

Development of Surface Treatment Composed of Chemical Conversion Treatment and Paint Coating for Black Bolts Used in Motorcycles

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ABSTRACT

This research relates to the development of black surface treatment bolts used for motorcycles. Conventionally, the surface treatments applied for black colored bolts have been, in many cases, the methods using hexavalent chromium. However, hexavalent chromium is designated as a hazardous substance, and its use is restricted. For this reason, the developments of technologies to replace the surface treatment using hexavalent chromium are under way. In the case of using such substitute technologies, the technology for realizing black-colored appearance did not fulfill the requirements, because of the obstacles to realize required appearance and fastening performances. As a result, those bolts were used only for limited applications. In order to cope with this situation, we developed black surface treatment for bolts which can be widely used for motorcycle applications. For the coating composition, a black trivalent chromium conversion coating film and a dip coating layer were formed on a zinc plating coating. The conditions that satisfy the requirements for individual films were also designed.

Moreover, the manufacturing conditions were examined and set as well. As a result, we established a surface treatment method that can satisfy the performance requirements as a black bolt for wider application to motorcycles.

1. Introduction

Bolts are frequently used to fasten mechanical parts of motor vehicles due mainly to the advantages such as the work efficiency, serviceability, and fastening performance. Also, in motorcycles, bolts are often used as parts of exterior parts. In such a case, bolts require adequate corrosion resistance, appearance quality, etc. in addition to the fastening performances. A surface treatment, therefore, is often applied to the bolts for motorcycles. To make the appearance matching with the parts in the proximity, the surface treatment that provides a metallic or black color is applied as an option to achieve an attractive styling design.

Conventionally, in order to impart corrosion resistance and appearance design to the bolt, it is common to combine electroplating and chemical conversion treatment using hexavalent chromium⁽¹⁾. For example, a target appearance

was attainable by overlaying various layers of chemical coating using the hexavalent chromium on the zinc or zinc-plated surface. The hexavalent chromium⁽²⁾, however, is an environmentally hazardous substance and its use is restricted throughout the world^{(3),(4)}. Accordingly, a chemical treatment using chemical compounds containing the hexavalent chromium is becoming virtually unlikely.

The chemical treatment using the trivalent chromium is an alternative for the chemical treatment using the hexavalent chromium^{(5),(6)}. In general, the trivalent chromium chemical conversion film is thinner than the hexavalent chromium chemical conversion film, and challenging to adequately color the surface by the coating itself. Therefore, the colorless chemical coating using the trivalent chromium aimed at providing of the metallic color of the base material was enhanced the quality of appearance. Contrary in the black chemical conversion film using the

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trivalent chromium, the base metal color has to be concealed by the black coating. The black chemical conversion film created by the trivalent chromium, however, is not adequately thick to conceal the base metal color, resulting in an inadequacy of blackness. Hence depending on the use site of the bolt applied to the motorcycle, there is a case that a sufficient black appearance can not be obtained.

On the other hand, as another method of imparting black appearance to bolts, there is a technique called dip coating⁽⁷⁾. Generally in a dip coating, the paint film thickness varies, causing color unevenness. The film thickness is often increased to deal with the said issue. Therefore, since a thick coating film is also applied to the threaded part of the bolt, it is not easy to obtain high thread accuracy.

It is therefore necessary to work out a new method that blackens the bolt without using the hexavalent chromium while obtaining both the appearance quality and the thread precision.

This project started to establish a black surface treatment method by combining a black chemical conversion film and a dip coating.

This paper describes the principle and design procedure of the newly developed surface treatment method and appropriate production conditions to achieve the target coating.

2. Issues in Conventional Method and Aims of Development

2.1. General Methods for Imparting Black Appearance to Bolts

The galvanization (also referred to as zinc plating) is the most commonly-applied surface treatment for bolts. The galvanization is a composite anti-rust treatment method that precipitates a zinc metal film on a material and precipitates a chemical conversion film on its surface. Firstly to create a metallic zinc film, the work piece is immersed in the plating solution containing zinc ions. Then, a certain electric charge is applied to cause metallic zinc to deposit on the surface by the effect of electro-reduction. As the surface easily becomes oxidized and discolored in the atmosphere if only a metallic zinc coating is provided, a chemical conversion film has to be overlaid. In other words, the work piece having a metallic zinc coating is dipped in the solution containing chemical compounds to have a film produced on the surface by chemical reactions to prevent oxidation of metallic zinc surface. To further enhance corrosion resistance, such a zinc alloy plating in that the metallic zinc is substituted by a zinc-nickel alloy or a zinc-iron alloy has been developed. Also in the case of these zinc alloy platings, it is common to apply a chemical conversion treatment film because the surface is easily oxidized. The chemical conversion treatment film permits adjustment of the color by control of chemical compounds in the solution. When black is required, the blackening chemical conversion treatment is applied⁽⁸⁾. Conventionally, hexavalent

Table 1 Blackening surface treatments for bolts

Hazardous material	Surface treatment	Requirement					
		Fastening		Appearance quality			
		Friction control	Thread precision	Appearance	Scratching resistance	Corrosion resistance	Weather resistance
Contained	Black Zn plating using Cr (VI)	3	3	3	3	2	3
	Black Zn alloy plating using Cr (VI)	2	3	3	3	3	3
	Black Cr plating using Cr (VI)	3	2	4	4	4	3
Not contained	Black Zn plating using Cr (III)	3	3	1	1	2	3
	Black Zn alloy plating using Cr (III)	2	3	1	1	3	3
	Dip coating	2	1	3	3	3	2

4 = excellent, 3 = good, 2 = average, 1 = poor

Cr (III): Trivalent chromium, Cr (VI): Hexavalent chromium

chromium was contained in this chemical conversion treatment film. However, at the present time, substitution with a trivalent chromium chemical conversion treatment film not containing hexavalent chromium is proceeding.

While the black chromium plating used to be applied in some cases for blackening, it is currently avoided because the treatment solution contains hexavalent chromium⁽⁹⁾.

Since the said method is a combination of electric plating and chemical conversion treatment, the control of film thickness is relatively easy. Accordingly, it is often used in bolts which are required to have high thread precision and more reliable fastening.

In the meantime, the blackening method by dip coating is also used in some cases. The dip coating is such a method in that the work piece is dipped in the paint, the extra paint is shaken off with a centrifuge or the similar, and the paint is finally baked or dried. As the paint film thickness is not easy to control, it is hard to ensure thread precision. When applying dip coating, it is therefore necessary to take special considerations in the thread shape design or perform additional machining to the bolt after the painting.

