

Development of a Chromium-free Pretreatment System for Aluminum Bodies

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ABSTRACT

A chromium-free surface treatment method was developed for aluminum bodies. By adding fluorine ions and iron complex compounds to the current zinc phosphate pretreatment bath, an improved zinc phosphate film is formed on aluminum. Also, increasing the manganese in the pretreatment bath improves the alkaline resistance properties of the zinc phosphate film. As a result of these changes, the zinc phosphate film has improved secondary adhesion after water conditioning and improved filiform corrosion resistance without using a chromium rinse. Therefore, chromium can be eliminated from the paint process of aluminum bodies. This, in turn, reduces environmental burdens previously posed.

1. Introduction

It is necessary to consider the post-painting corrosion resistance when using aluminum in automotive bodies just as is true with the use of steel. Thus, research is being conducted on various painting techniques. Painting methods for aluminum automotive bodies and their associated pretreatment processes developed to date are shown in Fig. 1. In Japan, chromating was briefly used as the pretreatment method. However, currently the main method applied for aluminum/steel mixed metal pretreatment is a zinc phosphate treatment, which enables the painting of hybrid bodies. With this treatment, a free fluorine ion (F^-) is added to the zinc phosphate solution used for steel bodies, allowing a zinc phosphate film to be formed on aluminum.

However, it is known that the addition of fluorine ions lowers the adhesion of the paint film. This is believed to be caused by fluorine compounds adhering to the surface of the zinc phosphate film and impeding the adhesion of the paint film. One method for improving adhesion is to apply a chromium rinse after phosphating to remove the fluorine compounds.

It is also difficult to form a zinc phosphate film on a sanded area of an aluminum body (an area where a body stamping deformation or welding irregularity has been corrected by grinding the surface with sandpapers, etc.). Even with the addition of fluorine ions, a comparison between such areas and normal areas, where no abrasion has been applied, shows them to be inferior in post-painting corrosion resistance. To solve this problem, a chromium corrosion-resistant pigment is added to the cathodic electrocoat (E-coat) to assist in corrosion resistance.

However, a surface treatment that utilizes chromium has

a negative impact on the environment and entails costly wastewater treatment, so the use of a chromium rinse is gradually declining. It has also been decided in Europe that the amount of hexavalent chromium used in corrosion-resistant coatings will be restricted in the future.

Therefore, we began the development of a surface treatment for aluminum that does not require the use of chromium. We report in this paper the development of a method for adding fluorine ions and an iron complex compound to the zinc phosphate solution as reaction accelerators. This method enables the elimination of materials containing chromium from the painting process.

2. Current Surface Treatment Methods

Corrosion resistance in automotive bodies must take into account various difficulties in paint adhesion such as paint film blisters, delamination and peeling, and resistance to such types of post-painting corrosion as scab and filiform corrosion. It is known that the corrosion resistance of aluminum is generally superior to that of steel in the untreated state. However, when a zinc phosphate solution for steel is applied to aluminum, an adequate film cannot be formed and the resulting corrosion resistance is inadequate.

When treating aluminum, therefore, fluorine ions have conventionally been added to the zinc phosphate treatment solution as an etching agent to accelerate the formation of the zinc phosphate film. Fluorine ions are added as fluorosilicic acid (H_2SiF_6) and sodium fluoride ($NaHF_2$), and controlling their concentration regulates the degree of film formation.

