High Corrosion Resistance Mechanism of Chrome-Free Zinc-Rich Paint

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In the zinc-rich paints used for corrosion protection of automotive parts, a chrome-free solution with superior performance is highly desirable, in part due to the impact of the ban of hexavalent chromium. In this paper, we will explain the high corrosion resistance performance mechanism of chrome-free zinc-rich paint, and compare the performance of this coating with other surface treatments.

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1. Introduction

Steel is a metal widely used in the automotive and construction sectors among others. As it also very easily corrodes, steel used in applications requiring corrosion protection is generally first given a surface treatment such as the application of a metal film or coating. Electroplating or thin film coating is normally applied to small parts because it is not appropriate to use molten zinc plating or a paint coating that develops a thick film, subsequently causing dimensional accuracy problems in these small parts.

Zink plating is commonly used as a metal surface treatment for small parts. However, thin-film zinc-rich paint is applied to numerous components especially requiring high corrosion protection such as those used for automotive brake/suspension systems.

Conventional thin-film zinc-rich paint had a chromium compound as a binder component. Although this type was widely used before, chromium compounds have been subject to several regulations in the global trend to reduce environmentally harmful substances, and the use of these substances is currently strictly controlled. Because of this, chrome-free zinc-rich paint without any toxic heavy metals has been gaining a lot of attention, and new processes have been developed and become available in the market.

In this study, we measured the polarization curves of zinc plating and non-chrome zinc-rich paint, and examined the high corrosion protection mechanism of the zinc-rich paint.

2. Experiment

2-1 Preparation of Test Samples

Most non-chrome zinc-rich paint products available in the market develop a film structure comprised of a base coat and top coat. Depending on the top coat specification, there are two broad types of zinc-rich paints. The first type uses a top coat comprised of aluminum powder and a binder made from organic resin to develop the coating film (referred to as the aluminum coating type hereinafter). The other has a top coat with a silica-base solution that reacts with and impregnates into the base coat (referred to as the silica reaction type hereinafter).

In this test, both the aluminum coating type and silica reaction type samples were prepared as zinc-rich paint test samples. Using a bar coater, the liquid coating was applied to cold-rolled steel coupons (JIS-G3141, 0.8mm×50mm×100mm). The coupons were then baked under the standard baking condition. Table 1 and Figure 1 below show an overview of the zinc-rich paint test coupons.

In addition, we also made 3 types of zinc-plated test plates with (1) zinc plating, (2) zinc plating + blue hexavalent chromium and (3) zinc plating + yellow hexavalent chromium. The film thickness of the zinc plating was 8μ, and general hexavalent chromium processes were used under the standard condition for each process.

Table 1 Zinc-Rich Paint Test Coupons

	Base Coat			Top Coat		
	Film thickness [μm]	Major components	Bake condition	Film thickness [μm]	Major components	Bake condition
Al coating type	8.0 – 10.0	Zn, Al, Si, Ti	260℃, 20min	2.0 – 3.0	Al, Organic resin	200℃, 20min
Silica reaction type	8.0 – 10.0	Zn, Al, Si, Ti	260℃, 30min	0.5 - 1.0	Si	100℃, 10min

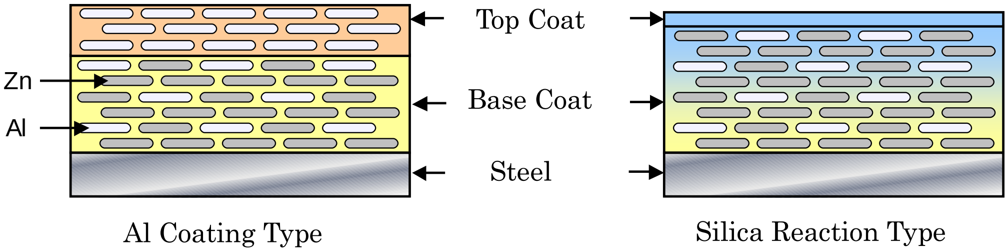

Figure 1 Zinc-Rich Paint Film Cross Section

2-2 Corrosion Protection Evaluation

In this study, a cyclic corrosion test (referred to as CCT hereinafter) was used as an accelerated test to evaluate the corrosion protection performance. The following indicates the CCT condition.