Table 1 shows various methods for blackening of bolts. As can be seen from this table, it can be seen that the surface treatment technology which imparts black without using hexavalent chromium can not satisfy the requirements of bolts used for motorcycles.

2.2. Issues in Current Blackening Method

2.2.1. Issues in chemical blackening using trivalent chromium

Figure 1 shows the cross section photographs of the films produced by typical blackening methods, i.e., the hexavalent chromium treatment and the trivalent chromium treatment. For easy comparison of chemically produced

films, the two pictures are of the same magnification rate. A zinc plating layer exists on the base metal surface of bolt, and a thin chemically-produced film is seen on it. While the thickness of film by the hexavalent chromium treatment is approximately 2 μm , it is as thin as 0.2 μm in the one by the trivalent chromium treatment. As the color has to be applied by a thinner film in the case of the trivalent chromium treatment than in the case of the hexavalent chromium treatment, it is challenging to realize uniform blackness.

The reason why the trivalent chromium chemical conversion treatment film can not be formed thick is explained hereafter from the principles of film formation while comparing to the hexavalent chromium chemical conversion treatment film. Figure 2 shows image pictures of chemical film formation in the hexavalent chromium chemical conversion treatment and the trivalent chromium chemical conversion treatment.

Regardless of hexavalent chromium contained or not, the formation of chemical conversion treatment film is triggered by the dissolving of zinc into the solution. As the zinc-plated work piece is immersed in the chemical treatment solution, a dissolving of zinc into the solution starts. In the case of hexavalent chromium, $\text{Cr}(\text{OH})_3$ and $\text{ZnCrO}_4(\text{H}_2\text{O})_x$, which serve as the matrix of coating, are produced as the chemical reactions take place⁽¹⁰⁾. While the $\text{Cr}(\text{OH})_3$ is a solid component, the $\text{ZnCrO}_4(\text{H}_2\text{O})_x$ is a soluble component, maintaining a semi-dissolved conditions in the solution. Accordingly, the chemical solution can come into contact on the zinc surface via the $\text{ZnCrO}_4(\text{H}_2\text{O})_x$, allowing continuation of the chemical reactions. As a result, the film can grow as thick as approximately 2 μm . In the case of trivalent chromium treatment, however, while the $\text{Cr}(\text{OH})_3$ is formed, the $\text{ZnCrO}_4(\text{H}_2\text{O})_n$ is not⁽¹¹⁾. As mentioned earlier, as the $\text{Cr}(\text{OH})_3$ is a solid component, it does not allow permeation of the chemical solution. Accordingly, once the zinc plating surface is covered with the $\text{Cr}(\text{OH})_3$, the chemical treatment solution cannot come in contact on the zinc plated surface, causing discontinuation of dissolving of zinc into the solution. Thus, the chemical reactions

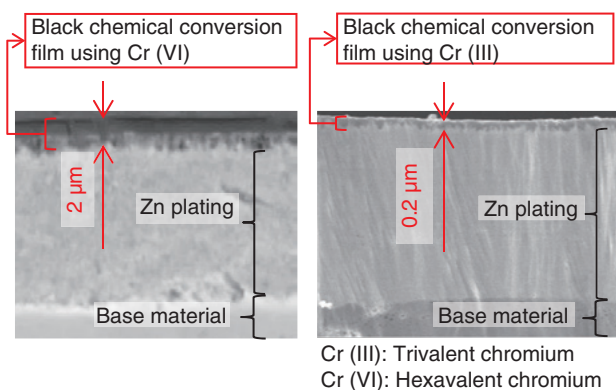


Fig. 1 Chemical conversion film using Cr (VI) and Cr (III)

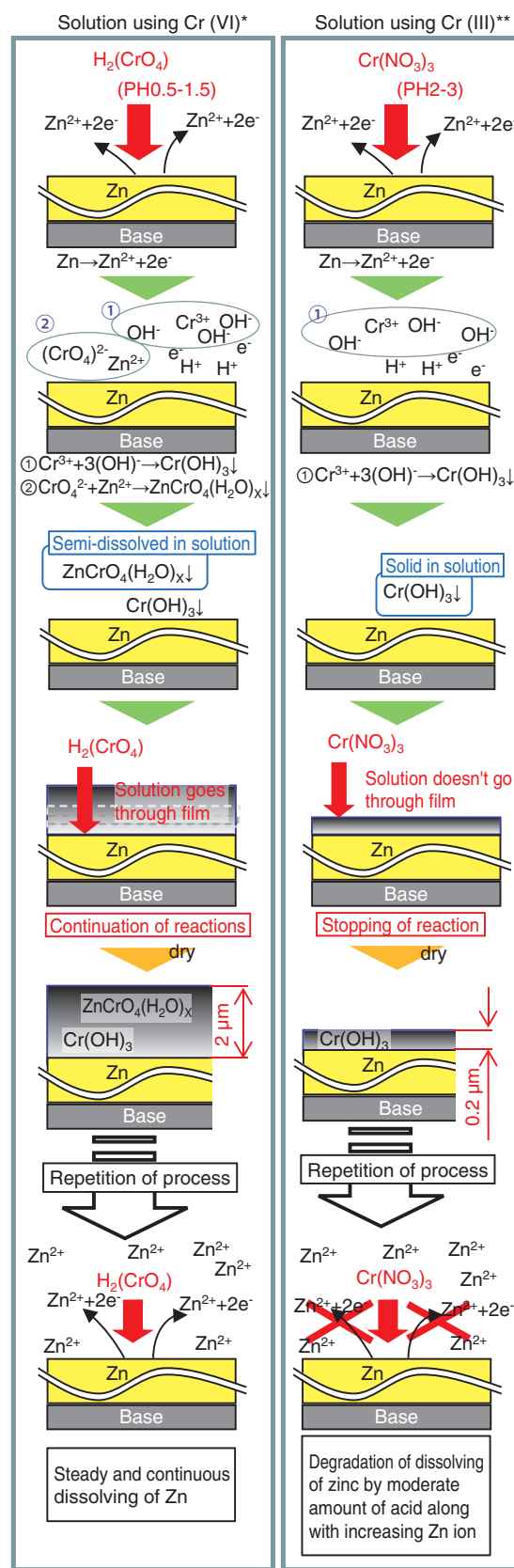


Fig. 2 Models of reaction of chemical conversion film using Cr (VI) or Cr (III)

finish when the chemical conversion film is as thin as approximately $0.2\ \mu\text{m}$.