When aluminum ions (Al^{3+}) are eluted in the treatment solution and accumulate beyond a fixed amount, they inhibit

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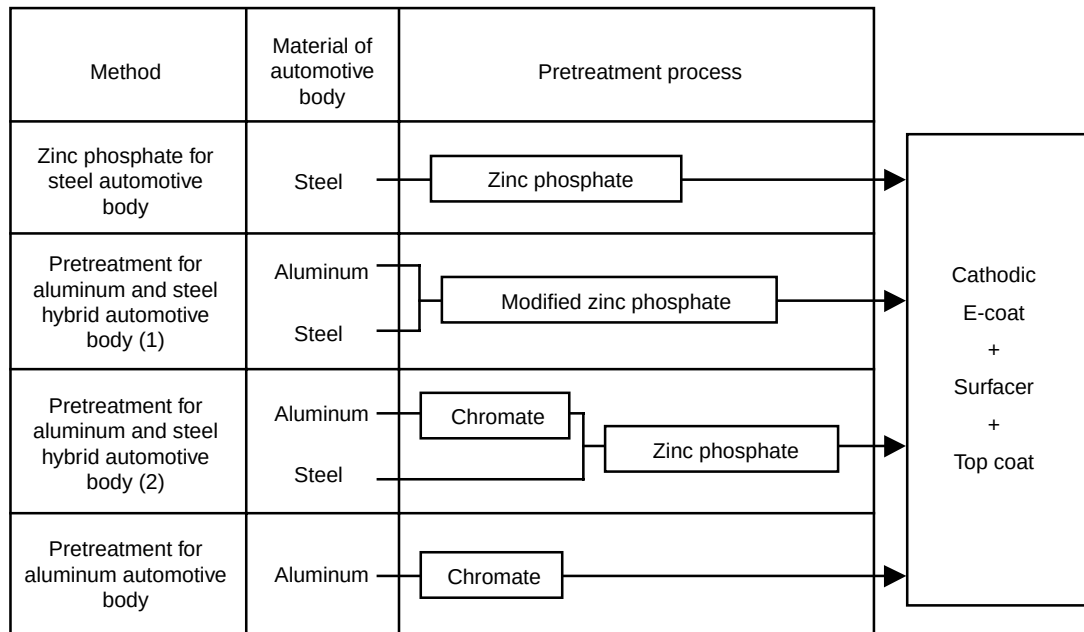


Fig. 1 Pretreatment methods for aluminum and steel bodies

the precipitation reaction of the zinc phosphate film. Thus, they must be removed.⁽¹⁾ The zinc phosphate reaction on aluminum and removal of the aluminum ions from the solution can be described by the following reactions:⁽²⁾

- (1) Etching the aluminum surface

$$2\text{Al} + 6\text{HF} \rightarrow 2\text{Al}^{3+} + 6\text{F}^- + 3\text{H}_2 \uparrow$$
- (2) Precipitation of a zinc phosphate film resulting from an increase in pH value of the aluminum surface

$$3\text{Zn}(\text{H}_2\text{PO}_4)_2 \rightarrow \text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} (\text{Hopeite}) + 4\text{H}_3\text{PO}_4$$
- (3) Removal of aluminum ions from the solution

$$\text{Al}^{3+} + 3\text{Na}^+ + 6\text{F}^- \rightarrow \text{Na}_3\text{AlF}_6 (\text{Cryolite}) \downarrow$$

In this way, the addition of fluorine ions to the current zinc phosphate treatment for aluminum and steel hybrid bodies improves the zinc phosphate properties on the aluminum and allows for a continuous treatment.

However, it is known that an excessive concentration of fluorine ions reduces the degree of adhesion of the paint film. This is thought to be caused by fluorine compounds

adhering to the surface of the aluminum blocking the adhesion of the paint film. To improve adhesion, it is necessary to carry out a chromium rinse in the post-treatment process to remove the fluorine compounds. Fig. 2 compares the results of a water-resistance test with and without a chromium rinse after the treatment. The results demonstrate that the chromium rinse improved the water resistance.

Even with the addition of fluorine ions, however, it is difficult to achieve sufficient film coverage over the scratches on a sanded aluminum surface, with the result that the filiform corrosion resistance is lowered on the sanded surface. It is known that the addition of a chromium corrosion-resistant pigment to the E-coat improves the filiform corrosion resistance. Fig. 3 shows the effect of this addition.

As already explained, it has been necessary to use materials containing chromium to maintain good paint adhesion and filiform corrosion resistance with the current zinc phosphate treatment for aluminum and steel hybrid automotive bodies.

