

Development of a Highly Anti-Corrosive Organic-Inorganic Hybrid Paint

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ABSTRACT

A highly anti-corrosive organic-inorganic hybrid paint for automotive steel parts has been developed. The inorganic component included in the paint is silicon dioxide (SiO_2), which has the capability to passivate zinc. By application of the paint on a trivalent chromate-treated zinc-plated steel sheet or a trivalent chromate-treated zinc-nickel-plated steel sheet, high anti-corrosion protection can be provided to steel materials. Particularly in the case of application over a zinc-nickel-plated steel sheet, 0 mm corrosion depth after a cyclic corrosion test (CCT) of 450 cycles was demonstrated. An investigation of the mechanism of this corrosion resistance leads to the following observations: 1) Even in an area where the paint coating is missing, SiO_2 is precipitated to cover the steel material and passivate the zinc. 2) The passive material is Simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$) and it fills the area from where the paint has been lost. 3) The deposition layer is closely packed by the effect of trivalent chromate and the passivation of the deposition is maintained by nickel. With this closely packed deposited layer, the painted material demonstrates a high corrosion resistance.

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INTRODUCTION

Paints have been developed for various purposes in recent years. One purpose is corrosion prevention of steel structures, which is also regarded as important in the automotive industry. Particularly in regions with heavy snow, higher corrosion resistance is required for steel parts because a snow-melting agent (salt) is used. The part that is targeted in this study, namely a fuel filler inlet pipe, is important for transporting fuel from the fuel filler to the fuel tank. To prevent corrosion of this part, automobile manufacturers changed the material of the part from iron-based materials to stainless steel-based or resin-based materials. However, because of the processability or material cost, there is still a deeply rooted demand for use of iron-based materials.

In the case of iron-based materials, the substrate is generally plated with zinc first, and then, the paint is applied. Because of the difference in the ionization tendency, zinc corrodes earlier than iron, delaying the corrosion of the substrate (Fe). However, if a conventional paint is applied over the steel materials, high-grade corrosion resistance such as stainless steel-based specification (stainless steel sheet + cathodic electrodeposition paint) cannot be

expected. Hence, there is a need to develop a paint that can achieve a corrosion resistance equivalent to that of the stainless steel-based specification for the iron-based materials.

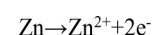
Although there was a previous report where SiO_2 improved the corrosion resistance of a zinc-plated steel sheet [1], the mechanism was not clarified.

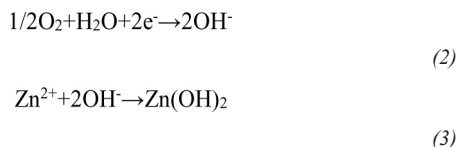
Therefore, a paint that utilizes the effect of SiO_2 was developed, and determination of the corrosion resistance for iron-based materials and an analysis of its mechanism were performed.

DEVELOPMENT CONCEPT

Utilization of Zinc Compound

Because of the difference in the ionization tendency between zinc and iron, zinc corrodes earlier. The corrosion of zinc is expressed by the following chemical reactions:





The Zn(OH)_2 formed in (3) is converted to ZnO after a dehydration reaction. After reacting with OH^- and Cl^- , it forms $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. Upon deposition over the surface of steel, ZnO and $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ delay the corrosion by restricting the oxidation-reduction reaction of iron [2], and the mechanism allowing these zinc compounds to precipitate early is considered to be effective for the development of the paint.

Effect of SiO_2

A Zn^{2+} forms a complex with H_2O and this complex releases H^+ to make OH^- . The OH^- and Cl^- react with Zn^{2+} to form $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. The release of H^+ has been reported to be affected by SiO_2 [1]. As shown in Fig. 1, H_2O close to the Si-O-Zn bond releases H^+ more easily because the electron is attracted more to the O side compared to a Zn-O-Zn bond. As a result, the OH^- necessary for $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ is likely to be formed. Then, as mentioned before, the Zn^{2+} complex reacts with OH^- and Cl^- to form $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$.