Also, the chemical treatment solution containing the hexavalent chromium is a strong acid of $\text{PH}0.5 - 1.5$, which allows steady dissolving of zinc into the solution. Meanwhile in the trivalent chromium treatment, the solution is a weak acid of $\text{PH}2 - 3$. As the zinc ion concentration increases in the solution, less zinc is dissolved into the solution, causing unstable chemical reactions for film formation, which is another cause of inconsistent blackness.

For the reasons stated above, in the trivalent chromium chemical conversion treatment solution used for present bolts for motorcycles, the treatment solution is frequently exchanged in order to prevent the reaction from becoming unstable. In order to satisfy the minimum appearance required for motorcycle application, exchange is carried out every time the concentration of Zn ions in the treatment liquid reaches $5\ \text{g/L}$ in the case of the treatment liquid condition with the highest replacement frequency. This hinders productivity and increases management cost.

Moreover, due to the thin film, the insufficient corrosion resistance and the vulnerability to damages from use of tool are also issues. A finish treatment is often applied to the black film produced by the trivalent chromium treatment to enhance corrosion resistance, which is another cause of additional cost.

2.2.2. Issues in black dip coating

The dip coating using a black paint is another option for blackening. Figure 3 shows an example of the procedures.

The dip coating processes can be divided to three sub

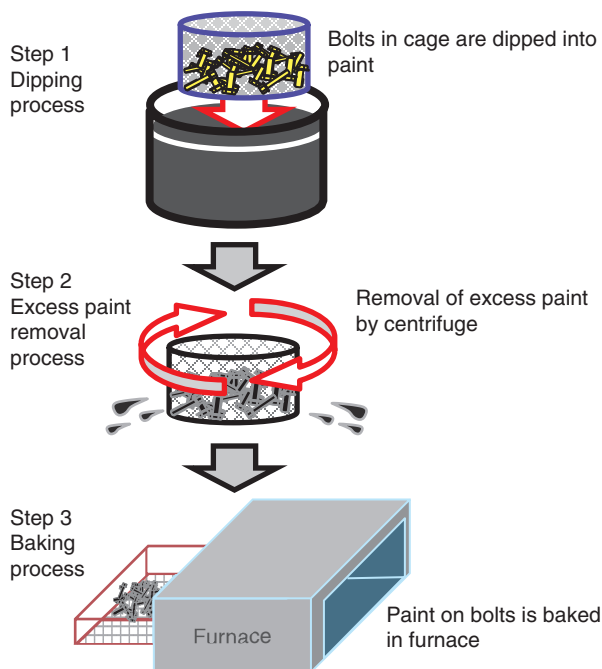


Fig. 3 Model of dip coating process

processes; the dipping process, the excess paint removal process, and the baking process.

In the dip coating, the necessary film thickness for coloring is attainable by the control of paint viscosity and the removing of excess paint using an appropriate centrifugal force. In actual practices, however, it is not easy to control conditions to attain uniform paint film thickness from the dip coating. The film becomes thin in some area of the bolt, causing exposure of base metal color. In other words, the bolt cannot be blackened uniformly in some cases. If the bolts are in contact with each other when dipping or removing, the paint will be inadequate or excessive in such a contacting area, causing a defect called the touch mark to occur in some cases. That means that some areas of the bolt are adequately colored while the base metal color is exposed in other areas. When an adequately colored area and an inadequately colored area come side by side, the color unevenness becomes apparent.

Therefore, in general, it is necessary to paint thick the entire bolt so that color unevenness does not occur, and in some cases it is necessary to paint more than twice as shown in Fig. 4. As a result, unnecessary coating films are formed on thread portions which are not subject to appearance requirements, and the threaded portions may not satisfy the standard tolerance in some cases⁽¹²⁾. To deal with the said issue, it is necessary to remove excessive paint on the thread after painting, to modify shape of the fitting female thread,

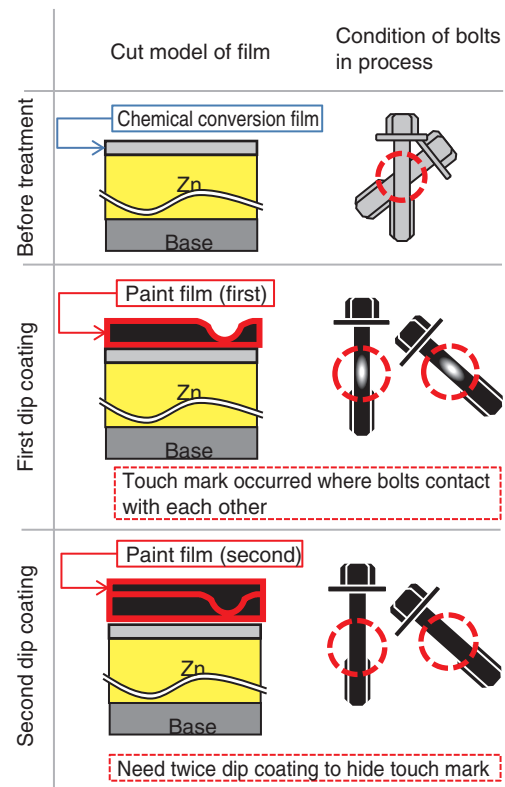


Fig. 4 Cross-sectional view of touch mark in conventional dip coating

or to modify the shape of blank material itself.

It is often the case that a paint not exclusively developed for motorcycle bolts is used for the dip coating. Accordingly, the durability requirements in sun light and/or corrosive environment are not satisfied in some cases. Moreover, the friction coefficient is often different from that of the conventional bolt surface treatment, sometimes requiring special processing conditions⁽¹³⁾.

2.3. Aims of Development

After sorting out the above-mentioned issues in the blackening operations taking into account the quality requirements of motorcycle bolts, the following requirements were set for the coloring of the bolts to be developed.

- An adequately black color shall be provided steadily without apparent unevenness of color
- Tool marks shall not be apparent after tightening of bolt
- The thread shall fit smoothly into the female thread
- An appropriate axial force shall be attainable from a bolt tightening torque
- The coloring shall be weather resistant and shall not be discolored by the sunlight
- The corrosion resistance shall be adequate
- The coloring shall not be deteriorated by the oil, fuel, and other chemicals used in a motorcycle

These requirements shall be satisfied without using the hexavalent chromium while coloring by such a method that allows mass production using the existing production equipment for low-cost manufacturing.