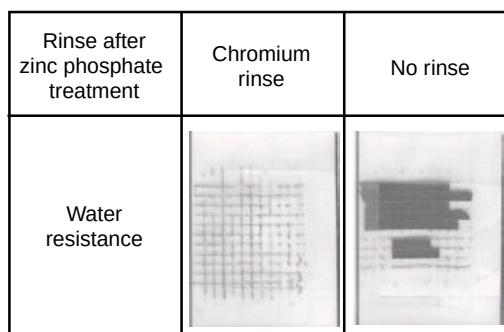


Fig. 2 Paint adhesion on sanded area after water resistance test

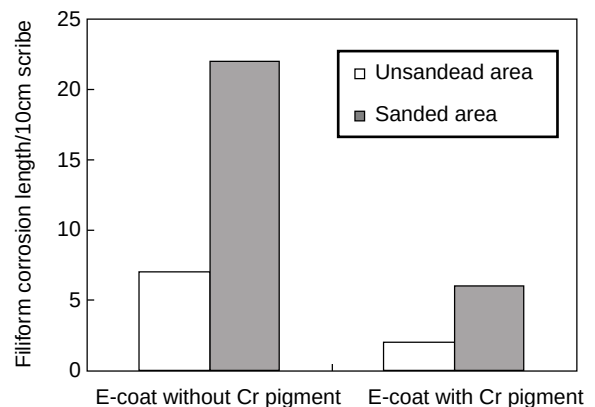


Fig. 3 Effect of corrosion-resistant pigment in E-coat

3. Improvement in Zinc Phosphate Treatment Properties with the Addition of an Iron Complex Compound

To ensure the post-painting corrosion resistance of aluminum without using a chromium rinse or chromium corrosion-resistant pigment in the E-coat, we concluded that it would be necessary to form a fine and uniform zinc phosphate film and improve its coverage (the percentage of the surface covered) by increasing the reactivity of the treatment solution.

The effectiveness of iron ions (Fe^{3+}) as an etching accelerator for aluminum in an acidic solution is well known.^{(3),(4)} It is also known that the addition of iron ions to the zinc phosphate solution forms a fine and uniform zinc phosphate film on a steel surface. However, iron ions in the zinc phosphate solution used on automotive bodies (pH 3 –

3.5, NO_2^- ions contained) form an iron phosphate sludge, making it impossible to stably maintain a fixed amount of iron ions over a long period of time.

We therefore attempted to reproduce the effect of iron ions as just described on the formation of a zinc phosphate film on aluminum, by maintaining the ions in the zinc phosphate solution as a complex. We used ammonium iron citrate ($[\text{Fe}\{\text{C}_6\text{H}_4\text{O}_7(\text{FeO})(\text{NH}_4)_2\}_2(\text{OH})_2\}_3\text{C}_6\text{H}_5\text{O}_7 \cdot x\text{H}_2\text{O}$) as the iron complex compound. Figs. 4 and 5 respectively show the phosphating time plotted against the change in coating weight and the precipitation of crystals in the film. The material used in both cases was a 6000 series aluminum alloy. The results show that the addition of the complex compound increased the precipitation of zinc phosphate film and improved the film coverage compared to the current treatment.

Fig. 6 shows the electrical potential during the etching of a 6000 series aluminum alloy. As the intention here was to observe the etching behavior during the zinc phosphate