Tester: Suga Test Instrument CYP-90
One Cycle: SST (50℃, 17hr.) → Dry (70℃, 3hr.)→ SST (50℃, 2hr.)
→ Dry (Room Temp., 2hr.）

Additional test coupons were cross-cut and respectively coated with each zinc-rich paint type to also evaluate corrosion protection over scratched areas.

2-3 Polarization Curve Measurement

We used a Potentiostat machine (Solartron Group Ltd. : 1285A) for measurements. This system is configured with 3 electrodes. Each test plate was attached as the test sample pole, and measurements were performed in a 5% NaCl solution (pH: 7±0.2). Refer to Figure 2. Platinum was used for the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The potential scanning speed was 1.0mV/sec.

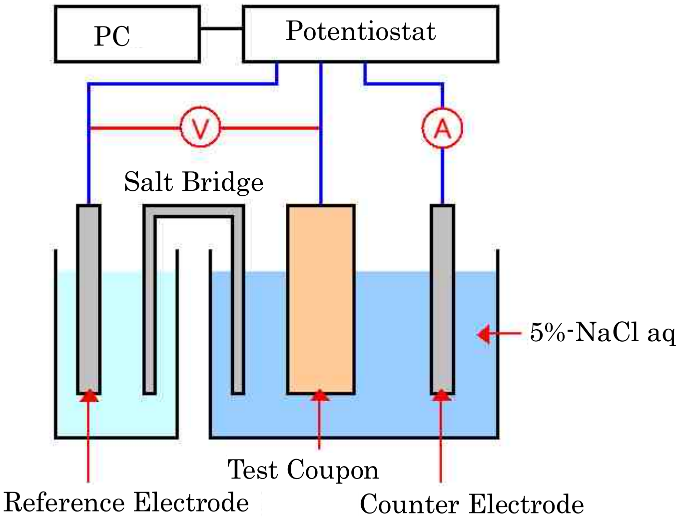

Figure 2. Polarization Curve Measurement Equipment

3. Results and Consideration

3.1 Results of Corrosion Resistance Performance Evaluation

Refer to Figure 3 for the CCT results of the corrosion resistance performance evaluation of each test coupon. In this evaluation, we were able to confirm that the zinc-rich paint demonstrated superior corrosion resistance against red rust to the zinc plating and hexavalent chromium. When the two types of zinc-rich paints were compared, we verified that the silica reaction type had better corrosion resistance over scratched areas than the aluminum coating type, and that the corrosion resistance performance of the aluminum coating type was reduced by half when there were scratches on the film.

