Effect of Pretreatment Film Composition on Adhesion of Organic Film on Zinc Coated Steel Sheet*¹

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It is known that chromate pretreatment films with dry-type silica adhere well to organic films such as paint and laminate films on a zinc coated steel sheet. The role of surface polarity in the adhesion mechanism has been investigated for a long time, but remains unclear. We examined the correlation between the composition of chromate pretreatment films with dry-type silica and their adhesion to a laminate film on a zinc coated steel sheet, for both the wet silica and without silica types of chromate pretreatment film. We also investigated the adhesion mechanism by analyzing the pretreatment films using SEM, AFM, BET, TEM and EDX.

The results were as follows. Not only the type and particle size of silica, but also the silica/chromate ratio and the coexistence of chromate affected the adhesion of laminate films. The highest adhesive strength was obtained for the pretreatment films formed in a pretreatment solution with SiO₂/Cr ratio of 4.0 and dry-type silica with a particle diameter of 7 nm. The good adhesion of chromate pretreatment films with dry-type silica is due to an anchor effect by sub-micron surface roughness and an increased number of interface bonding sites by a nano-porous structure. The formation of an insoluble Cr(III) compound layer plays an important role in binding silica particles to the zinc coating surface.

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1. Introduction

Surface finishing has been widely applied to steel materials to confer various functions such as corrosion resistance and ease of design at low cost. In order to make these functions remain effective for a long time, it is important to enhance the adhesion between the surface finishing layers such as metal plating, paint and laminate film at the interface or between these layers and the substrate. For painted or laminated steel sheets which have been widely applied to building materials and electrical appliances, the adhesion between paint or laminate films and zinc coatings has been greatly improved to reduce maintenance and improve the design, and the adhesion mechanism has been actively investigated.

Zinc phosphate treatment has been used to pretreat zinc coated steel sheet since the early 1950s. Zinc phosphate films, which are formed by the reaction of zinc and its treatment solution, are crystalline and porous. Their good adhesion is due to the anchor effect of holes which account for 0.1 to 10% of the total surface area. Since the crystal size of zinc phosphate affects the adhesion and corrosion resistance, surface adjustment and post-treatment are required. Surface adjustment is used to achieve adsorption of a titanium compound to decrease the size of zinc phosphate particles on the zinc coating by promoting nucleus formation, while in the post-treatment a chromate film is coated after the zinc phosphate treatment to achieve a seal. Thus, zinc phosphate treatment involves a complicated process. Accordingly, the dry-in-place chromate treatment was developed in the late 1980s. Since the chromate film is formed by drying a zinc coated steel sheet

which is coated with the treatment solution, treatment is easier than zinc phosphate treatment. Since the dry-in-place chromate treatment requires no washing process, unlike react-in-place and electrolysis chromate treatments, large-scale effluent treatment facilities are also unnecessary. Further, by adding phosphoric acid, silica and resin, this treatment can provide various functions such as anti-fingerprint, paint adhesion and lubrication, and so it is now widely used.

Paint adhesion is known to depend on the amount and type of silica in the chromate layer. It has been reported that optimizing the amount of silica caused it to condense on the surface of chromate films, and that the dry- or chain-type silica improves the paint adhesion.¹⁻⁵⁾ The adhesion mechanism involves many factors related to surface polarity, which is attributed to intermolecular forces such as hydrogen bonding. For example, the surface energy of a dry-in-place chromate film with silica and phosphoric acid was measured by the contact angle of water or methylene iodide, and the paint adhesion was considered to be influenced by the ratio of the polarity force and dispersion force to the film composition.⁶⁻⁸⁾ The results showed that adhesion is improved because the silica condenses toward the upper part of the film and the polarity component is increased. However, the superior adhesion of dry-type silica which has fewer silanol groups, which are the polarity groups on the silica surface, compared with wet-type silica in terms of manufacturing method cannot be explained by these considerations based on surface polarity alone. Moreover, the role of chromate in adhesion is not clear. On the other hand, in view of environmental regulations such as the RoHS Directive, chromate-free coatings are required for the pretreatment films of organic films such as paint and laminate films. Understanding how chromate and silica improve adhesion would assist the design of chromate-free films. In this work, we examined the correlation between the composition of

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Table 1 Composition of pretreatment solutions.

Treatment type	Cr(VI)/Cr(III)	Silica	
		Production Type	
A	+	—	—
B	—	+	Dry
C	+	+	Wet
D	+	+	Dry
E	Zn phosphate coating		

+: Constituent

—: Non-constituent

chromate pretreatment films with dry-type silica and their adhesion to an organic film on a zinc coated steel sheet. The sub-micron morphology was also considered.