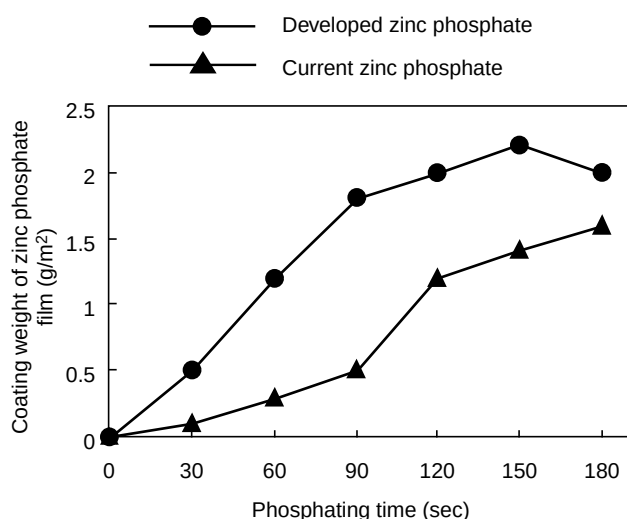


Fig. 4 Phosphating time vs. coating weight of the zinc phosphate film

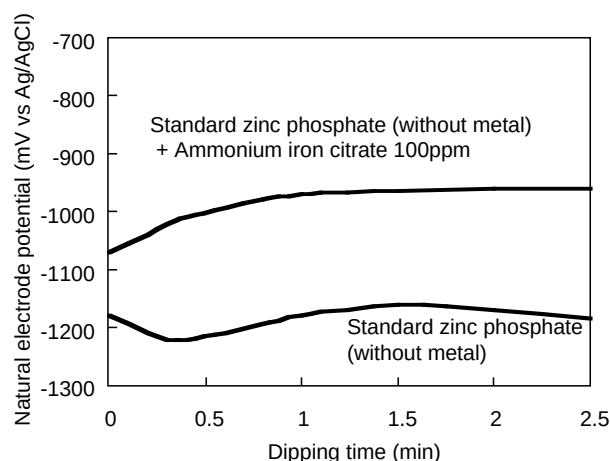


Fig. 6 Change of electrical potential during the etching reaction of aluminum

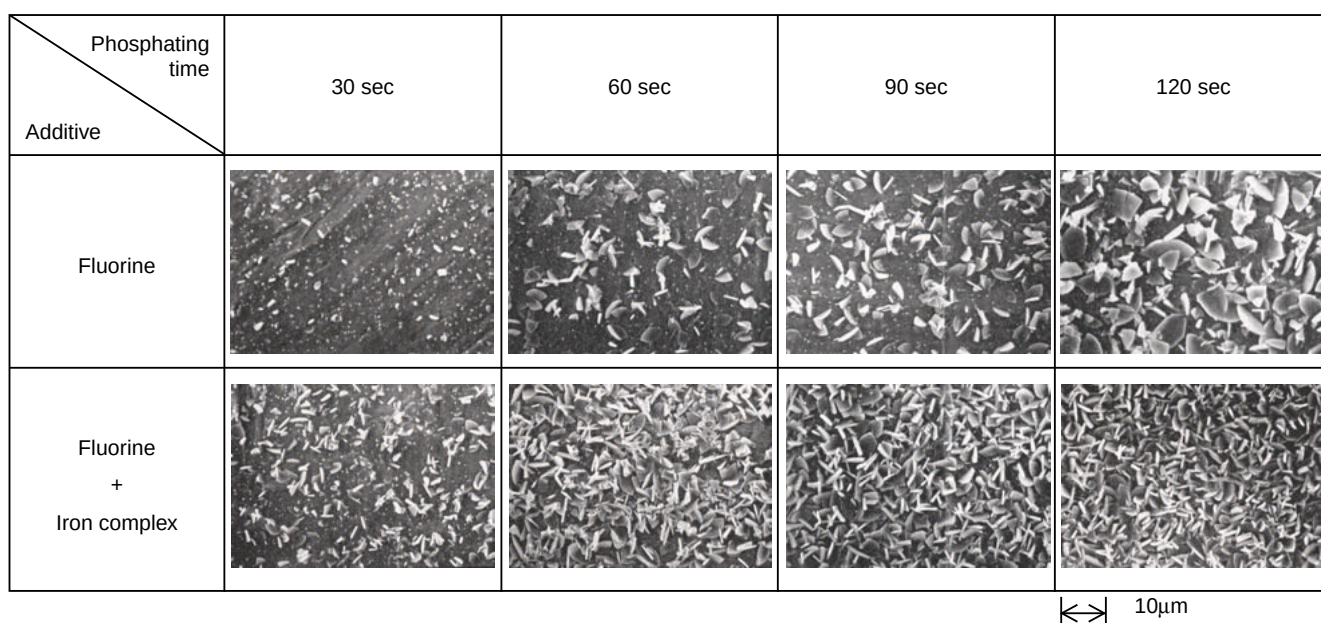


Fig. 5 SEM images of zinc phosphate films

reaction, we extracted the zinc (Zn), nickel (Ni) and manganese (Mn) (components of the film formation) from the treatment solution. With the addition of the complex compound, the electrical potential shifted to noble during the etching process. Based on this, we hypothesize that the aluminum etching reaction is accelerated due to the acceleration of the cathode reaction.

4. Improvement of Water Resistance

It is necessary to grant sufficient attention to paint film adhesion, because when it declines, the appearance of the body is compromised due to peeling, blisters, etc., eventually leading to the development of corrosion under the film.

It is thought that there are various controlling factors in paint film adhesion performance. These factors include the paint materials, the method of painting, the chemical conversion coating method and the metal materials. Various experimental methods have been devised to evaluate paint film adhesion. In this section, we will discuss the relationship between the zinc phosphate treatment and water resistance.

Various improvements have so far been made to the zinc phosphate solution for steel, with the aim of ensuring water resistance. For example, when galvanized steel was first used for vehicle bodies, Mn was added to the zinc phosphate solution. This improved the quality of the film by replacing part of it with Mn, and it limited condensation during warm-water dipping. As a result, the water resistance was improved.⁽⁵⁾