3. Structure and Method of Surface Treatment

3.1. Structure of Films Produced by Surface Treatment

Assuming that the above-mentioned goals were unachievable solely by the chemical blackening on the zinc plating or the dip coating, a combination of both methods were considered.

In order to obtain a sufficient black appearance while maintaining a thin film, firstly a black chemical conversion treatment film is applied on the zinc plating as an undercoat of painting. Further overlaying a thin black paint film, a three-layer structure should be employed. Conventionally, the purpose of a black chemical conversion treatment film was prevention of oxidation of the zinc plated surface. In this new method, the purposes are to provide coloring for suppressing color unevenness of paint applied as an undercoat of painting, and to ensure adhesion of the paint film. In the meantime, the purposes of painting are to be able to impart and maintain a sufficient black appearance while ensuring the fastening function of the bolt. With the said coating structure employed, since the black chemical conversion treatment film as the undercoat and the overlaid paint film are superimposed, it is possible to impart a sufficiently uniform black tint even if the paint film is thin, allowing to satisfy the appearance requirements. The bolt

colored by the newly-developed method can be treated in the same manner as for the conventional bolt when tightening.

3.2. Black Chemical Conversion Treatment Film as an Undercoat of Painting

3.2.1. Principles of coating design

As mentioned earlier, the black chemical conversion treatment film using the trivalent chromium is thinner than that of the hexavalent chromium and challenging to attain a sufficient black appearance. Accordingly, the chemical treatment is usually conducted two times to satisfy the quality of appearance while ensuring corrosion resistance. In the first chemical conversion treatment, a coarse surface film is formed, which intensifies the blackness taking advantages of the diffused reflection of light on the coated surface. However, on the coarse surface coating, water tends to accumulate on the surface, making it vulnerable to corrosion. To deal with this issue, the surface concealing treatment should be applied as the second chemical conversion treatment⁽¹⁴⁾, which smooths out the chemically coated surface to conceal the spots that trigger corrosion. As shown by Fig. 5, while the surface is coarse just after the first chemical conversion treatment, the surface is smooth after the concealing treatment. That said, as mentioned earlier, the purposes of chemical coating in this project are to color as an undercoat and to ensure adhesion of paint film. It was therefore considered that the second treatment for corrosion resistance could be eliminated.

It was also considered that as the coarse surface after the first chemical conversion treatment would have an anchoring effect to enhance adhesion of paint to be overlaid, the corrosion resistance would be better than painting after the second chemical conversion treatment. Figure 6 shows principles of the anchoring effect.

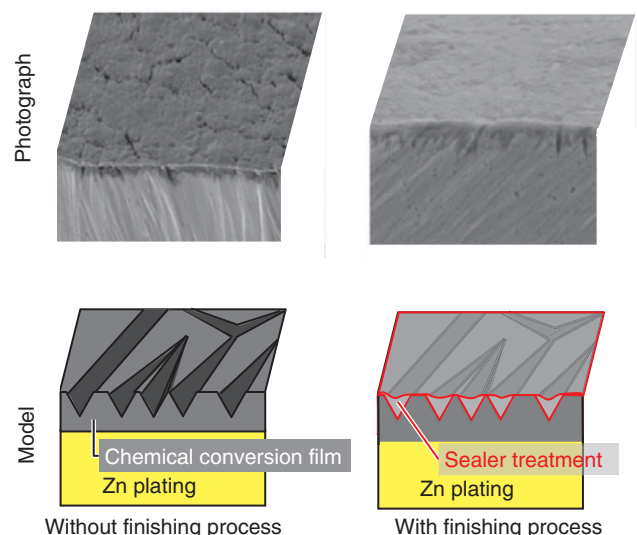


Fig. 5 Surface of chemical conversion films

To verify the model shown in Fig. 6, experiments were conducted using test pieces to measure the adhesion of paint film and the corrosion resistance. Surface And Interface Cutting Analysis System (SAICAS)⁽¹⁵⁾ was used for paint adhesion measurement. Figure 7 shows measurement

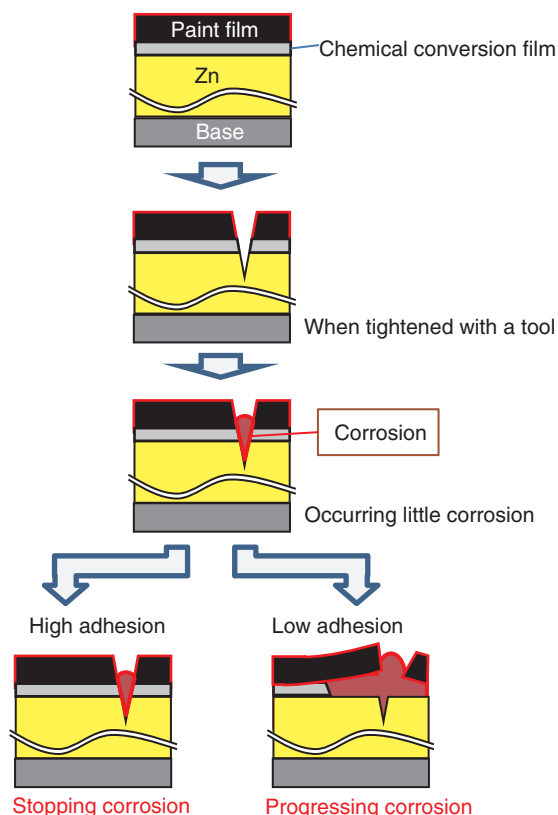
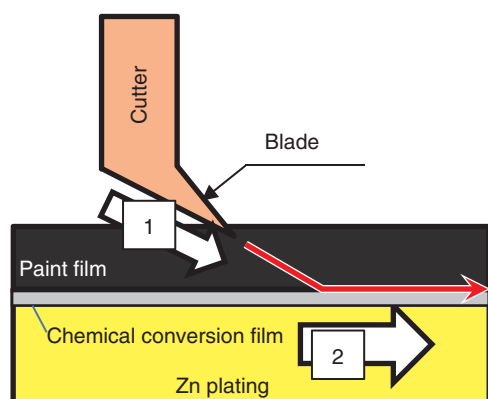


Fig. 6 Models of paint adhesion and corrosion resistance



1. The cutter advances along the direction of the blade.
2. Just after the blade touches the Zn plating layer, the cutter changes the direction to advance horizontally parallel to the paint surface.
3. The adhesion strength is measured by detecting the stress applied on the cutter.

