

Development of Hexavalent Chromium-free Surface Treatment

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ABSTRACT

A hexavalent chromium-free surface treatment has been developed for automotive parts which provides a coating possessing equivalent anti-corrosion performance and friction characteristics to conventional chromate layers containing chromium(VI). The treatment forms a passivation layer of trivalent chromium and metallic chelates at the interface with the zinc, while uniformly covering the surface with a protective zinc layer. It is an unusual feature of this process that a single procedure is able to form a double layer. Optimization of the amount of silica added has enabled the achievement of friction characteristics equivalent to those of conventional chromium(VI) chromate layers. The new surface treatment has resulted in a reduction in the amount of hexavalent chromium used in the production process and in finished parts.

1. Introduction

Demands for the reduction of the amount of environmental load substances used in automobiles are increasing with a growing focus on global environmental issues. Annex II of the EU End of Life Vehicle (EU-ELV) Directive bans the use of hexavalent chromium, employed in automotive applications as a rust inhibitor, from 1 July 2007^{(1),(2)}. This makes the development of a hexavalent chromium-free surface treatment as a substitute for chromate conversion coatings containing hexavalent chromium (referred to as hexavalent chromate coatings below) an urgent issue.

2. Development Goals

The purpose of the project discussed in this paper was to develop a substitute for hexavalent chromium in order to reduce the environmental load associated with scrapping and recycling vehicle parts at the end of vehicle life. Hexavalent chromate is often used as a coating on zinc in fasteners, where its corrosion resistance and

clamping performance (friction properties) fulfill an important function, making the development of a substitute particularly important.

2.1. Issues Associated with Conventional Technologies

The following treatments have recently been adopted as substitutes for hexavalent chromium:

- (1) Molybdate-phosphate coatings⁽³⁾, triazinethiol coatings, tannic acid coatings
- (2) Chromate coatings containing trivalent chromium compounds to which metallic salts have been added (termed trivalent chromate coatings below).
- (3) Organic and inorganic compound silicate coatings applied by dip-spin and baking

However, these methods generate a number of issues.

The cost of the materials for the substances listed in (1) is high, and they do not offer an equivalent level of corrosion resistance to hexavalent chromate coatings, due to the lower coating thickness. The reactivity of the substances listed in (2) in terms of coating formation is low. High temperatures (more than 50 °C) and long

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periods of time (more than 60 secs) are required to increase reactivity, making productivity low compared to hexavalent chromate coatings, which only require 15-30 secs at room temperature. In addition, the differences in chemical composition (low level of hydrates in the coatings, etc.) tend to have a high coefficient of friction, necessitating the addition of an extra coating treatment to adjust the coefficient of friction for the fastener. The coatings listed in (3) tend to generate a higher film thickness within the screw threads, leading to torque and fit concerns. Other issues associated with these substances include the high baking temperatures required to ensure that the coatings adhere, making it difficult to process in conventional plating processes.

Given these issues, the following goals were established for the development of a substitute:

- (1) From the environmental perspective, elimination of hexavalent chromium, lead, cadmium and mercury, which have become the targets of legislation.
- (2) From the performance perspective, the achievement of identical corrosion resistance and friction characteristics to those displayed by hexavalent chromate coatings.
- (3) From the production perspective, the achievement of an identical level of productivity to hexavalent chromate coatings while using the same production facilities.

2.2. Design and Development of Materials

2.2.1. Enhancement of corrosion resistance performance

Hexavalent chromate coatings are thick (0.2-1.0 μm) inorganic coatings composed of complex salt hydrates of soluble hexavalent chromium and trivalent chromium. Hexavalent chromium produces a shielding effect to prevent damage from external sources; when the coating is damaged by a scratch, a passivation film is formed by the reduction of the soluble hexavalent chromium to trivalent chromium. This shielding effect and self-healing characteristic of the coating gives it a high level of corrosion resistance performance^{(4),(5)}. Corrosion resistance performance therefore declines greatly when hexavalent chromium is not contained in the coating. The achievement of both a shielding effect and self-healing characteristic is important in ensuring an equivalent level of corrosion resistance performance in a replacement material. Self-healing ability in particular is essential, due to the likelihood of damage to the coating when fasteners are tightened and when gravel chipping contacts the coating during vehicle operation.