The zinc phosphate film on aluminum is also thought to be improved by Mn, but the water resistance declines on areas where it is difficult to form a zinc phosphate film such as sanded areas. It is also known, as already described, that if excess fluorine ions are added to improve the film coverage, fluorine compounds are precipitated on to the aluminum surface, causing a decline in the water resistance.

In contrast, a treatment with zinc phosphate to which iron complex compounds have been added demonstrates an improvement in the water resistance, as shown in Table 1. The figures shown as the surface F/Zn ratio represent the

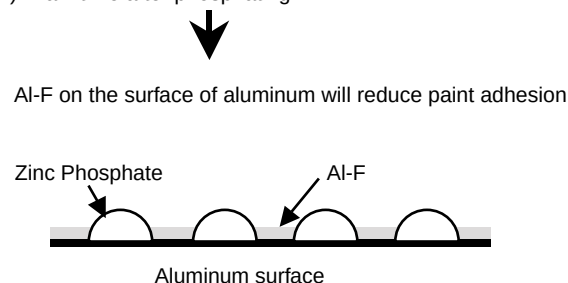
ratio of the atomic densities of fluorine (F) and zinc (Zn) on the aluminum surface after the zinc phosphate treatment. These figures were calculated from X-ray photoelectron spectroscopy (XPS) measurements.

A high water resistance resulted when the drain time (the time from phosphating to the water rinse) was less than 5 sec (i.e. immediate water rinse after phosphating) and when the phosphating time was 10 min. The resulting F/Zn ratio was zero in this case, so it is clear that fluorine compounds had not been formed.

These results enable the mechanism for the improvement in water resistance to be deduced. As Fig. 7 shows, when an area of the aluminum surface remains incompletely covered by the film, fluorine ions in the solution react with the incompletely covered area until the zinc phosphate solution is removed by the water rinse, and compounds of aluminum and fluorine (Al-F compounds) are precipitated. It is thought that these Al-F compounds inhibit adhesion. As Figs. 4 and 5 show, the phosphate film coverage was improved with a treatment by zinc phosphate to which an iron complex compound has been added, because Al-F compounds would not be readily produced in this case. When the water rinse was conducted immediately after phosphating, no Al-F compounds were formed because the fluorine ions had been removed. The coverage on the aluminum surface of the zinc phosphate film was sufficient with a treatment time of 10 minutes, so Al-F compounds had not been formed.