Fig. 7 Model of SAICAS and test method

principles of SAICAS.

In the measurement using this equipment, the treated surface is firstly cut downward at an angle with a small blade, and as soon as the blade reaches the chemical conversion film, the blade is moved along the surface of the film. After that, peeling of the paint film is started by peeling load. When the movement of the blade is further continued, the peeling load increases and decreases each time the shearing of the paint film is repeated. Figure 8 shows the image picture of the load fluctuation. In this project, the value obtained by dividing the minimum value of the load, when the blade is moving along the surface of the zinc plating layer, by the blade width was defined as the adhesion strength. The corrosion resistance was measured by the length of time until white rusts occur in the Salt water Spray Tests (SST) chamber.

For the preparation of test pieces, firstly the zinc plating was applied to the mild steel sheet. Then, test pieces only with the chemical conversion treatment and those with further concealing treatment were prepared. After that, the surface of the test piece was painted with the polysiloxane paint (to be mentioned later). The difference of adhesion strength was measured using the test pieces. The corrosion resistance was also measured using the test bolts having the similar surface treatment. Figure 9 shows the test results. It has been proven from the tests that the paint adhesion is stronger on those having only the chemical conversion treatment than the ones having the concealing treatment, and so is the corrosion resistance.

Based on the findings, it was decided to eliminate the concealing treatment. Considerations, however, are necessary for the environment in the processes up to the painting after the chemical conversion treatment because the corrosion resistance is low from only the single chemical conversion treatment using the trivalent chromium, which requires painting before a start of corrosion. For validation, the test pieces were soaked under the conditions shown in Table 2 after applying the chemical treatment, and after

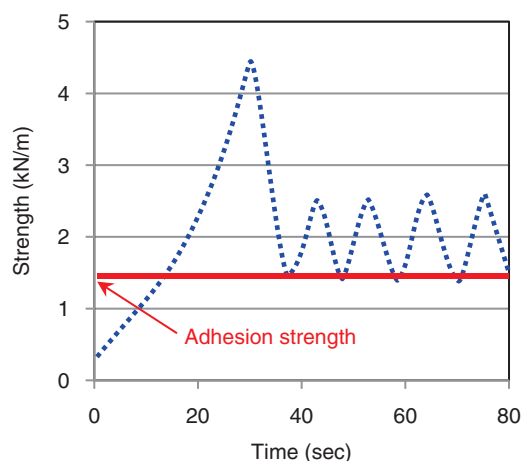


Fig. 8 Model data of SAICAS

Table 2 Storage condition until coating process after conversion process

	Finishing	Storage condition	
		Temperature	Humidity
Storage condition A	Dry	21°C	under 40%
Storage condition B	Dry	40°C	95%
Storage condition C	Not dry	40°C	95%

painting, the corrosion resistance and the paint adhesion were measured (Figs.10 and 11). After these tests, deterioration was found in those not dried after the under coating, i.e., the chemical conversion treatment, and those exposed to high temperatures and high humidity. It has thus been clarified that the work piece should be dried after the chemical treatment and should not be left in a high temperature, high humidity environment.

3.2.2. Blackness of black chemical conversion treatment film as undercoat

As mentioned earlier, in the method to be employed at this time, the final blackness of the surface is a mixture of the blackness of the undercoating black chemical conversion treatment film using the trivalent chromium and the blackness of the overlaid paint film. Therefore, in order to develop a paint for this application, it is necessary first to grasp the blackness that can be imparted by the black trivalent chromium chemical conversion treatment film, in particular, the level of the lowest blackness that can occur in the manufacturing process.

Meanwhile, as the thickness of black chemical conversion treatment film is affected by the zinc ion concentration in the chemical treatment solution, the resultant blackness depends on the zinc ion. It was therefore decided to clarify the zinc ion concentration in the most deteriorated chemical treatment solution, and quantifiably

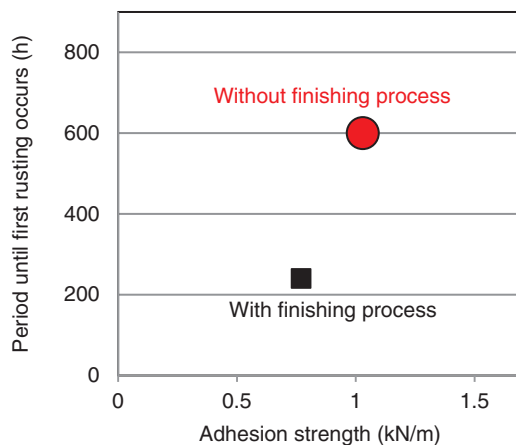


Fig. 9 Relationship between adhesion and corrosion resistance with and without finishing process after chemical treatment

evaluate the blackness of the black chemical conversion treatment film surface produced by the solution.

Usually, if the solution is not replenished at the time of chemical treatment, the zinc ion concentration keeps rising until saturation. However in an actual chemical treatment operation, some solution sticks on the work pieces and taken out of the treatment tank each time the treatment is completed as Fig. 12 shows. Consequently, the treatment solution is reduced slightly. By the replenishment of the same amount of solution as the consumed volume, a part of the treatment solution, in which the zinc ions are increasing toward saturation, is removed and replaced.

