

# Preparation and Property of Zr-series Nano-conversion Film on Metal Surface

## Abstract

Before electrochemical coating or powder coating on metal surface, chromate passivating techniques or phosphate passivating techniques are usually use to improve corrosion resistance property or coating film adhesion property, but problems in high toxicity for the former and in precipitate accumulation for the later are difficult to handle. This paper discusses the formation techniques of Zr-series transforming film and the film's corrosion resistant test. Results of corrosion resistant by neutral salt spray indicated Zr-series nano-conversion agent treated transforming film displayed prominent corrosion resistant property and can replace traditional chromate and phosphate passivating process.

## 1. Introduction

Chemical conversion treatment usually takes place before electro-coating or powder spray coating on the metal surface such as Fe, Zn, Al, etc. to increase samples' corrosion resistance and adhesion strength. In industry, chromate passivating treatment to elongate rust corrosion time is widely applied. Chromate layer is composed by complexed Cr(III) and Cr(VI) oxidates and hydroxides, eg., the  $\text{Cr}_2\text{O}_3$  film can prevent material base from corrosion in the external environment. Cr (VI) could react with the exposed metal base by reduction to produce Cr (III) compounds covering on the defect parts, reaching the ability of self-repairing to make the layer have good corrosion resistant function. Although the produced chromate effectively prevent the white rust, high toxicity of Cr (VI) and cancer inducing effect are harmful to environment safety.

With the environmental requirement and EU's ROHS, ELV and WEEE regulation taking into practice, limitation on import of Cr (VI) passivating products started from 2003. Additionally, zinc phosphate passivating has been widely applied. However, large amounts of precipitate accumulation could appear when using zinc phosphate treatment agents for metal surface treatment. Phosphate ions may nourish the environment, which increase the cost for eliminating accumulated precipitates and waste water treatment and hence has no economic advantages. Considering the environmental safety problems and economic advantages, non-P and non-Cr passivating agents are urgent to develop, especially Ti- and/ or Zr-series passivating techniques are potential research topics. Ti, Zr oxidates or hydroxides

are chemically stable with the acidic resistant and alkaline resistant property. The above metal oxides or hydroxides by metal and O<sub>2</sub> reaction could form network structure and precipitate on the surface of the metal base, hindering water, oxygen and corrosion inducing components to reach good corrosion resistant property.

This paper introduced nano-Zr-series transforming agent for passivating different kinds of metal surfaces, and the treatment provides high corrosion resistant property and coating adhesion strength

## 2. Process flow chart and Experimental methods

### 2-1 Process flow chart

Nano-conversion technique procedures:

Powder spray, painting process

Degrease → water wash → nano-conversion → water wash → wash by pure water → dry → spray painting → dry

Electrophoresis deposition process (ED)

Degrease → water wash → nano-conversion → water wash → wash by pure → ED → dry

### 2-2 nano-conversion agent technical parameters

Table 2-1 Technical parameters for working solution

Sample Lable	appearance	Free ion acidity	Total acidity	pH
Ching-Feng Zr-series nano-conversion agent	Colorless and transparent	0.8-1.2	2-3	3.0-4.0

Use according to volume ratio, original solution:water=1:19, adding water to stir and homogenize. Passivating temperature 20~40°C, time 90~180s, using ammonium or sodium hydroxide to adjust pH in the range of 3.0~4.0.

### 2-3 testing method

2-3-1 adhesion strength test: QFZ film adhesion strength analyzer was used.

2-3-2 nano-conversion film constant temperature and humidity corrosion resistant test: the nano-conversion treated metal material was put in the testing chamber with constant

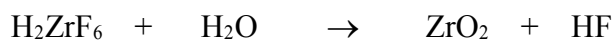
temperature of 35°C and constant humidity of 80%, evaluation on corrosion resistance of the nano-conversion treated film started from the appearance of rust on the surface of base materials.

2-3-3 neutral salt spray corrosion test: according to the method of GB/T1771-2007, continuous spray method was used. Half separate the coated samples along the direction of *duijiaoxian*, corrosion resistance of nano-conversion treated film was evaluated by the width of the peeled film on the two sides of the *duijiaoxian* samples or the size of bubbles.