We can further point to the surface F/Zn ratio as a good indicator for judging water resistance.

(1) Drain time after phosphating



(2) Al-F doesn't appear on the surface of aluminum covered with fine zinc phosphate film

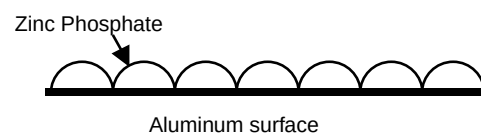


Fig. 7 Mechanism for the decrease in the paint adhesion

Table 1 Water resistance and F/Zn ratio

	Water resistance (Percentage of remained paint)	F/Zn ratio
Zinc Phosphate for aluminum and steel (STD condition)	0~50%	5.1
New zinc phosphate (STD condition)	100%	0.1~1.3
New zinc phosphate (Drain time < 5 sec)	100%	0
New zinc phosphate (Phosphating 10min)	100%	0

* STD condition : Phosphating time 2min, Drain time 30sec

5. Improvement in Filiform Corrosion Resistance

Filiform corrosion is one form of atmospheric corrosion that occurs with painted metals, etc., taking the particular form of corrosion growing from a damaged area or from the edge of the paint film in a thread-like form across the

surface. Filiform corrosion is particularly common with aluminum, and sufficient attention to the phenomenon is necessary in the body painting process. External factors that have been reported to influence the appearance and growth of filiform corrosion include relative humidity, paint materials, and pigments.⁽⁶⁾ As mentioned earlier, one method for improving the filiform corrosion resistance of aluminum when using the current zinc phosphate treatment is the addition of a chromium corrosion-resistant pigment to the E-coat.

A model of filiform corrosion on aluminum has been presented⁽⁶⁾ (see Fig. 8) in which the tip of the filiform corrosion (the anodic section) is in an acidic environment, while the area around the tip (the cathodic section) is in an alkaline environment.

Fig. 9 shows a comparison of the filiform corrosion resistance between the current zinc phosphate treatment for hybrid aluminum and steel bodies and the same treatment with an iron complex compound added. It is clear that the filiform corrosion resistance was improved by the newly developed treatment.

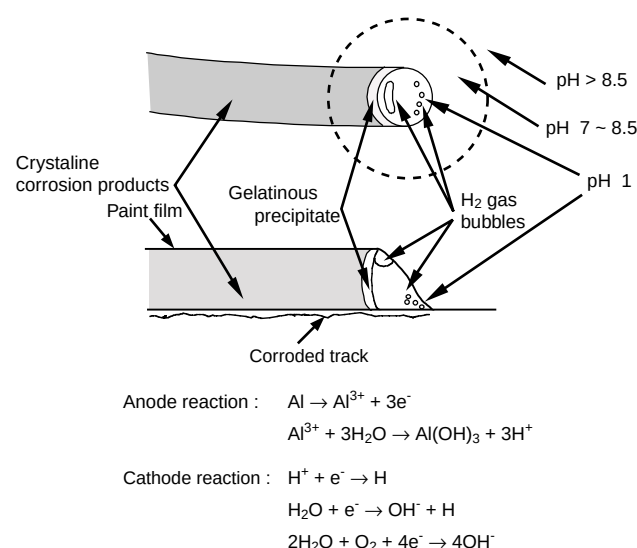
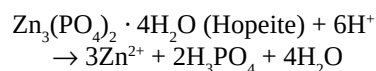


Fig. 8 Mechanism of filiform corrosion

We believe this improvement is due to the increased coverage of the zinc phosphate film causing the anodic section to be neutralized by the film according to the following formula, leading to suppression of the anodic reaction:



The filiform corrosion resistance was also improved by increasing the concentration of Mn in the zinc phosphate solution. We believe that increasing the amount of Mn in the film by increasing the concentration of Mn improved