As shown by Fig. 12, when the chemical reactions, removal and replenishment of solution are repeated,

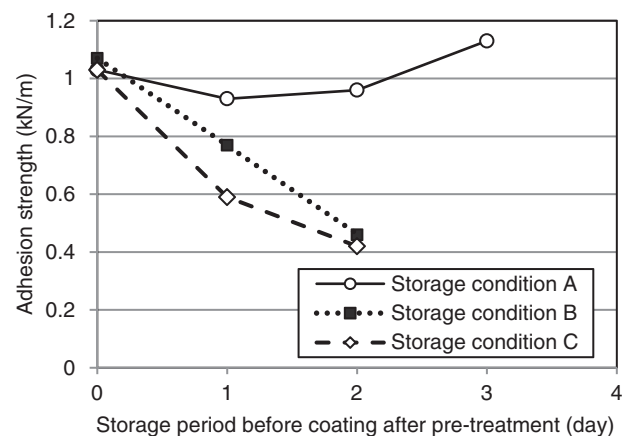


Fig. 10 Relationship between adhesion and storage period with various conditions

	Storage period			
	0 day	1 day	2 days	3 days
Storage condition A	 No rust	 No rust	 No rust	 No rust
Storage condition B	 No rust	 Whitening	 Whitening	—
Storage condition C	 No rust	 Whitening and peeling	 Whitening and peeling	—

Fig. 11 Relationship between corrosion toughness and storage period with various conditions

the amount of zinc ions at the n^{th} replenishment can be represented by Eq. (1).

$$A_n = A_{(n-1)} + x - y((A_{(n-1)} + x)/B) \quad (1)$$

- A_n : Amount of zinc ions [g] in the chemical treatment solution after treating n times.
 B : Amount of chemical treatment solution [L]
 x : Amount of zinc ions released in the solution during one treatment operation [g]
 y : Amount of solution taken out of the tank per one treatment operation (= replenishment volume) [L]

Equation (1) means that as the n increases, the zinc ion concentration gradually nears a certain level. When the n in Eq. (1) is increased infinitely large to calculate the amount of zinc ions that corresponds to the said level, the ultimate equation can be represented by Eq. (2).

$$\lim_{n \rightarrow \infty} A_n = x((B - y)/y) \quad (2)$$

Accordingly, when n is adequately large, the ion

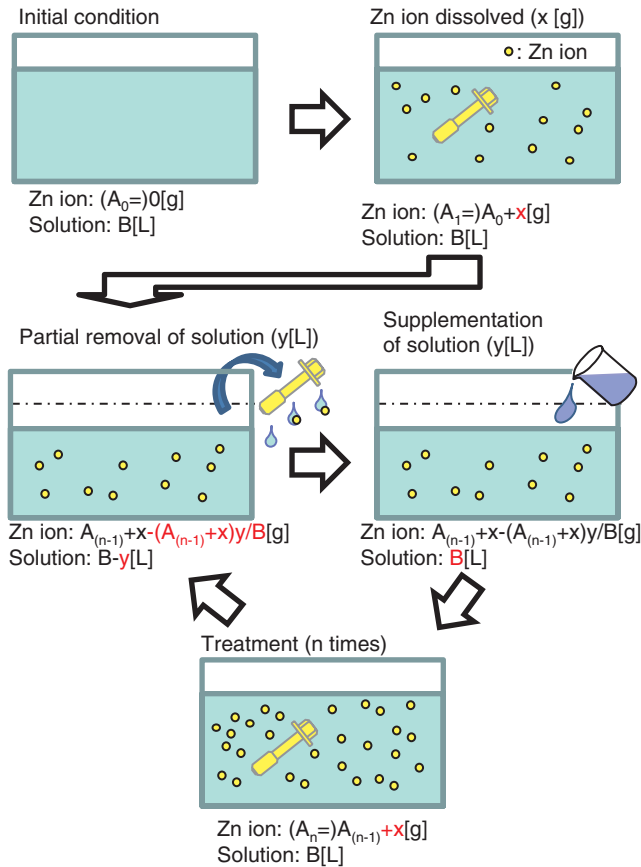


Fig. 12 Increase of zinc ion in solution and loss of solution in chemical treatment using trivalent Cr

concentration C_{Zn-ion} [g/L] can be represented by Eq. (3).

$$C_{Zn-ion} = x((B - y)/y)/B \quad (3)$$

The values x and y in Eq. (3) depend on the conditions of the treatment solution and the surface area of the work pieces. The zinc ion concentration becomes the highest when x is maximum and y is minimum. Upon the simulation under all the presumably conditions in mass production process, the highest zinc ion concentration has been determined as 14.7 g/L.

Assuming from these findings that the zinc ion concentration will not exceed 20 g/L even when estimated high in ordinary mass production operations, this level of concentration is considered as a precondition when determining the lower limit of the thickness of produced film. By setting this condition, it becomes possible to continue to use the chemical conversion treatment liquid which has been frequently replaced in the past almost without replacement, and it is possible to enhance the productivity.

For a quantitative evaluation of blackness of the black chemical conversion treatment film, it was decided to use L^* , which is the brightness index, of Hunter Color Scale. Note that the lower the L^* , the stronger the blackness.

The brightness of the black film produced by the chemical solution in which the zinc ion concentration reached the presumed upper limit of 20 g/L was measured. The L^* was approximately 33. Presuming from that finding that this brightness is the blackness when the film thickness becomes the smallest when designing the black paint for dip coating.

3.3. Designing of Paint Presuming Use of Chemically-produced Black Film as Undercoat

3.3.1. Paint film thickness

It was firstly decided to set a target film thickness for the dip coating. To determine the maximum film thickness, the target film thickness of the surface treatment was set from the thread precision standards (JIS B0209) of M6 bolt, which is the smallest bolt frequently used in motorcycles. Taking into account the conditions under which the clearance between the male thread and the female thread becomes the minimum, such a case is employed when the inside diameter of the female thread is at the lower limit and the outside diameter of the male thread is at the upper limit. At that time, the clearance becomes 13 μm . Under these conditions, the film thickness of the surface treatment on the male thread has to be 13 μm or less. As the total thickness of the zinc plating layer and the chemical conversion treatment film is 8 - 10 μm , the paint film thickness has to be 3 μm or less.

In view of the above, the target paint film thickness was set at 2 μm with a tolerance of ± 1 μm . As the film thickness in the thicker side is 2 - 3 μm in the time-proven chemical conversion treatment film using the hexavalent chromium,

the target film thickness set at this time is deemed appropriate.

3.3.2. Type of base paint material

Studies were continued for the type of base paint material. When selecting, from the standpoint of general applicability to motorcycles, it was decided to select from the conventional organic paint and the organically modified inorganic paint, and conducted evaluation.

Table 3 shows results of evaluation of various base paints from the standpoint of paint film quality requirements of dip coating of bolts.

Among the paint options, the polysiloxane paint, which features a low viscosity and allows easy control of thickness within the narrow range of $2 \pm 1 \mu\text{m}$, was selected as the base paint material. As the cross-link density of the paint film made of this material becomes high, a high blocking effect is attainable to protect the base metal from the oxygen in the atmosphere. The advantage of corrosion resistance is also considered as a benefit when selecting.

