Product Introduction

Cobalt-free Trivalent Chromium Passivation Film Treatment Agent

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Introduction

Hexavalent chromium regulations, which began in 1992 with the establishment of in-house regulations by VOLVO of Sweden, became global with the ELV Directive enforced in 2000 and the RoHS Directive enforced in 2006.

Conventionally, zinc and zinc alloy plating has generally been treated with chromate containing hexavalent chromium (hereinafter referred to as hexavalent chromate) as a means of significantly improving corrosion resistance at a low cost. However, in compliance with these regulations, there was a shift to trivalent chromium passivation, which does not contain hexavalent chromium and use trivalent chromium.

Hexavalent chromate contains hexavalent chromium in its coating and has a self-healing function whereby when the coating is damaged, the chromium seeps out and regenerates the coating on the damaged area. Trivalent chromium does not have the same function, and cobalt is used in many trivalent chromium passivation film to provide a similar function.

The REACH regulation enforced in July 2007 initially included only cobalt chloride as a SVHC (substances of very high concern) for cobalt compounds, but most cobalt compounds have recently been included. In addition, the environment surrounding cobalt, such as concerns about it as a conflict metal, has become more severe year by year, and the movement against its use is accelerating.

This paper describes the functional characteristics of typical trivalent chromium passivation film and the function of each component, as well as the current status and future prospects of cobalt-free trivalent chromium passivation film.

Trivalent chromium passivation films

Classification

Trivalent chromium passivation films for zinc plating are broadly classified into white and black types. (see Figure 1)

The white type mainly includes inorganic silica [*1] and organic [*1], which are used as alternatives to conventional colored and bright chromates.

The black type includes phosphoric acid containing[*1], sulfur compound containing[*1], and hybrid[*1] containing both phosphoric acid and sulfur compounds, and is used as an alternative to conventional black chromate.

[*1] Classification names are colloquial terms, and names differ depending on the industry, manufacturer, etc.

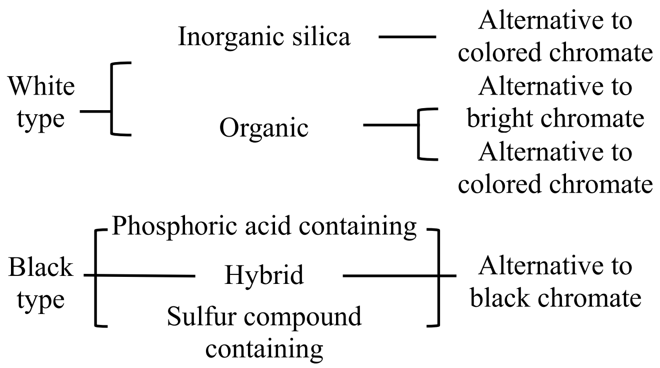


Figure 1 Classification of trivalent chromium passivation films [1]

Film structure

1. Organic trivalent chromium passivation films

Organic trivalent chromium passivation films have a monolayer structure with uniform oxides and hydroxides, e.g. chromium, cobalt, and zinc.

The XPS depth profile of the organic trivalent chromium passivation films is shown in Figure 2.

2. Inorganic silica trivalent chromium passivation films

The inorganic silica trivalent chromium passivation films have a two-layer structure with silicon and oxygen (present as silica) in the upper layer and oxides and hydroxides, e.g. chromium, cobalt, and zinc in the lower layer. The main feature of the inorganic silica trivalent chromium passivation films is that such a two-layer structure can be constructed in a single immersion treatment.

The XPS depth profile of the inorganic silica trivalent chromium passivation films is shown in Figure 3.

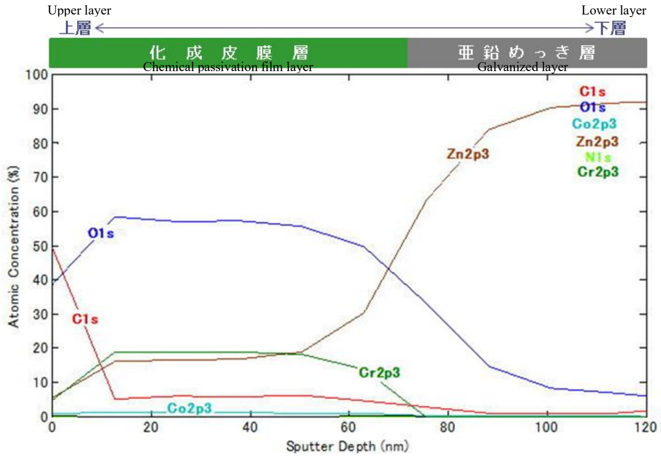


Figure 2 Organic trivalent chromium passivation film[1]