While reports concerning various development projects for hexavalent chromate replacements exist in the literature⁽⁶⁾, few report development of a replacement possessing both a good shielding effect and self-healing ability. The project discussed in this paper therefore attempted to design a coating which would combine two materials which each guaranteed one of these characteristics in a single production process.

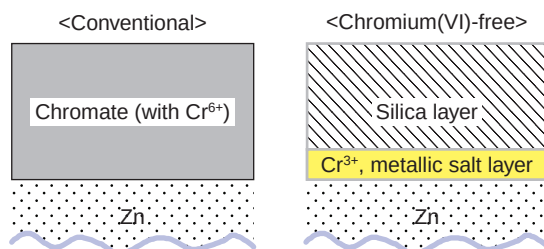


Fig. 1 Chromate layer

The top layer of the projected material would be a silica layer with colloidal silica as the main component. Silica has superior shielding properties compared to conventional trivalent chromate coatings and it also possess good coating formulation properties. The bottom layer, which is in contact with the zinc-coated substrate, would act as an inhibitor via the chelating effect of trivalent chromium salt and metallic salts and could be expected to display self-healing properties. The coating is shown in Fig. 1.

2.2.2. Control of friction properties

Sufficient attention to the friction properties produced by the surface treatment is important in ensuring that the axial tension acting on the bolt when the fastener is tightened as close as possible to the design value. Because it is not practical to directly measure the axial tension on the bolt, a calibrated wrench method, which measures tightening torque, is generally employed for tightening control. The torque produced by tightening and the axial tension generated are proportional; in the calibrated wrench method, the torque coefficient is read from the gradient of the torque-tension line. The relationship between torque and axial tension in this range of elasticity⁽⁷⁾ is shown by Eqs. (1) and (2). Figure 2 shows a typical example of a torque-tension line.

$$T_f = T_s + T_w = K \cdot F_f \cdot d \quad (1)$$

$$K = \frac{1}{2d} \left(\frac{P}{\pi} + \mu_s d_2 \sec \alpha + \mu_w D_w \right) \quad (2)$$

T_f : Tightening torque	T_s : Screw torque	T_w : Flange torque
K : Torque coefficient	F_f : Axial tension	d : Nominal diameter
P : Screw pitch	μ_s : Screw surface friction coefficient	
d_2 : Effective diameter of screw	μ_w : Flange friction coefficient	
$\sec \alpha$: Flank angle of thread		
D_w : Equivalent diameter of friction torque on flange		

The equations above are used to convert friction coefficient to torque coefficient. Torque coefficient varies according to the characteristics of the surface treatment. If a new surface treatment with a higher torque coefficient is used, tightening with identical torque will produce less axial tension, possibly leading to the fastener dropping out due to looseness or loss of function due to stress fractures and the like. The replacement substance is therefore required to possess a similar torque coefficient to the existing surface treatment.

This development project focused on the upper corrosion-preventing silica layer. The concentration and properties of the colloidal silica added to the chromate treatment solution were studied to enable the achievement of an equivalent torque coefficient to that of hexavalent chromate coatings^{(8),(9)}.

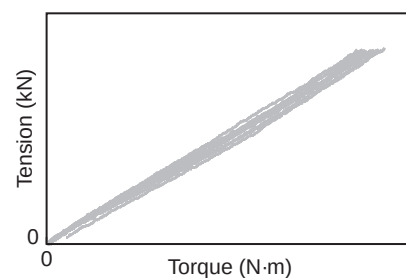


Fig. 2 Example of torque-tension line

3. Composition of Newly Developed Coating

To apply the newly developed coating (trivalent chromate coating below), first a uniform mixture of chromium nitrate, metal chelate salts and a dispersed solution of colloidal silica is created. This is applied to a zinc coating in an immersion treatment at 30-40 °C for 15-40 seconds. Glow discharge spectroscopy (GDS) was used to analyze the concentration of elements in the depth direction. The results are shown in Fig. 3.