2. Experimental

2.1 Specimens

The basic composition of the pretreatment solutions is shown in Table 1. Partially reduced chromic acid solutions were prepared by reducing Cr (VI) to Cr (III) by adding cane sugar to chromic acid solution (50 g/L) till the Cr (III)/Cr (VI) mass ratio became 40/60. Both dry- and wet-type SiO₂ were used. In the basic condition, the primary particle size of silica is 12 nm. Treatment type solutions C and D were prepared by adding SiO₂ to partially reduced chromic acid solution till the SiO₂/Cr ratio became 4.0. Furthermore, pretreatment solutions with varying SiO₂/Cr mass ratio and particle size of silica were prepared as treatment type D. The SiO₂/Cr mass ratio in this paper means the ratio of SiO₂ concentration (mass%) to metallic Cr concentration (mass%) in the treatment solutions and the ratio of films is varied with the ratio of solutions. As a comparison, zinc phosphate film (treatment type E, coating weight: 2.0 g/m²), which is widely used as the pretreatment layer for laminated steel sheet, was prepared.

The specimens were prepared by drying (peak metal temperature: 120°C) after coating these solutions on hot-dip zinc coated steel sheets (sheet thickness: 0.5 mm, zinc coating weight: 120 g/m² at one side) by a bar coater. The basic Cr coating weight of treatment types A, C and D was 35 mg/m² as metallic Cr. The basic SiO₂ coating weight of treatment types B, C and D was 140 mg/m². These coating weights were controlled by the concentration and wet amount of the pretreatment solutions.

2.2 Evaluation of adhesion

Adhesion was evaluated using laminated specimens. The structure of specimens used for the adhesion test is shown in Fig. 1. These specimens were prepared by crimping vinyl chloride films (thickness: 3 µm) at 200°C after forming olefin adhesive films on these specimens.

Adhesion was evaluated by two methods, as shown in Fig. 2.

2.2.1 Peel-off strength after stretching

The peel-off strength was measured by peeling off the laminate film of 2 cm width after stretching the specimen to 20% of its length.

Fig. 1 Structure of specimen used for adhesion tests.

Fig. 2 Evaluation methods of film adhesion strength.

2.2.2 Adhesion at bent section

Adhesion at the bent section was evaluated by categorizing the extent of film exfoliation into five levels after heating (150°C × 1 h) the specimens after cutting off the laminate film with a knife and bending the specimens around a metallic bar (diameter: 2 mm). The extent of film exfoliation was rated as five points when the film on both sides, which had been cut off by a knife, stuck to the steel sheet after heating, and was rated as one point when these films exfoliated in parallel without following the steel sheet after heating. If the extent could not be judged according to this rating, it was evaluated by categorizing the area of exfoliated film according to three levels. The grades were defined by the average of two specimens having the same film composition.

Furthermore, C and Si X-ray images of the exfoliated parts of the specimens after evaluating the peel-off strength were measured by EPMA in order to identify the exfoliation face (measurement area: 1.0 × 1.0 mm).

2.3 Analysis of film structure

Structural analysis of the pretreatment films was carried out by the following methods.

2.3.1 Analysis of surface structure

Secondary ion images of the specimen surfaces were observed by FE-SEM (Hitachi S-510). These images were taken by tilting the specimens at 30 degrees (acceleration voltage: 2 kV).

The AFM images of these surfaces were observed by AFM (Digital Instrument Nano Scope II). The following roughness parameters were calculated from the cross-sectional profiles (length: 7000 nm).

Average roughness (R_a): average of roughness curve for center line

Maximum height (R_{max}): height difference between highest point and lowest point

Fig. 3 Influence of pretreatment composition on film adhesion. (A, C, D) Cr coating weight: 45 mg/m², (B, C, D) SiO₂ coating weight: 180 mg/m².

2.3.2 Measurement of specific surface area

The specific surface areas of the specimens were measured by the BET multi-point method. The BET specific surface areas were calculated by applying multi-molecular adsorption theory to the adsorption isotherm of Kr at 77 K, which was obtained by automatic gas adsorption measurement (BEL Japan BELSOP36). The molecular occupied area of Kr used in this measurement is estimated to be 0.2 nm² at 77 K, which is regarded as the lower limit of detection (resolving power) in the measurement result by this method. The specific surface area of the hot-dip zinc coated steel sheet was 1.1.

2.3.3 Analysis of cross-sectional structure and its composition

Cross-sectional specimens were prepared by the microtome method. Morphology observation by cross-sectional TEM images (acceleration voltage: 250 kV) and composition analysis by EDX were carried out by TEM (Philips CM30T).