3.3.3. Amount of pigment in paint film

The selection was continued for the pigment to color the paint film black. As the bolts for retaining of exterior parts of a motorcycle are often exposed to sunshine, the black pigment mainly consisting of the carbon black has been selected as a pigment less prone to color fading. The amount of black pigment was determined as per the following steps.

The target of appearance quality was set at the same level as of the black chromium plating. Although the black chromium plating is no longer applicable as the hexavalent chromium is contained in the coating, it was the surface treatment that used to provide the highest appearance quality to bolts. Upon measurement of the blackness with the Hunter Color Scale, the L^* was approximately 28. Accordingly, the target blackness by L^* was set at 28 or lower.

To achieve the target figure, attempts were made to determine the amount of black pigment in the paint. Firstly in the black chemical conversion treatment process, the test pieces were prepared by producing a black chemical conversion treatment film using the chemical solution in which the zinc ion concentration was adjusted at 20 g/L. Then, preparing paints having various contents of black pigment, each paint was applied on five test pieces in such a manner that makes the paint film thickness $1 \mu\text{m}$, which is the lowest limit of specified film thickness.

Figure 13 shows the measured highest, lowest, and average L^* of the samples.

It is understood from the graph that the L^* will be under 28 if the black pigment is 2.3% or more in the paint. The level of appearance quality same or better than the black chromium plating is attainable if the chemical coating and the newly-developed paint film are combined.

However, while the pigment is dispersed in the paint matrix, it is not chemically combined with the components

Table 3 Assessment of base paint material for bolts

	General organic paint			Organically-modified inorganic paint	
	Acrylic paint	Epoxy paint	Urethane paint	Silicon paint	Polysiloxane paint
Thin film	1	1	1	1	3
Corrosion resistance	2	3	1	2	3
Pot life	3	3	1	3	3
Hardness	1	1	1	2	3
Coloring	3	3	3	3	2
Weather resistance	3	1	3	3	3

3 = good, 2 = fair, 1 = poor

of the matrix. There are areas where the material structure is non-continuous between the matrix and the pigment. Such an area permits easy permeation of water and/or component that accelerates corrosion. In other words, it can be considered that the corrosion resistance lowers when the non-continuous areas of matrix increases due to an increase of pigment. Accordingly, the confirmation tests were conducted to check if the earlier-specified pigment amount was appropriate from the viewpoint of corrosion resistance.

Using the treatment solution having a zinc ion concentration of 20 g/L, the test pieces were produced by providing the black chemical conversion treatment film. There, preparing paints having various rates of black pigment content, each paint was painted on five test pieces in such a manner that the film thickness became $1 \mu\text{m}$, which was the lowest limit of the specified film thickness. Figure 14 shows the average, maximum and minimum of the measured rate of corroded surface area after allowing the test pieces of various black pigment contents to corrode for 480 hours in SST chamber.

From these finding, it is considered that the corrosion resistance does not lower significantly if the rate of black pigment in the paint is 3.0% or lower. Combining the minimum amount of black pigment determined earlier, the content of black pigment is specified between 2.3% and 3.0%.

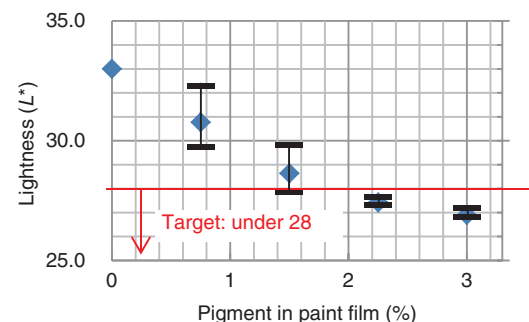


Fig. 13 Relationship between pigment content and L^* (Film thickness: $1 \mu\text{m}$)

3.3.4. Amount of friction modifier in the paint film

Then, taking into account the dispersibility in the paint, the friction modifier was selected to control friction coefficient. The relationship between the amount of friction modifier in the paint and the friction coefficient was measured, and the average value, the maximum value, and the minimum value in 5 samples are shown in Fig. 15.

From these findings and aiming at the same level of friction as of the conventional surface treatment, the rate of friction modifier in the paint has been set at 6 - 18%.

As the friction modifier is also dispersed in the paint matrix, the corrosion resistance may lower if the amount increases. Accordingly, it was decided to verify from the standpoint of corrosion resistance. Preparing paints having various contents of friction modifier, each paint was applied

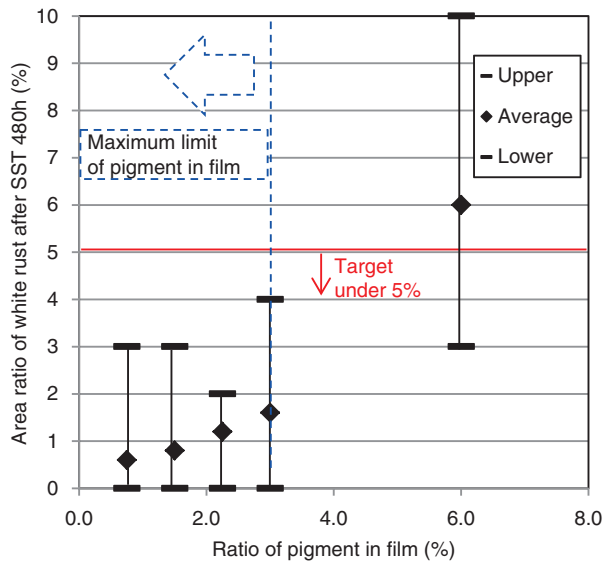


Fig. 14 Relationship between pigment content and corrosion toughness

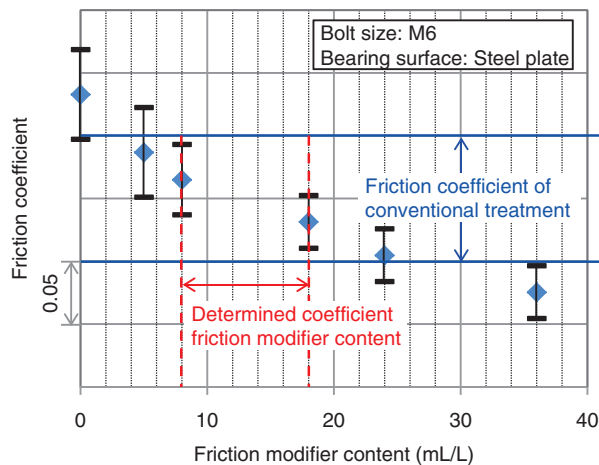


Fig. 15 Friction coefficients to friction modifier content

on five test pieces in such a manner that makes the paint film thickness 1 μm , which is the lowest limit of specified film thickness. SST of 480 hours was performed on these test pieces, and the area ratio of rust generated on the surface was measured. Figure 16 shows the average value, the maximum value and the minimum value.