The analysis confirmed a two-layer structure, with silicon present in the silica component at a depth of 100-150 nm from the surface layer and chromium and metallic elements derived from the metal chelate salts in a 50 nm-thick layer observed at the zinc interface.

A cross-section of the coating was also studied using scanning electron microscopy (SEM). SEM images are shown in Fig. 4. Observation under the SEM showed microscopic particles of silica distributed throughout the entire surface layer.

The results show a trivalent chromium and metal chelate salt layer deposited at the zinc interface and a uniform distribution of silica throughout the surface layer, indicating the achievement of a two-layer structure in the trivalent chromate coating. Figure 5 shows a diagram of the structure of the trivalent chromate coating.

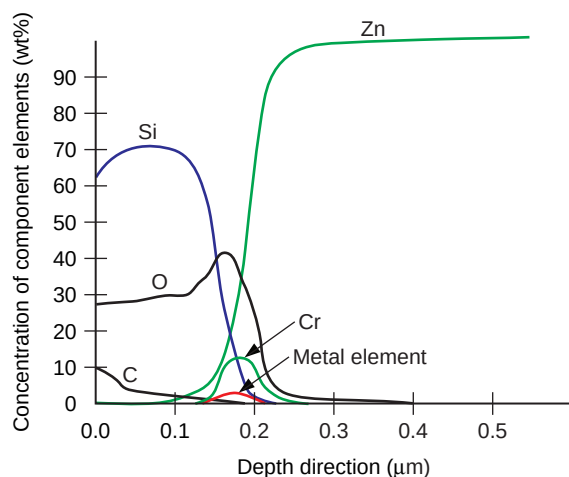


Fig. 3 Depth profile of element concentration in chromium(VI)-free chromate on zinc

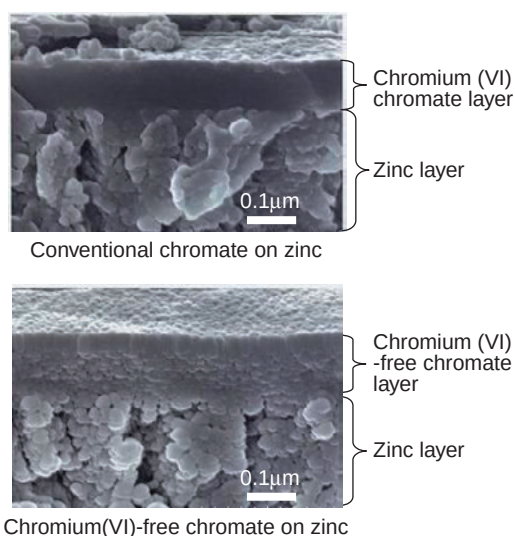


Fig. 4 Surface cross-sectional structure of chromium(VI)-free chromate on zinc

The formation mechanism of the trivalent chromate coating is believed to be as follows:

- (1) Dissolution and activation of the surface of the zinc by the acid components
- (2) The pH rises at the boundary between the zinc and the treatment solution
- (3) Formation of chromium hydrate compounds and complexes of metal chelate salts and zinc at the zinc interface, together with deposition of colloidal silica and film formation in the upper layer
- (4) Fixing of the coating by drying

4. Characteristics of Components of Newly Developed Coating

4.1. Contribution of Silica to Corrosion Resistance Performance

The corrosion resistance performance of the silica layer was evaluated to verify the shielding effect. Figure 6 shows the relationship between the silica content of the trivalent chromate treatment solution and the thickness and corrosion resistance performance of the coating, as measured in a saltwater spray test (SST).

In addition to making the coating thicker, the addition of silica has enhanced the corrosion resistance performance. The results of the tests can be assumed to indicate that the silica has produced a shielding effect.