3. Results

3.1 Evaluation of adhesion

The peel-off strength after 20% stretching and adhesion at the bent section of the laminated specimens are shown in Fig. 3. The chromate pretreatment films with dry-type silica D group (D1 and D2) exhibited remarkably high peel-off strength and film adhesion in comparison with the chromate (silica-free) pretreatment film A, dry-type silica (chromate-free) pretreatment film B and chromate pretreatment film with wet-type silica C. In particular, D2 (SiO₂ particle size: 12 nm, SiO₂/Cr mass ratio: 4.0) exhibited higher adhesion than D1 (SiO₂ particle size: 700 nm, SiO₂/Cr mass ratio: 1.5), which simulated the commercial pretreatment films for paint undercoats. Thus, not only the type and particle size of silica but also the silica/chromate ratio and the coexistence of chromate greatly affect the adhesion of laminate films.

The effects of SiO₂ particle size, SiO₂/Cr mass ratio and Cr coating weight on adhesion were investigated using chromate pretreatment films with dry-type silica D. Figures 4 and 5 show the influence of SiO₂/Cr ratio and size of SiO₂ particles in pretreatment solutions on peel-off strength and Figs. 6 and 7 show the influence of SiO₂/Cr ratio and size of SiO₂ particles in pretreatment solutions on rating of adhesion.

Fig. 4 Influence of SiO₂/Cr ratio of pretreatment solutions on peel-off strength.

Fig. 5 Influence of size of SiO₂ particles in pretreatment solutions on peel-off strength.

Fig. 6 Influence of SiO₂/Cr ratio of pretreatment solutions on rating of adhesion.

Fig. 7 Influence of size of SiO₂ particles in pretreatment composition on rating of adhesion.

Fig. 8 EPMA elemental mapping at exfoliated parts of specimens after peel-off tests.

adhesion, respectively. The results for the zinc phosphate pretreatment film (treatment type E) are included in the figures. The peel-off strength increased and the adhesion at the bent section improved as the SiO_2 particle size decreased. It was found that these properties declined when the SiO_2/Cr mass ratio was over 4.0 and hardly changed when the Cr coating weight was between 20 and 55 mg/m^2 . According to these results, the adhesion of the chromate pretreatment films with dry-type silica D depends on SiO_2 particle size and SiO_2/Cr mass ratio, and does not depend on the Cr coating weight between 20 and 55 mg/m^2 . The highest adhesive strength was obtained for the pretreatment film with SiO_2/Cr ratio of 4.0 and dry-type silica with a particle diameter of 7 nm, which was equivalent to the conventional zinc phosphate film.

Figure 8 shows X-ray images of the surface of the substrates by EPMA after evaluating the peel-off strength. In the case of the dry-type silica pretreatment film B, the intensity of Si, which is thought to derive from the pre-

treatment film component, and the intensity of C, which is thought to derive from the adhesive layer, were generally low. However, parts on which both elements were detected at high intensity were also recognized. Furthermore, the intensity of Cl, which is thought to derive from the laminate film, was low for the same part. These results suggest that the exfoliation mode of this specimen is predominantly interface exfoliation between the pretreatment film and the zinc coating, and that cohesive destruction in the adhesive film partly occurred.

In the case of the chromate pretreatment film with wet-type silica C, it was found that the intensity of Si was strong and that of C was weak overall. These results suggest that the exfoliation mode is interface exfoliation between the adhesive film and the pretreatment film.

In the case of the chromate pretreatment film with dry-type silica D2, it was found that the intensities of both Si and C were strong and that the parts of high intensity of Si almost matched the parts of high intensity of C. It can therefore be

presumed that the exfoliation mode is cohesive destruction across the interface between the pretreatment film and the adhesive film.

3.2 Film analysis

3.2.1 Analysis of surface structure

SE images of the surfaces of the specimens by FE-SEM are shown in Fig. 9. The dry-type silica (chromate-free) film B and the chromate pretreatment film with dry-type silica D2 have fine surface roughness in comparison with the chromate (silica-free) film A and the chromate pretreatment film with wet-type silica C. The chromate pretreatment film with dry-type silica D2 shows a high coverage and uniformity with rough parts. In contrast, the dry-type silica (chromate-free) film shows a low coverage and even has parts where the substrate is exposed.

AFM images, cross-sectional profiles and the roughness parameter (R_a , R_{max}) on these diagonals of the specimen surfaces are shown in Fig. 10. It was found that the chromate pretreatment film with dry-type silica D2 had rough surface in comparison with the chromate (silica-free) film A and the chromate pretreatment film with wet-type silica C as shown in Fig. 9, and that its R_{max} value was approximately 400 nm.