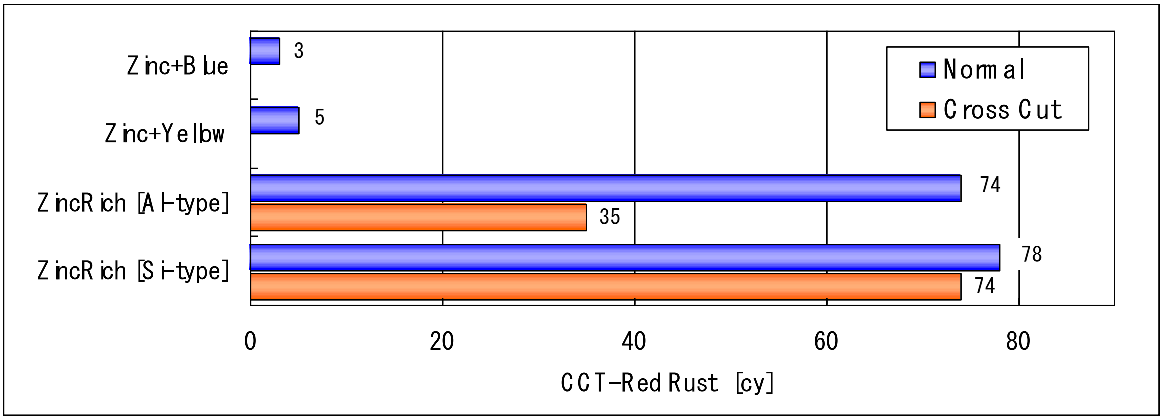

Figure 3 CCT Corrosion Resistance Evaluation Result

3.2 Natural Corrosion Potential Measurement

The following is generally considered as the corrosion process of zinc-rich paint. On the surface of the zinc-rich paint film, a corrosion battery is first formed with the film components (mainly zinc) only, causing corrosion (dissolution) of the film. Furthermore, when the steel surface is exposed due to defective zinc-rich paint film or to a dissolution of the film components, a corrosion battery is formed with zinc in the film contacting iron. Zinc subsequently starts to dissolve, as it is a more base material than iron (sacrificial corrosion protection effect). When the steel is further exposed due to the loss of the zinc-rich coating film, there will be areas where the sacrificial anode does not work, resulting in the corrosion of iron.

Based on the above-described notion, the following two factors are required to achieve a high corrosion resistance of zinc-rich paint.

(1) Effectiveness of zinc-rich paint film (zinc) corrosion (dissolution) control
(2) Effectiveness of zinc/iron metal battery formation control

In this study, we focused on these two factors, and analyzed each film based on the polarization curve measurement results.

Figure 4 below shows the polarization curve near the natural corrosion potential of each test sample.

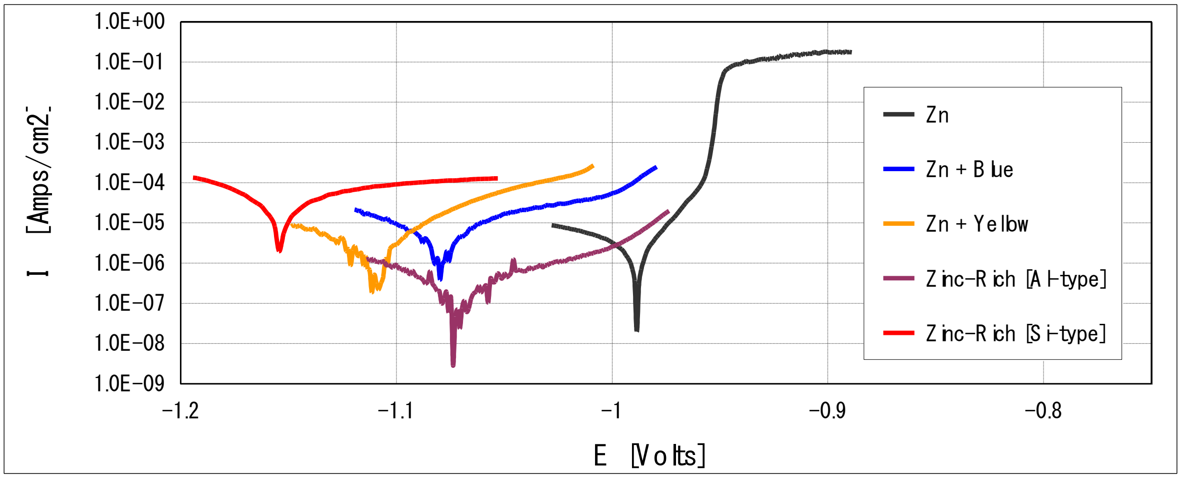

Figure 4. Polarization Curve Near Natural Corrosion Potential

As an example, looking at the polarization curve of the zinc plating film, -0.988V is the potential indicated when the test coupon is soaked in the test solution. At this time, in the zinc plating film surface, anode reaction and cathode reaction are well balanced. The potential at this point is called the natural corrosion potential. The natural corrosion potential of iron in this test solution is -0.445V. Because the natural corrosion potential of zinc is more base than that of iron, a sacrificial corrosion protection mechanism is established with a zinc plating film over iron.

Each polarization curve shows the relationship between the test sample and the electrical current when the potential is changed to the cathode (minus) side or to the anode (plus) side from the natural corrosion potential, using the potentiostat. Cathode and anode reactions respectively occur on the test sample.

When we examine the natural corrosion potential of test coupons plated with zinc and processed with blue or yellow hexavalent chromium, the blue one shows -1.079V and the yellow shows -1.108V. What this means is the higher the corrosion resistance of the film, the more base the natural corrosion potential. When the natural corrosion potential is shifted to be more base, we consider that the sacrificial corrosion resistance mechanism for iron will work better. This shifting of the natural corrosion potential is one element of the corrosion protection mechanism of the film made of zinc plating and hexavalent chromium.

