

Development of Black Surface Treatment Applicable to Bolts for Motorcycles

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ABSTRACT

A black surface treatment without using hexavalent chromium and applicable to bolts of motorcycles has been developed. The surface treatment also satisfies the requirements of bolts for motorcycles such as fastening performance, corrosion resistance, weather resistance and appearance of outer finish.

There is a method of coating a black chemical conversion film using trivalent chromium on the zinc-plated surface as one of the surface treatments that do not use the hexavalent chromium. Such a black film, however, is thinner than the film using hexavalent chromium, and unable to ensure satisfactory black appearance. Meanwhile, although the dip-coating using a black paint can provide a sufficient black color, it is necessary to apply coating two times to eliminate an irregular color. As a result, thick paint films are formed on the roots of thread, making it difficult to fit into the internal thread. To simultaneously solve the above-mentioned two issues, two measures were executed. One was to apply the black film using trivalent chromium as an undercoat of dip-coating. The second was to develop paints that the amount of pigments in paints was adjusted on the assumption of the color of the undercoat. Thus a proper fit of thread was ensured when fastening in addition to a satisfactory black appearance even with the dip-coating only once. Also, the friction coefficient was controlled at an appropriate level by the selection of friction modifier. Moreover, the adhesion was improved by the enhancement of anchor effect of coating with the elimination of finishing process of the black chemical conversion film, and the requested corrosion resistance was achieved.

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INTRODUCTION

A large number of bolts are used in a motorcycle to fasten parts from the needs of workability and serviceability. A bolt is often considered as one of the appearance-conscious parts in a motorcycle. In such a case, as the bolt is required to have a good appearance in addition to the fastening performance, corrosion resistance and weather resistance, a surface treatment is generally applied to the bolt. Especially, the surface treatment that applies a metallic or black color is often used to make the bolt color same as the nearby parts.

In the past, the hexavalent chromium (here after Cr (VI)) was often used for the surface treatment of bolts. One of those treatments includes that for the zinc plating with Cr (VI), in which the surface of the zinc plating is chemically converted by Cr (VI). As the zinc plating using Cr(VI) is corrosion resistive, low in cost and a number of colors such as black, metallic are attainable, it has been applied to various types of bolts for used in outdoor environment.

Recent trends, however, are toward worldwide restriction of use of Cr (VI), which is an environmentally hazardous material [1] [2] [3]. Accordingly, the surface treatment has been shifted to ways without using Cr (VI) [4] [5].

One of the typical examples of those substituting treatments is that for the zinc plating with trivalent chromium (here after Cr (III)), in which the surface of the zinc plating is chemically converted by Cr (III) [6]. Since the chemical conversion film with Cr (III) is thinner than that of hexavalent counterpart, less coloring occurs on the base material. Accordingly, a better appearance is attainable from the colorless chemical conversion film using Cr (III) to take advantages of the appearance of base metal than from that using Cr (VI), thereby used widely. However, the black chemical conversion film using Cr (III) cannot obtain sufficient black. Also, the black film gradually becomes thinner as the chemical solution is used repeatedly and the black appearance gradually turns worse. Meanwhile, a black appearance is obtainable by application of a black paint film with dip-coating [7]. Such a dip-coating, however, has to be applied two times to ensure evenness of color, causing thick paint films to be formed on the root of thread, which makes it difficult to fit into the internal thread in some cases. The surface treatment that applies a black color without using

hexavalent chromium was unable to satisfy the appearance requirements while maintaining the necessary thread preciseness. The use of appearance-conscious parts therefore was limited.

In this study, we developed a black-finish treatment that simultaneously satisfies all the requirements of bolts for motorcycles without using Cr (VI).

Firstly to attain a satisfactory black appearance while maintaining adequate thread preciseness, it was decided to use the chemical conversion film, which used to be applied as a finish treatment on a zinc plating, as an undercoat before dip coating. Then, taking advantages of the color of the undercoat, such a paint has been developed that can ensure evenness of color even from one-time painting by controlling the amount of pigment in the paint.

SETTING OF DEVELOPMENT AIMS

Reviewing of Methods to Apply Black Appearance to Bolts

The zinc plating is the most popular surface treatment to apply to bolts. Zinc plating is the plating created through the process of placing a zinc metal layer, on the surface of base material, created by a deposition by electrically induced reduction process with application of an electric current to the target part material, which is immersed into the plating processing solution containing ionized zinc. Also developed to further improve corrosion resistance is the zinc-alloy plating in which the zinc-nickel alloy or zinc-iron alloy is coated [8]. It should however be noted that the surface of zinc plating or the zinc-alloy plating discolors easily by oxidation. A chemical coating therefore is generally applied to prevent discoloration. When a black color is necessary, a black chemical conversion film is provided. While the Cr (VI) used to be used in the chemical treatment, it has recently been substituted by the Cr (III).