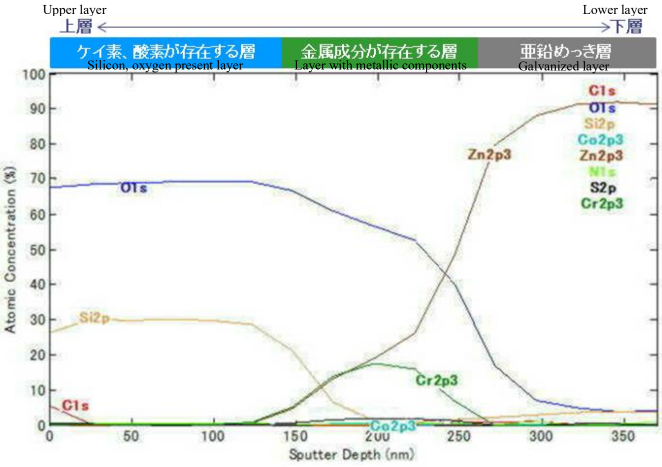


Figure 3 Inorganic silica trivalent chromium passivation film[1]

Mechanisms of film formation

The basic mechanism for the formation of trivalent chromium passivation films is the deposition of metal hydroxides caused by the increase in interfacial pH resulting from etching of the plated surface, but there are many differences between organic and inorganic silica in the film formation.

1. Reaction of organic trivalent chromium passivation film formation (estimated)[1, 2]

1) Etching of zinc surface occurs due to immersion. (Battery action, dissolution)
2) Increase in pH at the interface between zinc and treatment solution.
3) Formation and deposition of chromium compounds such as chromium hydroxide and formation and deposition of double salts of chromium, cobalt, and zinc.
4) Thick film formation. (maintenance of the film formation reaction due to the presence of cobalt)
   Incorporation of unreacted components into the film.
5) Fixation by drying.[2]

2. Reaction of inorganic silica trivalent chromium passivation film formation (estimated)[1, 2]

1) Etching of zinc surface occurs due to immersion. (Battery action, dissolution)
2) Increase in pH at the interface between zinc and treatment solution.
3) Formation and deposition of chromium compounds and silica film. At the same time, chromium hydroxide and double salts of chromium, cobalt, and zinc are formed and incorporated into the film.
4) Thickening of the film, destabilization of silica* due to the rise in pH. (maintenance of the film formation reaction due to the presence of cobalt)
   Incorporation of unreacted components into the film.
5) Fixation by drying.

*Destabilization of Silica

The stability change of colloidal silica as a function of pH is shown in Figure 4.

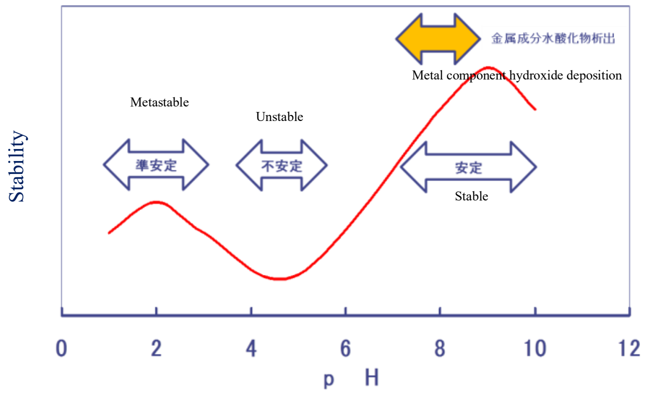


Figure 4 The stability of colloidal silica [1]

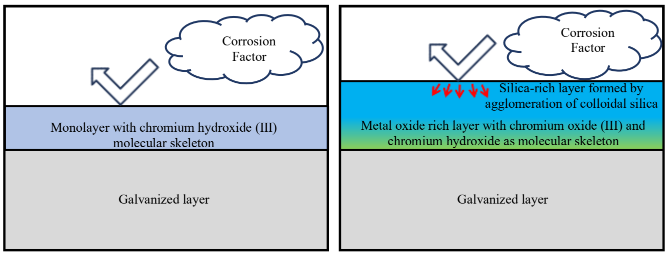
Colloidal silica is in a metastable region in the treatment solution, but becomes unstable due to the increase in pH caused by etching of the zinc surface, resulting in agglomeration and deposition. Since colloidal silica is solid, it cannot pass through the previously deposited gel layer and is deposited on the gel layer. On the other hand, the components other than colloidal silica are ions, so they can pass through the gel and reach the interface between the zinc and the passivation films, maintaining the reaction.