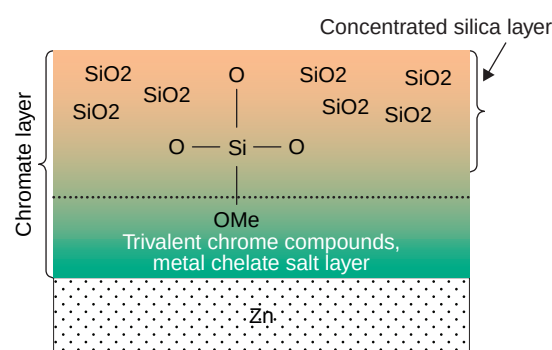


Fig. 5 Diagram of structure of chromium(VI)-free layer on zinc

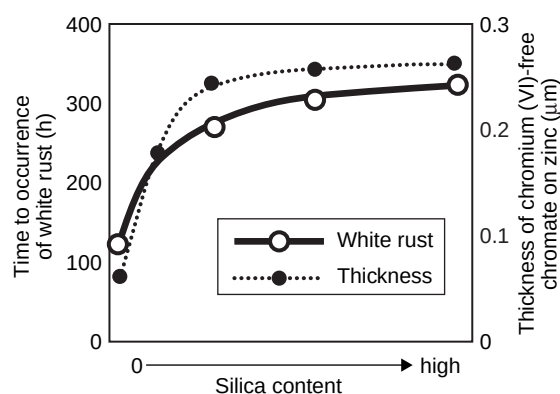


Fig. 6 Relation between amount of silica added and time to occurrence of white rust

4.2. Contribution of Metal Chelate Salts to Corrosion Resistance Performance

To test the effectiveness of the metallic salts in producing a self-healing characteristic, trivalent chromate coated test pieces were produced with and without the added metallic salts. Scratches reaching to the substrate were generated on these test pieces, after which they were subjected to combined cyclic corrosion tests (CCT) to evaluate corrosion resistance. Figure 7 shows external views of corrosion after 7 and 22 test cycles.

The addition of metal chelate salts was shown to have increased corrosion resistance performance at the scratch site to a level equivalent to or greater than that displayed by a hexavalent chromate coating. These results can be assumed to indicate that the addition of metal chelate salts produces a self-healing characteristic and generate a passivating effect.

The following tests were further conducted to verify the passivating effect:

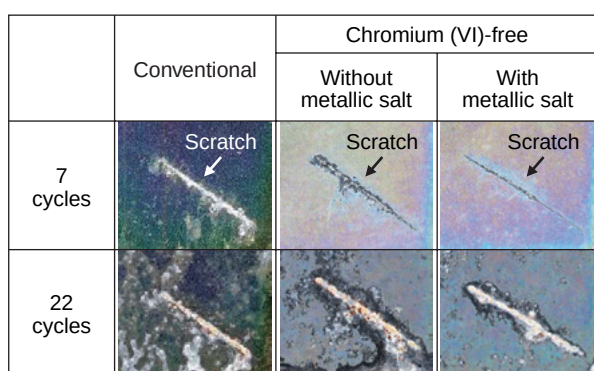


Fig. 7 Corrosion resistance of chromate on zinc with metallic salt around scratch (CCT)