Though no longer used because of containment of Cr (VI), the black chromium plating was sometimes used [9]. The black chromium plating is one of the plating techniques for forming a black layer composed of metallic chromium and chromium compounds on the nickel-plated surface that contains sulfur by electrolytic reduction. Because of its capability of presenting jet black appearance, it has been used for applying good appearances, but the application was limited for only when there's a specifically high demand due to its extremely high cost.

Another option is the trimanganese tetroxide process in which the surface of base steel is oxidized. Though a black finish is attainable from the treatment, it is less corrosion resistive, not for use in outdoor environment.

Various blackening methods by plating are analyzed from the perspectives of processing cost, corrosion resistance and appearance, and shown in Figure 1. The cost of quality control is high in the chemical treating using Cr (III) due to the difficulty of control of solution in addition to the inferior appearance.

In the meantime, the dip-coating is sometimes used for blackening. It is such a treatment in which the work piece is immersed in the paint, then excess paint is removed by a centrifuge or the similar, and finally baked or dried.

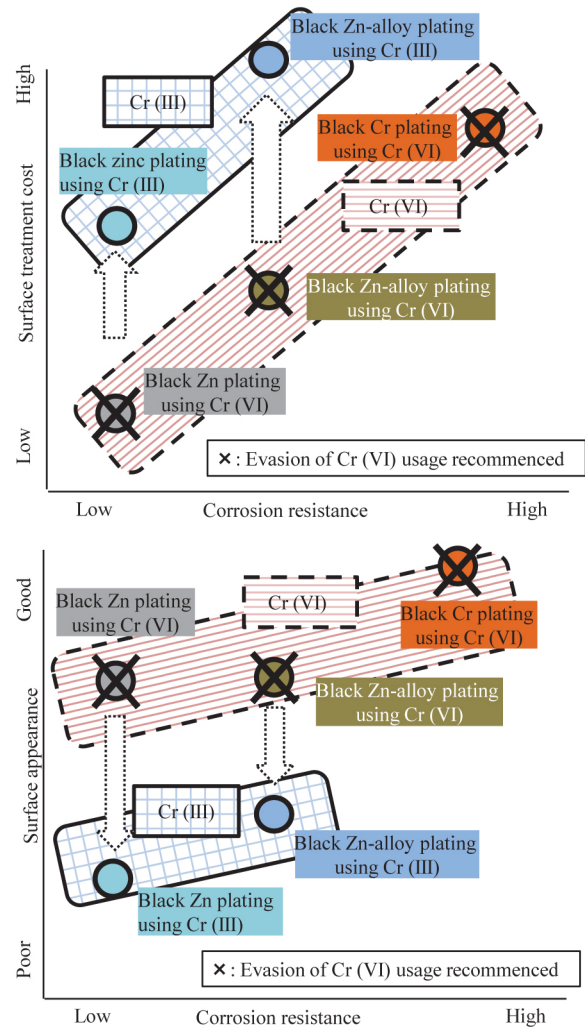


Figure 1. Trend of blackening methods for bolt under containment of Cr (VI)

Issues in Current Blackening Treatment

Issues in Chemical Conversion Film Using Cr (III)

Cross-sectional views of black chemical conversion film using Cr (VI) and the black chemical conversion film using Cr (III) are shown in Figure 2.

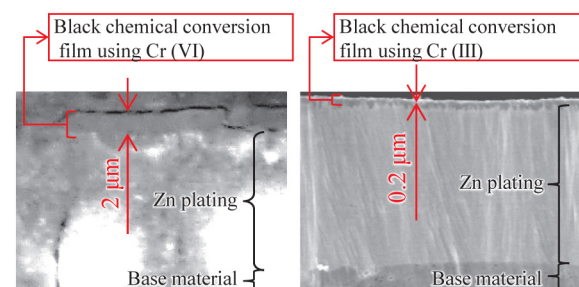


Figure 2. Chemical conversion film using Cr (VI) and Cr (III)

The base shows the bolt material, and the zinc plating is extracted above it. Seen further up on the zinc plating is a thin layer, which is the chemical conversion film. While the film created by the chemical treatment using Cr (VI) is approximately 2 μm , it is as thin as 0.2 μm in the case of treatment using Cr (III). Accordingly, as the material has to be colored by a thin layer, it is difficult to attain an adequate black color.

The reason why the film using Cr (III) is thin as explained hereafter. The image pictures of chemical reactions that create film using Cr (VI) and Cr (III) are shown in Figure 3.