This mechanism is thought to be responsible for the formation of the two-layer structure.

Anti-corrosion mechanism

1. Basic anti-corrosion mechanism

Both organic and inorganic silica have a basic corrosion inhibiting ability due to their barrier effect on corrosive substances. However, in the case of inorganic silica, the silica-rich surface layer is thought to have the additional effect of dispersing the corrosion current and suppressing the corrosion rate.[1] (see Figure 5)



Organic trivalent chromium passivation coatings   Inorganic silica trivalent chromium passivation coatings

Figure 5 Basic anti-corrosion mechanism

2. Mechanism of maintaining corrosion resistance when film is damaged

When both organic and inorganic silica coatings are damaged, the film is regenerated (self-healing) by a film-forming reaction between unreacted substances in the coating and exposed zinc. This ability is higher for organic, where unreacted components are relatively stable due to the presence of chelating agents. On the other hand, although inorganic silica has a weaker self-healing effect than organic. But the corrosion current dispersion effect of the silica-rich layer has the effect of suppressing the corrosion rate of the damaged area of the film itself.

Cobalt Effects

The addition of cobalt to organic trivalent chromium passivation solution increases the amount of chromium deposited as passivate film.

Cobalt has the effect of accelerating the formation reaction of passivate film, and this effect is also effective in regenerating the film when the film is damaged. Since the scratch resistance of organic trivalent chromium passivate depends largely on the film formation promoting effect of cobalt, cobalt is an essential component of organic trivalent chromium passivate. (see Tables 6 and 7)

The scratch resistance of the inorganic silica trivalent chromium passivation treatment is mainly due to the corrosion current dispersing effect of the silica-rich layer, so the decrease in corrosion resistance due to the removal of cobalt is not as great as with the organic trivalent chromium passivation treatment. However, since a slight decrease in corrosion resistance is observed, it can be said that cobalt is indispensable to obtain the same level of corrosion resistance as the current treatment. (see Tables 6 and 7)

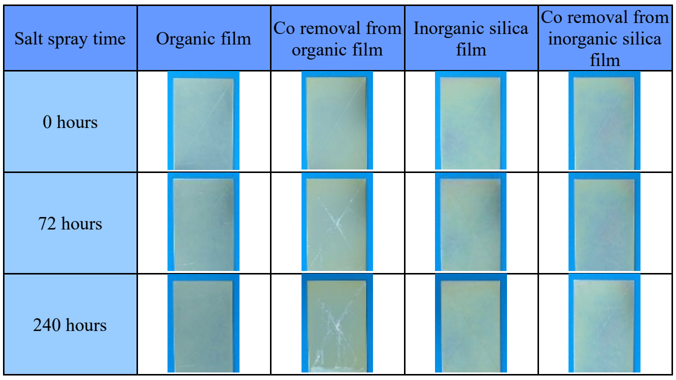


Figure 6 Corrosion resistance when Co is removed from the current treatment agent (rack and cross-cut tests)

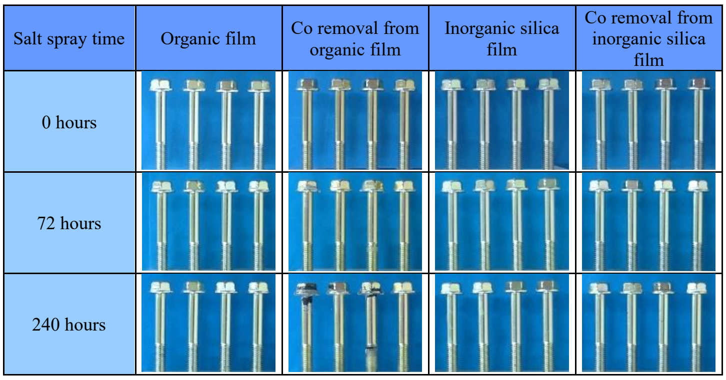


Figure 7 Corrosion resistance when Co is removed from the current treatment agent (barrel)

Cobalt-free

To make trivalent chromium passivation coatings cobalt-free, it is necessary to construct a system with scratch resistance equivalent to that of cobalt. In our research, we found that certain components exhibit cobalt-like behavior, and we have developed a treatment that incorporates these components. Figures 8 and 9 show the results of a salt spray test of the developed product.