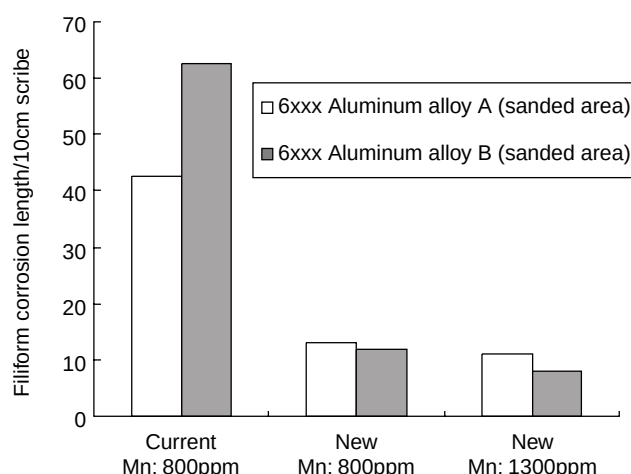


Fig. 9 Evaluation of filiform corrosion for each treatment

Table 2 Relationship between the concentration of Mn ions and alkaline resistance properties

Concentration of Mn (ppm)	Dissolved weight in alkaline (g/m ²)
800	0.2036
1300	0.0643

Current zinc phosphate treatment system

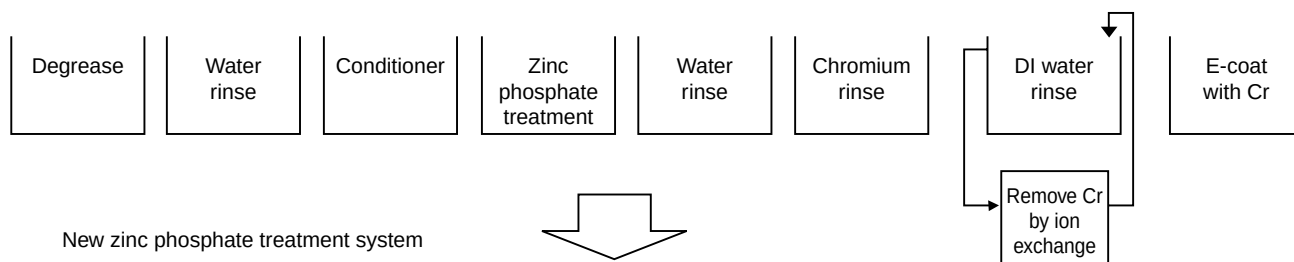


Fig. 10 New zinc phosphate treatment process

the alkaline-resistant property of the film, thus suppressing the filiform corrosion.

Table 2 shows the relationship between the concentration of Mn and the alkaline-resistant property of the zinc phosphate film.

The results of this study indicate that it is possible to obtain sufficient water and filiform corrosion resistance from body paint without the use of chromium. The removal of chromium from the painting process will contribute to a reduction in environmentally harmful substances. Fig. 10 shows an outline of the surface treatment systems.

6. Conclusion

In addition to the currently used fluorine ions, an iron complex compound was introduced as an additive to the zinc phosphate treatment for hybrid aluminum and steel bodies to increase reactivity. We also conducted studies on the concentration of Mn that would be required to improve the film.

- (1) The addition of the iron complex compound accelerated the zinc phosphate precipitation reaction, thus improving the coverage of the phosphate film on aluminum. This enabled the zinc phosphate film to be precipitated on to sanded areas which has been difficult with the current treatment.
- (2) Thus, it was possible to suppress the precipitation of Al-F compounds, which negatively affect paint film adhesion, and to ensure sufficient water resistance without a post-treatment chromium rinse. The filiform corrosion resistance was also improved in comparison with the current treatment.
- (3) We obtained a zinc phosphate film with superior alkaline-resistant properties by increasing the concentration of Mn in the treatment solution.
- (4) These results make it clear that it is possible to ensure sufficient filiform corrosion resistance without the addition of a chromium corrosion-resistant pigment to the E-coat.

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