Since the SiO_2 particle size and SiO_2/Cr mass ratio greatly influence the adhesion, SE images and AFM cross-sectional profiles of the specimens for varying SiO_2 particle size and SiO_2/Cr mass ratio were observed.

SE images and AFM cross-sectional profiles of the chromate pretreatment films with dry-type silica with a primary particle size of 12 nm or 40 nm D are shown in Fig. 11. There was a large difference in adhesion between the two specimens. Though these surfaces had fine surface roughness, there was no large difference in morphology. SE images of the chromate pretreatment film with dry-type silica and with SiO_2/Cr mass ratio of 1.5 or 4.0 are shown in Fig. 12. It is found that the flat substrate area is exposed in the case of $\text{SiO}_2/\text{Cr} = 1.5$ and that there is a uniform covering of rough films in the case of $\text{SiO}_2/\text{Cr} = 4.0$.

3.2.2 Measurement of specific surface area

The specific surface areas of the chromate pretreatment films with dry-type silica D for varying primary particle size of SiO_2 are shown in Fig. 13, measured by the BET multi-point method. Though it is not possible to clarify any difference in surface roughness between the particle size of 12 nm and that of 40 nm by SE images and AFM images in Fig. 11, it was found that the specific surface area remarkably increased as the primary particle size of dry-type silica decreased.

3.2.3 Analysis of cross-sectional structure and composition

TEM images of the cross-sectional specimen of the chromate pretreatment film with SiO_2/Cr mass ratio of 4.0 and dry-type silica with a particle diameter of 12 nm are shown in Fig. 14. Dark parts were observed and the crystal silica was condensed in the D2 coating which had a thickness of approximately 0.3 μm . The depth profile of the film, which was measured by EDX, is shown in Fig. 15. It was found that Cr condensed toward the interface between the D2 film and zinc coating and that SiO_2 condensed toward the interface between the adhesive film and D2 film.

Fig. 9 SE images of pretreatment surface.

The state transition of Cr with depth of the chromate films was observed by XPS measurement of obliquely polished cross-sectional specimens,⁹⁾ XPS measurement with ion sputtering,¹⁰⁾ and XPS measurement using synchrotron radiation as the X-ray source,¹¹⁾ which has a wide energy range and high luminance. All results indicated that Cr(III) condenses in the lower part of the chromate film near the zinc

Type	Surface image 1000nm	Cross-sectional profile 500nm 1000nm
A		Ra=2.87nm, Rmax=22.40nm
C		Ra=5.45nm, Rmax=36.14nm
D2		Ra=38.06nm, Rmax=404.78nm

Fig. 10 Surface morphology of pretreatment layers by AFM.

Type	Particle size of SiO ₂	SE image 2μm	Cross-sectional profile by AFM 500nm 1000nm
D	12 nm		Ra=38.06nm, Rmax=404.78nm
	40 nm		Ra=52.94nm, Rmax=404.35nm

Fig. 11 Influence of SiO₂ particle size on surface morphology of type D treated samples.

coating and that Cr(VI) condenses in the upper part. With the D2 film, the Cr that condensed near the interface between the D2 film and zinc coating seemed to be Cr(III).

4. Discussion

4.1 Improved adhesion by adding dry-type silica

Venables *et al.*¹²⁾ investigated the adhesion mechanism of

pretreatment for Al and found that fine surface roughness at submicron level was formed on the surface of Al by high resolution SEM and concluded that the adhesion resulted from an anchor effect between the porous oxide film and adhesive because there was a correlation between the fineness of the surface roughness and the adhesion. It is thought that a zinc phosphate coating, which has long been used as a pretreatment film for paint undercoats, produces adhesion by the anchor effect of zinc phosphate crystals at the micron level.

According to morphology analysis by SEM and AFM, since the chromate pretreatment film with dry-type silica D group, which was shown to have good adhesion, has fine surface roughness, it is thought that its roughness contributes to the anchor effect and that the good adhesion results from cohesive destruction across the interface between the pretreatment film and the adhesive film. In the case of the chromate pretreatment film with wet-type silica C where fine surface roughness was not observed, since the anchor effect was not exhibited and exfoliation occurred at the interface

Fig. 12 SE images of pretreatment surface of type D treated samples.

Fig. 13 Influence of SiO₂ particle size on specific surface area.

Fig. 14 Cross-sectional TEM image of a type D treated sample.

