance of the newly developed chrome-free thin organic coatings for elctrogalvanized steel sheets. The main results are summarized as follows;

(1) The corrosion resistance of nonchromated steel sheets was superior to that of conventional chromated steel sheets and found to be influenced, e.g., by the type of organic polymers, incorporation of silica and type of corrosion inhibitors.

(2) An excellent spot weldability was obtained up to film thickness of 2 μm.

(3) Formability judged by draw bead test was comparable to the conventional chromated steel sheets.

(4) Overall chemical resistances including fingerprint resistance and paint adhesion property were satisfied with the test according to Sony technical standard of SS-00260-2002.

Therefore, it is concluded that the newly developed chrome-free product can replace the conventional chromated product. It is, in future, needed to extend the application of the design concept of the present work to develop chrome-free coatings for other metal substrates like hot-dip galvanized, galvannealed, and Al-Zn alloy coated steels.

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