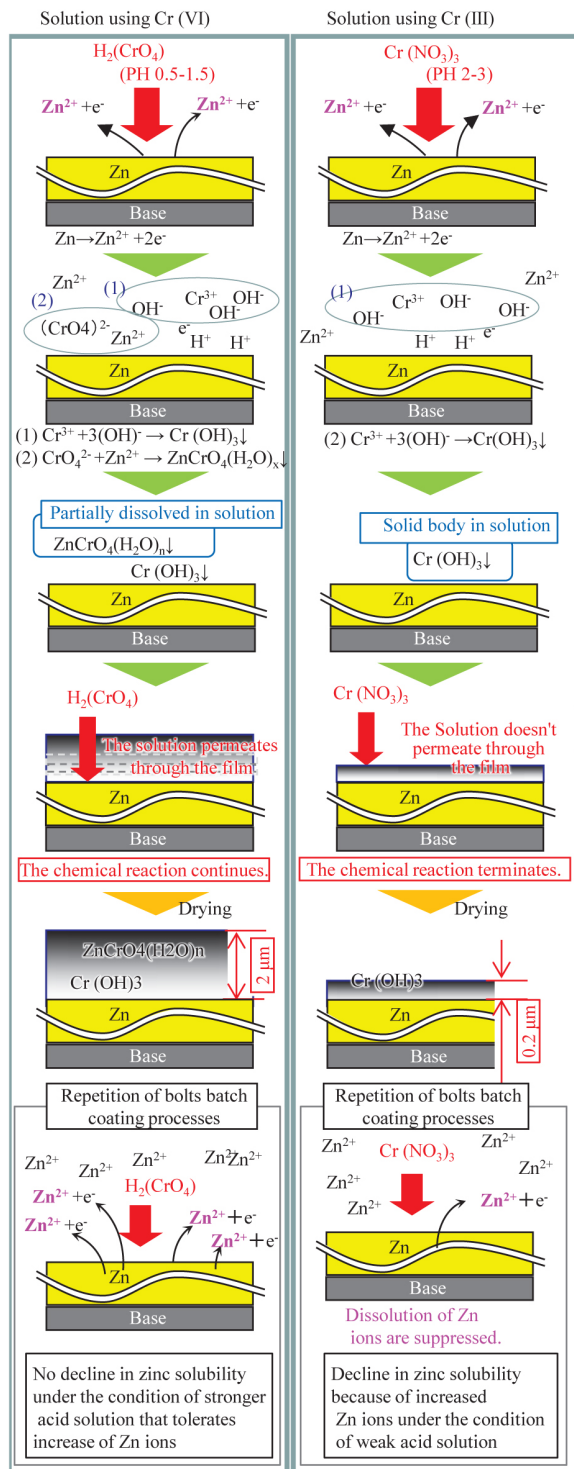


Figure 3. The models of reaction of chemical conversion film using Cr (VI) or Cr (III)

The formation of chemical conversion film starts with the layer-forming reactions triggered by dissolving of zinc. As a work-piece plated with zinc is immersed in the chemical solution containing Cr (VI), $\text{ZnCrO}_4(\text{H}_2\text{O})_n$ is produced along with $\text{Cr}(\text{OH})_3$ which serves as the matrix of coating. While $\text{Cr}(\text{OH})_3$ is a solid component, $\text{ZnCrO}_4(\text{H}_2\text{O})_n$ is soluble and in a semi-dissolved state when in the chemical solution. Accordingly, the chemical solution can contact on the zinc surface via $\text{ZnCrO}_4(\text{H}_2\text{O})_n$, allowing continuation of the reactions [10]. In the case of reactions in the chemical solution containing Cr (III), although $\text{Cr}(\text{OH})_3$ is produced, $\text{ZnCrO}_4(\text{H}_2\text{O})_n$ is not. Consequently, as the chemical solution cannot contact on the zinc-plated surface as soon as the surface is covered with $\text{Cr}(\text{OH})_3$, the dissolving of zinc finishes, causing the layer-forming reactions to stop. That is why an adequately thick film is unobtainable from the chemical treatment using Cr (III) [6].

Another issue is that in both ways of chemical treatment, as zinc ions are released in the solution each time the work-piece is treated, the zinc ion concentration increases gradually. The solution using Cr (VI) is very acid with a PH of approximately 0.7-1.5, allowing steady and continuous dissolving of zinc. In the solution using Cr (III), however, as it is moderately acid with a PH of 2-3, as the zinc ion concentration in the solution increases, the dissolving of zinc slows, reducing the layer-forming capability.

Consequently, the thickness of film decreases gradually, causing the blackening effect to lower. Accordingly, the chemical solution is frequently changed in the current chemical treatment using Cr (III) to prevent lowering of layer-forming capability. To satisfy the appearance requirement as a bolt for motorcycles, the solution is changed as soon as the zinc ion concentration becomes as high as 5 g/L. The frequent change of solution lowers production efficiency, causing an increase of cost to maintain quality.

Due to the thin film, the surface is vulnerable to damages when tightened with a tool. Accordingly, when used where the appearance demand is high, it is necessary to touch up with paint after tightening.

Issues in Black Dip-Coating

As mentioned in the preceding paragraph, another way to blacken a work-piece is the dip-coating using black paint. In this method, however, a lack of paint occurs where the bolts are in contact with each other when dipping in paint or removing the paint by a centrifuge, sometimes causing a fault referred to as "touch mark" shown in Figure 4.

To prevent such a fault, the dip-coating is applied two times in many cases. As a result, a thick film is formed on the root of thread, making a proper fit into the internal thread difficult in some cases. Accordingly, when the dip-coating is applied to bolts, the excessive paint on the external thread is removed after finish, the shape of internal thread is altered, or the shape of blank material is modified in some cases.