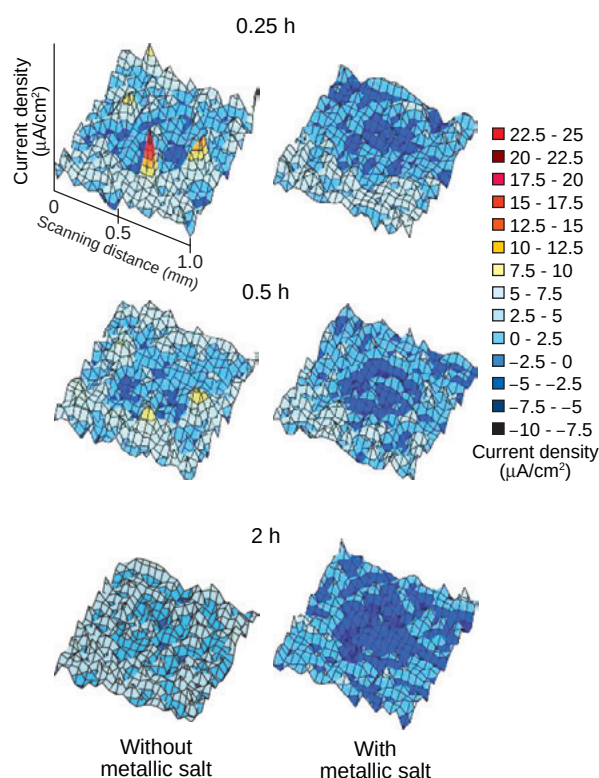


Fig. 8 Time variation of corrosion current density around micro-hole on zinc chromate

(1) Scanning vibrating electrode technique (SVET)⁽¹⁰⁾

Micro-holes of 1 mm in diameter were artificially produced on test pieces, after which the test pieces were immersed in a 10 ppm NaCl solution and the density of the corrosion current around the hole was measured. Figure 8 shows the corrosion current density at 0.25 hr, 0.5 hr and 2 hr from immersion.

Immediately after immersion, a local cell, in which the center of the hole acted as a cathode and the surrounding area as an anode, was formed on the test piece coated without the addition of metallic salts, producing a maximum current of 20 $\mu\text{A}/\text{cm}^2$. As a result of the protective effect of substances formed in a reaction between the dissolved zinc, trivalent chromium and silica, the corrosion current decreased with immersion time, until it was virtually nonexistent at 2 hr.

By contrast, despite the fact that the center of the hole formed a cathode on the test piece with a coating containing metal chelate salts, a distinct anode section could not be identified, and the maximum corrosion current density was 5 $\mu\text{A}/\text{cm}^2$, indicating the occurrence of a passivation effect at the damaged section of the coating.

(2) Measurement of polarization

When polarization measurements were conducted using the same test pieces, a passivation potential range (−1.1 – −1.0 V) was recorded on the anode section of the test piece with a coating containing metallic salts (Fig. 9). These results indicate that a passivation effect and self-healing characteristic like that occurred by a hexavalent chromate coating can be achieved through the addition of metallic salts⁽¹¹⁾.

The results discussed above enable the mechanism of corrosion resistance in the trivalent chromate coating to be theorized as follows:

(1) Corrosion prevention by shielding effect

The surface silica layer prevents the corrosion promoters H_2O , O_2 and Cl^- from contacting the zinc layer, and the trivalent chromium at the boundary with the zinc layer functions as a passivation coating. This prevents penetration of the corrosion promoting anion Cl^- from an external moist environment, in addition to preventing fluxion of cations (Zn^{2+}) from the zinc layer.

(2) Corrosion prevention by self-healing characteristic

At the scratch site, where the zinc layer is exposed to the atmosphere, corrosion first produces a dissolution reaction in the zinc.

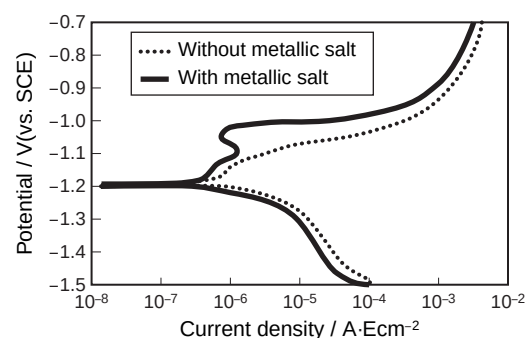
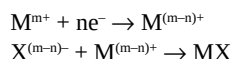
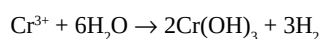


Fig. 9 Polarization curves of chromate on zinc with metallic salt

At the same time as reducing the dissolved metal ions (M^{n+}), the e^- produced by the dissolution reaction of the zinc reacts with the unreacted chelates in the metallic salts (X) to form insoluble metallic salts.



The dissolution reaction of the zinc raises the pH at the zinc coating interface, and the presence of unreacted trivalent chromium in the coating causes deposition of complex ions of trivalent chromium, forming a film. This self-healing characteristic produces a passivation reaction.



