

# The research of improved zirconium system nano-ceramic agent

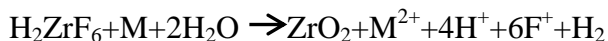
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Summary:

In order to improve the **PH value of zirconium system nano-ceramic film when it formed the film stable after the tank liquid was aged. It will have the metal ion remaining to cause the zirconium ion unable to form the film on the surface of metal and decrease its adhesion. This article is to use chelant as adding agent to extend the life of tank liquid and make the research for coating.**

Introduction:

Since 2002, Germany's Henkel Group developed many kinds of **zirconium system nano-ceramic agent to replace traditional phosphate products all over the world for a variety of materials and it already widely used in the marketplace. The theory is to use zirconium ion to form sol-gel** in the liquid and put the metal in it which will produce erosion as battery reaction. Meanwhile, it produces metal dissolving in anode and the PH will elevate on the metal surface to improve the Fluozirconic Acid to be separated and release the main component of zirconium oxide (ZrO)



This M represents different metals.

From the above reaction, as the treatment time is increased from the tank liquid, it will have more metal ion to lose the balance of the reaction. It will also make the zirconium ion fail to form the zirconium oxide to have the appearance of peeling off during coating. Currently, most products of **zirconium system ceramic agent are forming at pH3.5-4.5** in the marketplace. The acidity can be dissolving the metal surface effectively and make the zirconium oxide sedimentation. However, the higher acidity leads to more metal ions in the tank liquid and these will combine with zirconium oxide to become the situation of sol-gel. In addition, it will also lead to less and less free zirconium and have the appearance of peering off after coating. Our research is to use adding agent to chelate with metal ion to make the tank liquid more stable and increase its treatment life.

1.Test

1.1 Material and treatment

1.1.1 Q235 steel plate、 6067 aluminum plate

1.1.2 the component of improved **ceramic agent**

Fluozirconic Acid 50~100g/L

Organic Acid 15~30g/L

Chelant 5~10g/L

Corrosion inhibitors 5~10g/L

Polymer dispersion agent 1.0~3.0g/L

Use dilute alkali for neutralization pH at 4.5~5.5

## 1.2 Test process:

### 1.1 Liquid and powder paint:

Degreasing → water rinsing → **nano-ceramic** (pH4.5~5.5、room temperature、3min) → water rinsing → pure water rinsing → drying(120℃、10min) → coating

### 1.2.2 Electrophoresis paint

Degreasing → water rinsing → **nano-ceramic** → (pH4.5~5.5、room temperature、3min) → water rinsing → pure water rinsing → electrophoresis → drying

水洗 → 纯水洗 → 电泳 → 烘干

## 1.3 Test method:

### 1.3.1 Neutral salt spray test:

Based on GB/T1771-2007, use continuous spraying to slice the trial workpieces as 60 angle to see the adhesion according to the width of erosion and the volume of the bubbles.

### 1.3.2 Aged test:

Put Q235 into the **ceramic liquid after degreasing and immersion time is 8hr/day** to see the change of the liquid and the concentration of zirconium and ferric ions.

## 2. Test result

### 2.1 6067 aluminum salt spray test:

	<b>100 hr</b>	<b>200 hr</b>
<b>Without phosphate</b>	Oxide	Oxide
<b>Traditional ceramic</b>	Without oxide	Oxide
<b>Improved ceramic</b>	Without oxide	Without oxide

Improved ceramic liquid has good corrosion resistance for 6067 aluminum plate and it is better than traditional one.

### 2.2 Test of corrosion resistance after coating:

#### 2.2.1 Liquid paint:

##### ◆ Q235

	<b>100 hr</b>	<b>200 hr</b>
<b>Without phosphate</b>	Peeling off	Peeling off
<b>Traditional ceramic</b>	Without peeling off	Without peeling off
<b>Improved ceramic</b>	Without peeling off	Without peeling off

##### ◆ 6067

	<b>100 hr</b>	<b>200 hr</b>
<b>Without phosphate</b>	Peeling off	Peeling off
<b>Traditional ceramic</b>	Without peeling off	Without peeling off

<b>Improved ceramic</b>	Without peeling off	Without peeling off
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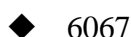


The corrosion resistance of improved ceramic liquid for liquid paint is the same as traditional one.