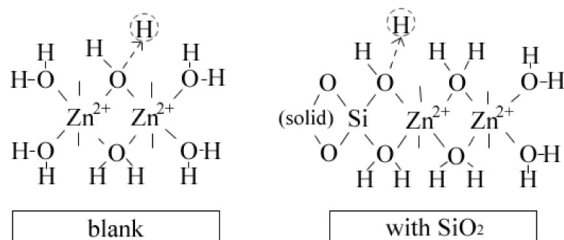


Figure 1. A model for release of H^+ from the aqua complex of Zn^{2+}

Since the conductivity of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ is lower than that of ZnO , improvement in corrosion resistance is anticipated.

Paint Design

Developing a new paint was used by the colloidal silica as inorganic agent (SiO_2) and the synthetic resin emulsion as organic agent. The test piece (T.P) was made under the condition as table.1 and evaluated the corrosion resistance by CCT under the condition as fig.2.

For the paint mixed with SiO_2 , peeling occurred at 90 cycles of CCT. It is believed that the adhesive force of the paint film was insufficient because there were few points of adhesion between the inorganic component and the base material. Therefore, an organic-inorganic hybridization that binds an organic component with an inorganic component was studied to allow the inorganic component also to have good adhesion. A coupling agent was used to provide a chemical bond, and no peeling of the paint film occurred upon evaluation of the T.P. made from this paint.

It is believed that the adhesive force of the paint film improved because points of adhesion were generated between the inorganic component and the base material, in a form that is shown in Fig. 3, by the bonding of the inorganic and organic component, which restricted the peeling.

Table 1. Surface treatment of test piece

Specimen	Plating	Coating	Scribe
Specimen.1	Zn alloy plating (8 μm) Chromate (0.1 μm)	Conventional paint (20 μm)	with cross-cut reached the plated surface
Specimen.2	Zn alloy plating (8 μm) Chromate (0.1 μm)	Organic-inorganic hybrid paint (20 μm)	with cross-cut reached the plated surface

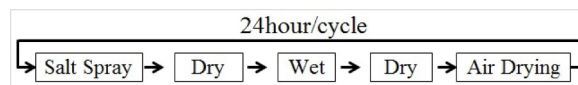


Figure 2. Testing condition of cyclic corrosion test

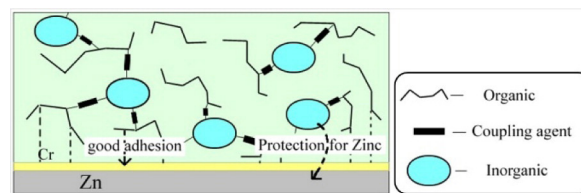


Figure 3. Schematic illustration of the organic-inorganic hybrid film

Corrosion Resistance

Corrosion Resistance of Zinc-Plated Steel Sheet with Developed Paint

Next problem is corrosion resistance. CCT cycle number when corrosion pits are observed is an alternative value of corrosion resistance. The pits mean the state that the corrosion pierces the base material. Before being pierced by corrosion, corrosion depth is measured by a microscope after removing the paint film and rust from the test piece randomly chosen.

Compared to conventional paints, application of the developed paint extended the number of CCT cycles until pitting but red rust occurred at 120 cycles and pitting occurred at 330 cycles for the developed paint (Fig. 4).

When the T.P. was evaluated according to the stainless steel-based specification as a comparison of the corrosion resistance, no progress in the corrosion depth was seen even at 330 cycles. Therefore, a further improvement in the corrosion resistance of the zinc-plated steel sheet + developed paint was required for application to the parts.

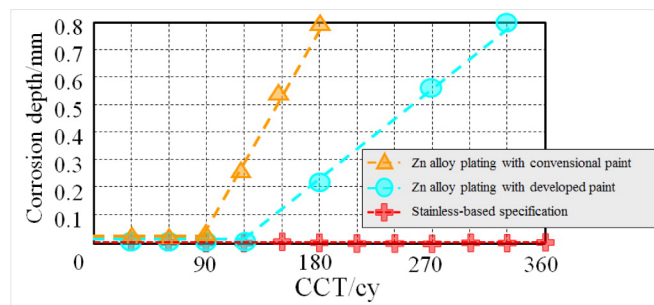


Figure 4. Corrosion depth of the developed paint and conventional paint on zinc-plated steel and stainless-based specification