4.3. Heat Resistance

Due to the high quantity of hydrates in hexavalent chromate coatings, cracks tend to occur at temperatures of 80 °C and above, causing corrosion resistance performance to decline. Figure 10 shows the surface property of trivalent and hexavalent chromate coatings after heating at 80 °C and 120 °C.

The trivalent chromate coating contains less hydrates than the hexavalent chromate coating, and therefore virtually no cracks caused by evaporation of the moisture content were observed.

Figure 11 shows the results of an SST conducted after heating. The corrosion resistance of the hexavalent chromate coating drops rapidly at 80 °C, while the trivalent chromate coating displays only a gentle decline, demonstrating that the trivalent chromate coating possesses high heat resistance.

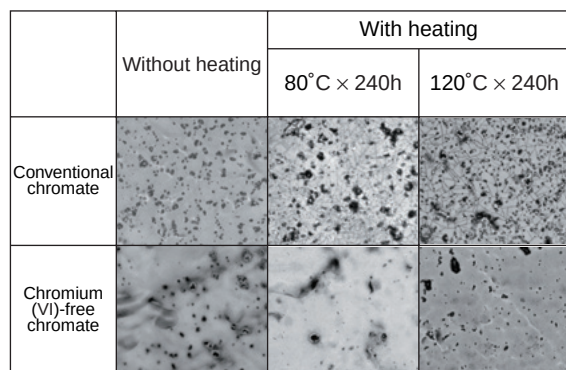


Fig. 10 Surface property of chromate after heating

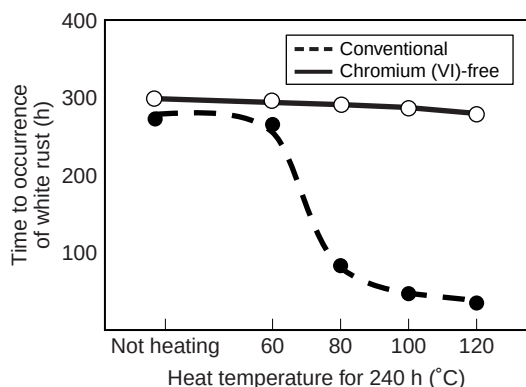


Fig. 11 Heat resistance of chromium(VI)-free on zinc (SST)

5. Effect of Processing Conditions on Corrosion Resistance Performance

A saltwater solution test (SST) was used to evaluate the effect of processing temperature and processing time on corrosion resistance, in order to establish optimum processing conditions for the trivalent chromate coating. Figures 12 and 13 show the relationship demonstrated between processing temperature and corrosion resistance and dipping time and corrosion resistance respectively.

The results showed that film thickness increases with an increase in processing temperature and dipping time, and there was a consequent increase in corrosion resistance. This indicated that good performance could be achieved with the trivalent chromate coating at low processing temperatures and with short dipping times.

6. Control of Torque Coefficient by Variation of Amount of Added Silica Content

Torque coefficient was measured in zinc plated nuts and bolts coated with trivalent chromate coatings containing varying concentrations of silica. The results are shown in Fig. 14.

The measurements showed that the torque coefficient became lower as the silica content was increased, and indicated the existence of an optimum range of concentration enabling the achievement of an equivalent torque coefficient to that displayed by hexavalent chromate coatings. However, if silica was added in excess quantities, the torque coefficient was observed to increase again.

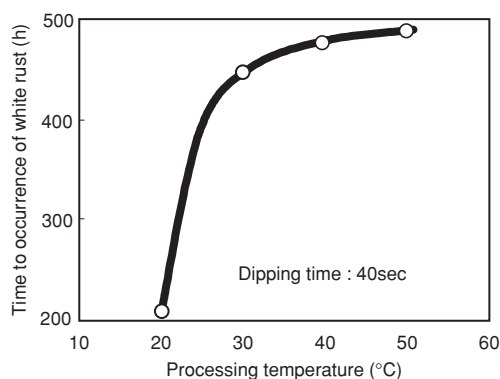


Fig. 12 Relation between processing temperature and time to occurrence of white rust (SST)