### 2.2.2 Powder paint



	<b>800 hr</b>	<b>1000 hr</b>
<b>Without phosphate</b>	Peeling off	Peeling off
<b>Traditional ceramic</b>	Without peeling off	Without peeling off
<b>Improved ceramic</b>	Without peeling off	Without peeling off

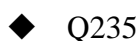


	<b>800 hr</b>	<b>1000 hr</b>
<b>Without phosphate</b>	Peeling off	Peeling off
<b>Traditional ceramic</b>	Without peeling off	Without peeling off
<b>Improved ceramic</b>	Without peeling off	Without peeling off



The corrosion resistance of improved ceramic liquid for powder paint is the same as traditional one.

### 2.2.3 Electrophoresis paint:



	<b>800 hr</b>	<b>1000 hr</b>
<b>Without phosphate</b>	Peeling off	Peeling off
<b>Traditional ceramic</b>	Without peeling off	Without peeling off
<b>Improved ceramic</b>	Without peeling off	Without peeling off



	<b>800 hr</b>	<b>1000 hr</b>	<b>1500 hr</b>
<b>Without phosphate</b>	Peeling off	Peeling off	Peeling off
<b>Traditional ceramic</b>	Without peeling off	Without peeling off	Without peeling off
<b>Improved ceramic</b>	Without peeling off	Without peeling off	Without peeling off

The corrosion resistance of improved ceramic liquid for electrophoresis paint is the same as traditional one.

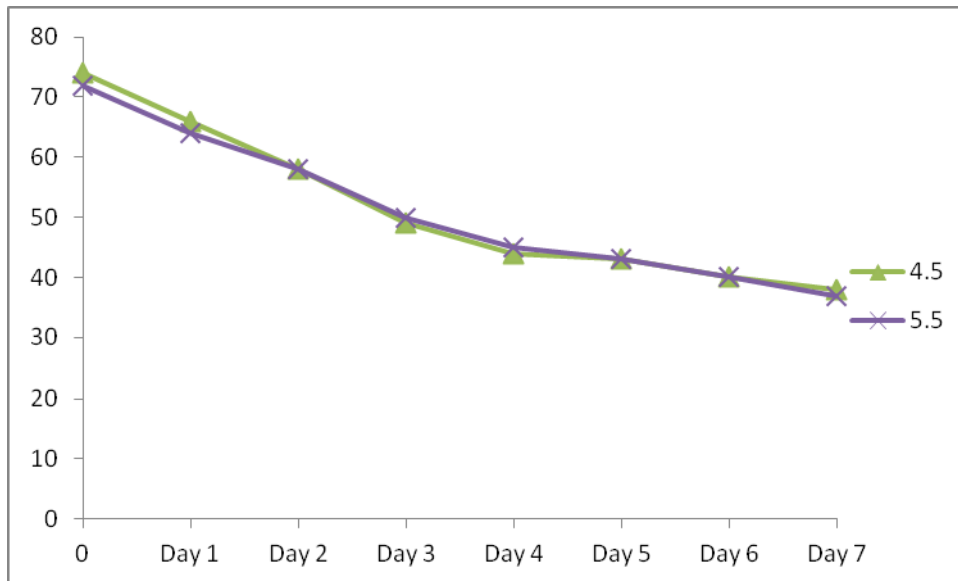
### 2.3 The determination for the age of ceramic liquid

<sheet 1> The consumption of zirconium ion

(unit: mg/L)

	0	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
traditional	74	66	58	49	44	43	40	38

improved	72	64	58	50	45	43	40	37
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<chart 1>the concentration's change of zirconium ion

<sheet 2>The outline's change of ceramic liquid

	<b>Turbidity</b>	<b>Red</b>	<b>sediment</b>
<b>Traditional</b>	Day3	Day3	Day4
<b>Improved</b>	Day6	Day4	Day8

From <sheet1> <sheet2> and <chart1>, no matter what improved or traditional ceramic agent, the adhesion and consumption for ferric are concerned with the surface area of workpieces. If there is a turbidity occurred, the battery reaction is proceeding in the tank liquid and its pH value is higher and higher. As the effective zirconium ions sedimented little by little, the amount of these will be less and less and the construction of film layer will be loose and decrease the corrosion resistance. However, the improved one is able to extend the treatment life of tank liquid due to its adding agent.

**Conclusion:**

The adhesion and combination with paint for ferric and aluminum of the improved ceramic agent is the same as traditional one. However, the time of age for the tank liquid is better than traditional one and it can improve the aged issue of the tank liquid to achieve the effect of cost down.