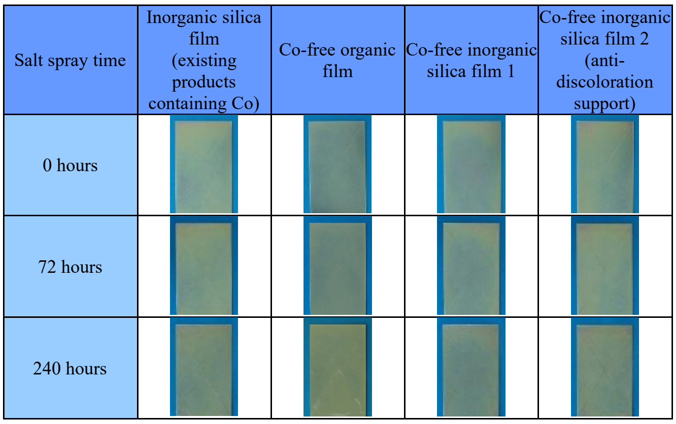


Figure 8 Corrosion resistance of newly developed Co-free passivation coating (rack and cross-cut tests)

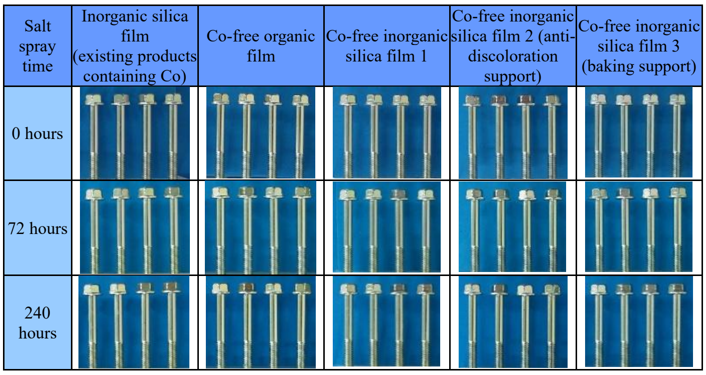


Figure 9 Corrosion resistance of newly developed Co-free passivation coating (barrel)

Compare Figures 8 and 9 with Figures 6 and 7. It can be seen that even for organic trivalent chromium conversion coatings, the corrosion resistance of crosscut areas, threads, and flanges has been improved compared to those in which Co is simply removed.

As shown above, development toward cobalt-free coating has been steadily progressing, and it is now at a level that can meet the required specifications of automobile manufacturers.

Product Summary

We offer cobalt-free treatments for zinc plating and zinc-nickel alloy plating in the Tryner series of trivalent chromium passivate coatings. (see Tables 1 and 2)

Table 1 For zinc plating

Appearance	Plating type	Passivate film treatment agent (Tryner)	Post dip agent
Blue	Rack, Barrel	TR-160A	－
Colored	Rack, Barrel	TR-173CF	－
	Rack, Barrel	TR-175CF	－
Black	Rack	TR-187FG	FT-192G
	Barrel	TR-185CF	FT-190CF

Table 2 For zinc-nickel alloy plating

Appearance	Plating type	Passivate film treatment agent (Tryner)	Post dip agent
Colored	Rack, Barrel	TRN-988CF	－
Black	Rack	5W115MB	FT-192G
	Barrel	5W115MB	FT-190W

In closing

In conventional trivalent chromium passivate coatings, cobalt was an essential component to give the passivate film self-healing properties, but as mentioned in the introduction, various circumstances are driving the trend toward cobalt-free passivate coatings. Cobalt-free trivalent chromium passivation coatings are a new technology that has only just reached the level of practical application. We believe that further improvement and maturation are needed to achieve higher performance and lower cost.

Literature

1 Nano plating No.50 (total No.114) (2014)

2 Hideo Susa; *J. Surf. Finish. Soc. Jpn.* Vol.70, No. 8, pp. 388-393 (2019)