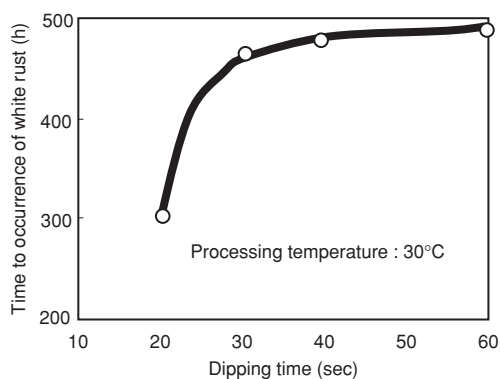


Fig. 13 Relation between dipping time and time to occurrence of white rust (SST)

This is believed to be caused by coagulation of the excess silica in the trivalent chromate surface layer, causing the surface to become rough.

This indicated the necessity of achieving a uniform distribution of silica within the treatment solution. There is a possibility of significant variations in torque coefficient being produced because of the surface roughness caused by silica flocculation.

7. Productivity

The occurrence of variations in corrosion resistance and torque coefficient in trivalent chromate-coated bolts produced in a mass-production coating facility was studied. Random samples of fasteners were taken from consecutive barrels. Figure 15 shows the results of SST of corrosion resistance and Fig. 16 shows measurements of torque coefficient.

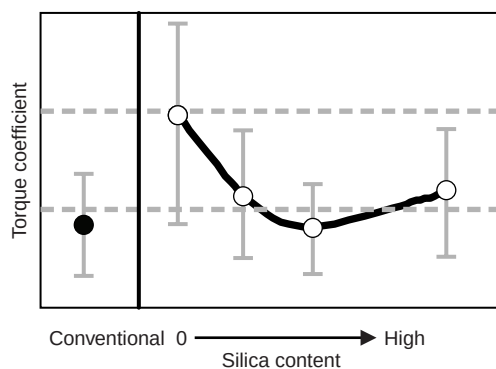


Fig.14 Relation between amount of silica added and torque coefficient

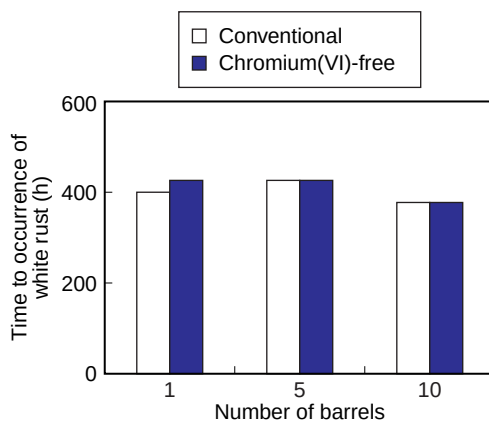


Fig. 15 Corrosion resistance of 10 consecutive barrels in facility

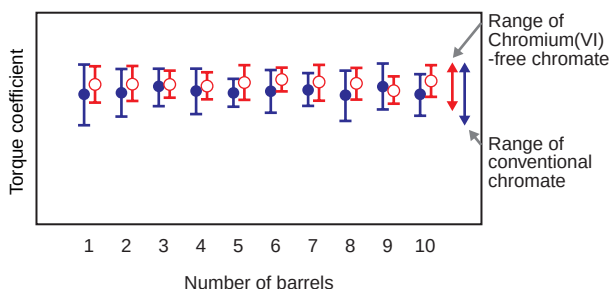


Fig.16 Torque coefficient of 10 consecutive barrels in facility

The trivalent chromate-treated bolts showed an equivalent range of torque coefficient as displayed by hexavalent chromate-treated bolts.

The results of measurements confirmed the achievement of a level of corrosion resistance and torque coefficient equal to those shown by hexavalent chromate coatings.

8. Evaluation of Durability in Actual Vehicles

Trivalent chromate-coated parts were fitted into a vehicle and put through comprehensive durability testing in corrosion-promoting environments to evaluate the durability of the new coating. For purposes of comparison, hexavalent chromate-coated parts were used in the right side of the vehicle and parts coated with the new trivalent chromate coating were used in the left side. Figures 17-19 show external views of the parts after testing.