Therefore, when we examine the natural corrosion potential of the zinc-rich paint, the aluminum coating type shows -1.073V, and it is just about the same as that of the blue hexavalent chromium. The silica reaction type zinc-rich paint shows -1.154V, and it is more base than that of the yellow hexavalent chromium. The potential of either type of zinc-rich paint is shown to be more base than that of the zinc plating film.

When these two zinc-rich paints are compared, the silica type shifts to be more base by 0.081V than the aluminum coating type, and therefore, the sacrificial corrosion protection seems to more easily occur with the silica type. We believe that this qualitative difference lead to the differing results in the corrosion resistance performance in the cross cut test.

In addition, a reason why zinc-rich paint has a better corrosion resistance than the film comprised of zinc plating and hexavalent chromium is due to the difference in film thickness. The film thickness of the blue hexavalent chromium is 0.1~0.2µm and the thickness of the yellow material is 0.4~0.6µm. On the other hand, the top coat of the aluminum coating type zinc-rich paint is 2.0~3.0µm. We can also expect the same effect from the base coat below the top coat.

Furthermore, as the silica reaction type top coat impregnates into the base coat and reacts with it, the top coat and base coat are considered to be consolidated. Therefore, we can expect a similar level of sacrificial corrosion resistance effect from the entire 10µm-thick film.

In other words, the fact that a thicker film with better sacrificial corrosion resistance is present over iron is one reason for the high corrosion resistance mechanism of zinc-rich paint.

3.3 Dissolution Behavior of Polarization Curve Near Natural Corrosion Potential

Figure 5 below indicates the anode polarization curve near the natural corrosion potential of each test sample (+250mv).