### 3. Results and Discussion

#### 3-1 mechanism of film formation

Film forming mechanism is mainly according to the balance of  $H_2ZrF_6$  和 HF in the reaction, precipitated nano-conversion film on the surface of base materials. Generally, Zr salt exists as  $H_2ZrF_6$  in the solution with enough amounts of HF. The reaction is as follows:



When the metal plate sample put in the Zr salt acidic solution, corrosion micro-electrical reaction occurs on the metal surface immediately.

Metal solubilization in the yang ji:



Reduction in the yinji to reduce jihua agent such as  $O_2$ 、 $H^+$



The reduction reaction in the cathode causes the increase in pH at some areas of metal surface layer, which promotes the decomposition of zirconium fluoride, and the main component of the precipitated surface film is  $ZrO_2$ . In the meantime, fluorion ( $F^-$ ) capture agent in the solution can form stable Fluorine complex with  $F^-$ . This reduced the concentration of  $F^-$  released by zirconium fluoride and it enhances the formation of passivated film.

### 3-2 Property test for Zr-series nano-conversion film

#### 3-2-1 Property test for cold plate uncoated and coated film

process	Base material	Uncoated film constant temperature and humidity test	Electro-phoresiss Painting 500h NSS	Powder Painting 500h NSS	Liquid Coating 200h NSS
Ching-Feng Zr-series nano-conversion agent	Cold plate	48h	<3.0mm	<3.2mm	<3.5mm

#### 3-2-2 Property test for galvanized plate after coating

process	Base material	Powder spray 100h NSS	Powder spray 300h NSS	Coating 300h NSS	Electro-phoresiss 500h NSS
Ching-Feng Zr-series nano-conversion agent	Galvanized plate	<1mm	<3.5mm	<8mm	<5mm

#### 3-2-3 Property test for the uncoated and coated film of aluminum plate

process	Base material	Uncoated film 72h NSS	Uncoated film 120h NSS	Powder spray 500h NSS	coating
Ching-Feng Zr-series nano-conversion agent	Aluminum	No rust	Corrosion area <10%	<1mm	<1mm

Note: (1) metal material and coating were provided by customers

(2) passed different tests for all kinds of coatings

(3) values represent the level of rust or bubbles(galvanized plates) spreading around the scratches.



cold plate painting   cold plate electrophoresis   galvanized plate/coating   galvanized plate/ spray   Al plate powder spray

### 3-3 Feature of Zr-series nano-conversion film

#### 3-3-1 comparison of Zr-series nano-conversion film with conventional treatment

Generally, procedures for conventional phosphating pretreatment system are relatively complicated, such as surface adjusting before filming and the passivating in the end. Besides procedures, costs in setting production line and reagents are not beneficial to economic competition, comparing to the Zr-series nano-conversion film.

#### Conventional conversion

Degrease → water wash → water wash → surface adjusting → water wash → passivating → wash by pure water

#### Nano-ceramic conversion

Degrease → water wash → water wash → nano-conversion → wash by pure water

#### 3-3-2 advantages of Zr-series nano-conversion film

\* it does not contain heavy metals such as Ni, Cr, and reduces the burdens on waste water treatment and environmental concerns.

- \* enhance coating binding strength and increase corrosion resistance, comparable to traditional phosphating.
- \* suitable to the metal surface pretreatment such as steel, zinc, aluminum, etc., different kinds of metals.
- \* compatible to current pretreatment production line (dipping or spraying), saving equipment cost.
- \* operate at room temperature, treatment time is short, no need for surface adjusting and passivating, saving process cost.
- \* almost no precipitates, no blocks on the top of sprayer, reduce the cost for waste handling.

#### 4. Conclusion

Zr-series nano-conversion film developed in Ching-Feng company is a kind of non-harmful non-chromate treatment agent, nano-conversion film can be formed on the surface of different types of metal by liquid precipitation method; provide good corrosion resistance and improve the tightness with coatings. This product can replace chromate treatment agents and be used in the areas of automobile, home electronics, and building materials. As surface treated base materials without phosphorus and chromium, the product can also be used in the extended areas, eg., container, cooker and interior building materials.