The corrosion resistance of the trivalent chromate coatings was equivalent or superior to that of the hexavalent chromate coatings, and no impairment of fastener function was displayed in the course of testing.

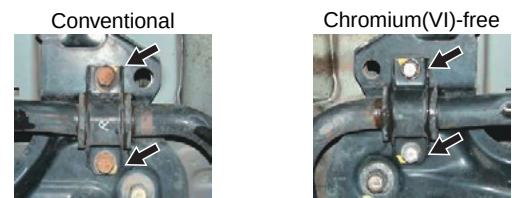


Fig. 17 Attachment bolt for stabilizer (front)

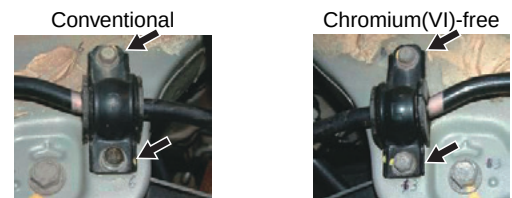


Fig. 18 Attachment bolt for stabilizer (rear)

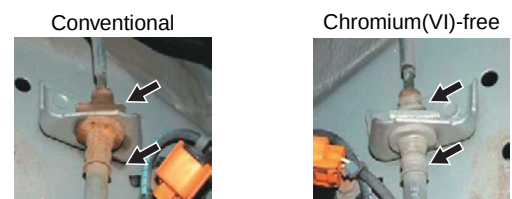


Fig. 19 Brake hose attachment nut (front)

9. Conclusion

A trivalent chromate coating possessing equivalent corrosion resistance and friction properties to conventional hexavalent chromate coatings has been developed a substitute for hexavalent chromate coatings. The following are the salient points of this development:

- (1) In the new coating, silica shields the substrate from corrosion inducement factors in the external environment and metal chelate salts form a passivation coating, enabling the achievement of an equivalent level of corrosion resistance to the conventional hexavalent coating.

- (2) The new coating has a two-layer structure: trivalent chromium and metal chelate salt layer at the boundary with the zinc coating, and a silica surface layer. These two layers are formed in a single production process.
- (3) An equivalent range of torque coefficient (friction coefficient) to that of hexavalent chromate coatings has been achieved by optimizing the added silica content.
- (4) Tests carried out on the production line to determine the suitability of the new coating to mass production demonstrated that the trivalent chromate coating process produced equivalent corrosion resistance and friction properties to the existing hexavalent chromate coating process.
- (5) Durability tests of trivalent chromate-coated fasteners conducted in a vehicle, operating within a corrosion-promoting environment showed equivalent or superior corrosion resistance to hexavalent chromate coatings. There were no issues associated with clamping performance or function.

10. Afterword

The newly developed coating discussed in this paper has been applied on parts used in the 2005 model year LEGEND. For reference, Table 1 shows a list of other technologies employed in the new LEGEND and the main parts to which they have been applied.

Table 1 Application of chromium(VI)-free materials and relevant parts

Base materials	Conventional chromium(VI)	Chromium(VI)-free development	Application
Zn plating	Yellow chromate	Chromium(III) white chromate	Fastener
	Black chromate	Chromium(III) black chromate	Pipe Caliper
Zn-Ni plating	Yellow chromate	Chromium(III) white chromate	Brake pipe Fuel pipe
Sn-Zn plating	Yellow chromate	Chromium(III) white chromate	Hose metal parts
Zinc Aluminum composite coating	Chromate binder	Silicate binder	Fastener Stay
anti-corrosion primer	SrCrO ₄ pigments	Epoxy resin Mg pigments	Brake pipe Fuel pipe
Aluminum	Chromate	Zirconium salt Titanium salt	Al wheel
		Anode oxidation	Wiper arm
Magnesium	Chromate	Zirconium salt	Engine head cover
			Oil pan

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