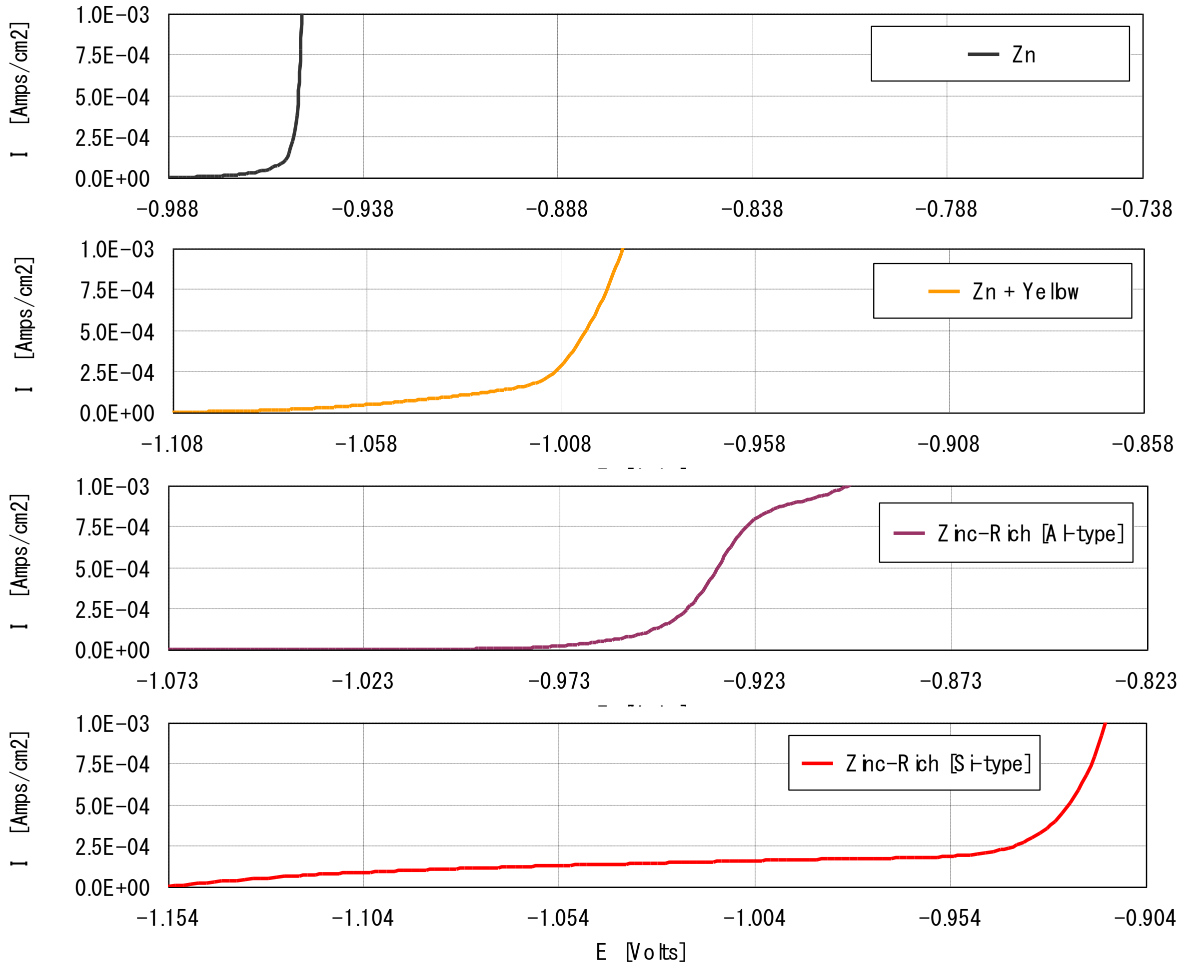

Figure 5 Dissolution Behavior Near Natural Corrosion Potential (+250mV)

We can evaluate the corrosion control effectiveness based on the configuration of the polarization curve near the natural corrosion potential on the anode side. As an example, when the curve of the zinc plating is polarized by approx. 40mV toward the anode side from the natural corrosion potential, the current density reaches 1.0mA/cm^2. In the zinc plating with yellow hexavalent chromium, unless the curve is polarized by approx. 100mV, the current density does not reach 1.0mA/cm^2. This indicates that the film dissolution is more controlled in the zinc plating with yellow hexavalent chromium than in the zinc plating only.

In other words, in the simple zinc plating film, a large corrosion current is likely to flow when there is even slight polarization. In the film processed with hexavalent chromium after zinc plating, a large corrosion current is unlikely to run when polarization is small.

When we look at the polarization curve of the zinc-rich paint on the anode side, the current density increase in the aluminum coating type is extremely small if the polarization is up to approx. 100mV. We can confirm that approx. 170mV polarization is required to reach 1.0mA/cm^2. In the silica reaction type, even if 200mV is polarized, the current density can reach approx. 0.2mA/dm^2, demonstrating that the film dissolution is well controlled.

In other words, the zinc-rich paint film can control the dissolution of film better than the film processed with hexavalent chromium after zinc plating. Even when there is polarization, there is only a small amount of corrosion current. This contributes to the high corrosion resistance mechanism of zinc-rich paint.

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4. Conclusion (Summary)

In this study of the high corrosion protection mechanism of the zinc-rich paint, we focused on the effect of corrosion control and the effect of sacrificial corrosion protection for iron that the zinc-rich paint film possesses. We conducted analyses by measuring the polarization curve of each film.

As a result, we obtained the natural corrosion potential of each film and verified that the zinc-rich paint demonstrates a sacrificial corrosion protection effectiveness superior to that of the film comprised of hexavalent chromium over zinc plating. In addition, by analyzing the polarization curve on the anode side near the natural corrosion potential of each film, we confirmed that the zinc-rich paint film has better corrosion control effectiveness than that of the film comprised of hexavalent chromium over zinc plating.

In conclusion, we believe that the following two factors contribute to the high corrosion protection mechanism of the zinc-rich paint.

(1) The natural corrosion potential of the film is more base than that of the hexavalent chromium film over zinc plating. Therefore, sacrificial corrosion protection for iron works more easily.
(2) As the film corrosion control effectiveness is excellent, it is not easy for corrosion current to run due to polarization.

In addition, when the two types of zinc-rich paints are compared, the silica reaction type is better in terms of the above two points than the aluminum coating type. We believe that this superiority resulted in the better test results for corrosion resistance over scratched areas.

In the future, we hope to further examine the high corrosion protection mechanism of the zinc-rich paint. We are planning to measure the corrosion current density uniformity of cross-cut test samples over a defined time period using SVET (scanning vibrating electrode technique), not to mention more work doing polarization curve measurements with the potentiostat unit.