Fig. 15 Depth profile of Si and Cr in pretreatment layer (Type D treated sample).

between the pretreatment film and the adhesive film as shown in Fig. 8, adhesion was poor and equivalent to chromate pretreatment film A. These morphological differences by type of silica are thought to be due to the differences of silanol density on the surface of silica, resulting from the differences in manufacturing method. Namely, the dry-type silica, which is manufactured by flame hydrolysis which is a dry process, has a lower surface density of OH groups than the wet-type silica, which is manufactured by an ion exchange method, etc., which is a wet process. It has been reported that the OH group density of dry-type silica was 2.6 pieces/ nm^2 and that of wet-type silica was 5.7 pieces/ nm^2 by measurement using the LiAlH_4 method.^{13,14)}

Since dry-type silica does not have much electrostatic repulsive force by OH groups in comparison with wet-type silica, it is thought that the former is easily condensed¹⁵⁾ and that the anchor effect is exhibited when an organic film is formed at the top of the pretreatment film. It is considered that the peel-off strength and adhesion at the bent section are improved as the SiO_2/Cr mass ratio increases because the coverage of the rough film with the dry-type silica increases as shown in Fig. 12.

Furthermore, the reason why the adhesion improved as the particle size of the dry-type silica decreased is thought to be due to the increase in surface polarity and the increase in interface bonding sites for adhesion, as already reported⁶⁻⁸⁾ since nano-porous films with high specific surface area are formed as shown in Fig. 13, in addition to the anchor effect by the above-mentioned fine surface roughness.

4.2 Improvement effect of adhesion by compositing chromate

The dry-type silica (chromate-free) film B has lower coverage than the chromate pretreatment film with dry-type silica D2 for the same coating weight of SiO_2 as shown in Fig. 9. In the case of the B film, since exfoliation occurred mainly at the interface between the pretreatment film and the adhesive film as shown in Fig. 8, the adhesion of the interface between the pretreatment film and zinc coating is suggested to be extremely weak. In the case of the D2 film, SiO_2

condenses toward the interface between the adhesive film and D2 film and Cr condenses toward the interface between the D2 film and zinc coating as shown in Fig. 10, and the Cr is assumed to be insoluble Cr(III) near the interface of the zinc coating.⁹⁻¹¹⁾ Thus, the insoluble Cr(III) fixes SiO_2 as binder and enhances the adhesion between the zinc coating and the pretreatment film. However, in the case of the silica-rich film with SiO_2/Cr mass ratio of more than 4.0, since the binder effect by Cr(III) condensing toward the lower part of the pretreatment film becomes insufficient and the part of SiO_2 condensing toward the upper part of the pretreatment film is not fixed, the adhesion decreases.

5. Conclusion

The correlation between the composition of chromate pretreatment films with dry-type silica and the adhesion to an organic film on a zinc coated steel sheet was examined by measuring the peel-off strength after stretching and the adhesion at the bent section. The adhesion mechanism was also investigated morphologically at the sub-micron level and the surface area at the nano level by analyzing the pretreatment films using SEM, AFM, BET, TEM and EDX. The results are summarized as follows:

- (1) Not only the type and particle size of silica, but also the silica/chromate ratio and the coexistence of chromate affected the adhesion of laminate films. The highest adhesive strength was obtained for the pretreatment films formed in a pretreatment solution with SiO_2/Cr ratio of 4.0 and dry-type silica with a particle diameter of 7 nm which is equivalent to that of the zinc phosphate films widely used today.
- (2) For the dry-type silica pretreatment films and chromate pretreatment films with wet-type silica which had poor adhesion, cohesive destruction occurred at the interfaces of the pretreatment film/zinc coating, and the adhesive film/pretreatment film respectively. In contrast, for the chromate pretreatment films with dry-type silica, cohesive destruction occurred across the interface of the pretreatment film and the adhesive film.
- (3) Compared with the chromate pretreatment (silica-free) films and the chromate pretreatment films with dry-type silica, the dry-type silica pretreatment (chromate-free) films and the chromate pretreatment films with dry-type silica showed fine surface roughness. As the particle size of silica in the chromate pretreatment films with dry-type silica decreased, these specific surface areas increased remarkably.
- (4) Cr condenses toward the interface of the pretreatment films/zinc coating, while SiO_2 condenses toward the interface of the adhesive films/pretreatment films.
- (5) Consequently, the good adhesion of chromate pretreatment films with dry-type silica is due to the action of the dry-type silica and the effect of the chromate. The action of the dry-type silica consists of an anchor effect by fine surface roughness and an increased number of interface bonding sites by high specific surface area due to the nano-level fine structure and nano-porous structure. The chromate serves to fix (a binder effect) the silica by insoluble Cr (III).

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