It is clarified from the findings that the corrosion resistance does not lower significantly when the content is 22% or lower, and that the corrosion resistance is not affected if the rate of friction modifier is 6 - 18% as specified earlier.

3.4. Conditions of Dip Coating

3.4.1. Conditions of paint removal by flinging

The newly developed method is designed to maintain appearance and ensure quality when the paint film thickness is between 1 μm and 3 μm . Accordingly, proper conditions should be set in the processes where the bolts are immersed in the paint and the excess paint is removed by a centrifuge, which are the key processes of the dip coating to control film thickness.

To achieve the target paint film thickness steadily, we considered to select parameters highly affecting the film thickness. Accordingly, we decided to investigate the dip coating process into a simplified model.

In the dip coating, the work pieces are held in a cage, and after immersing in the paint, the excessive paint is flung off by the centrifuge to control film thickness. It is considered that the surface tension of paint on the work pieces maintains continuous flow of paint, allowing the paint to flow virtually freely on the work piece surfaces. Accordingly, the paint on the work pieces move toward the outer circumference of the cage due to the centrifugal force as shown by Fig. 17.

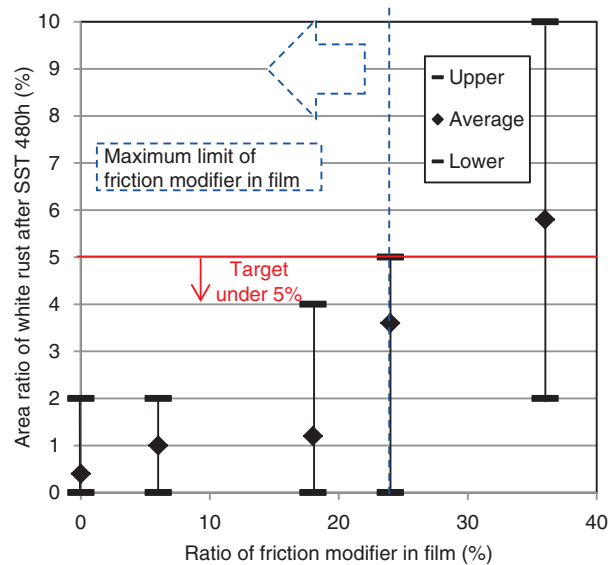


Fig. 16 Relationship between friction modifier content and corrosion toughness

In the outer-most part, the paint is flung off toward the outside of cage. Even when the paint on the bolt located near the outer circumference is flung off, the paint on the inner bolts moves toward the outside through the work piece surfaces due to the surface tension, replenishing paint. While the paint film thickness on various parts of the work piece decreases in the said manner, the paint stops flowing when the thickness reaches to a certain level due to the viscosity of paint, causing the paint to stay on the work pieces. Although the final paint thickness differs depending on the location of work piece in the cage, it is presumed that eventually the paint thickness of all work pieces in the cage is virtually determined by the balance of the centrifugal force F_c and the viscous force F_v in the outer most part of the cage due to the earlier mentioned effect of surface tension. Figure 18 shows image pictures of the principle.

On the basis of these presumptions, attempts were made to indicate the relationship among the parameters that affect film thickness using equations.

Firstly, the centrifugal force F_c can be represented by Eq. (4).

$$F_c = \rho \times S \times h \times r \times (2\pi N)^2 \quad (4)$$

ρ : Specific gravity of paint

S : Unit area where paint is adhering

h : Thickness of paint

r : Distance from the center of cage

N : Number of rotation of centrifuge

r is represented by the outer-most radius of cage r_{max} that affects film thickness.

Using Newton's law of fluid friction, the viscous force F_v can be represented by Eq. (5).

$$F_v = \frac{(\eta \times v \times S)}{h} \quad (5)$$

η : Viscosity of fluid

v : Flow speed of fluid

S : Unit area of area where paint is adhering

h : Thickness of paint

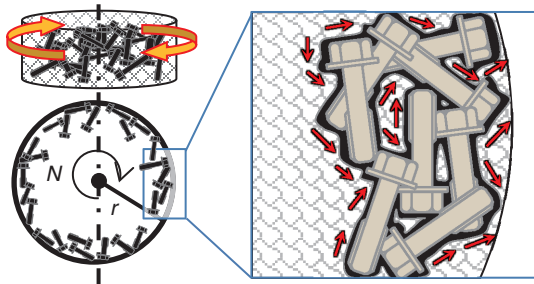


Fig. 17 Image of movement of paint in excess paint removal process by centrifugal force

v is the flow speed of paint. Since v is induced by the centrifugal force, it becomes maximum in the outer-most part where the centrifugal force becomes maximum. Also in the proximity of the outer-most part, the thickness gradually decreases, and the paint stops flowing when reaching a certain thickness. From Eq. (4) and Eq. (5), the centrifugal force acting on the paint on a unit area decreases along with a decrease of paint thickness while the viscous force increases. It can be considered that the flow of paint stops when the forces are balanced. If presumed $F_c = F_v$, the following Eq. (6) can be obtained to indicate paint thickness.

$$h = \sqrt{\frac{\eta \times v}{\rho \times r_{max} \times (2\pi N)^2}} \quad (6)$$

If the spinning of centrifuge is stopped under these conditions, the paint flows again on the work pieces, and the thickness of paint film becomes uniform. The paint is baked in the later process to form solid paint films. If the conditions are controlled in such a manner that the paint film thickness h becomes constant in the outer-most part when the flinging off of paint is discontinued, a constant paint film thickness is attainable on all the work pieces. Among the affecting parameters, controllable ones are the paint viscosity η and the spinning speed of centrifuge n . Although influences of other factors are obviously conceivable in actual practices, the validation was conducted in this project presuming the two parameters as the principal factors that determine film thickness.

In order to set processing conditions to attain the target film thickness on the basis of this theory, tests were conducted to analyze the relationship between the paint viscosity and the spinning speed of centrifuge. Figure 19 shows the test results.

The viscosity was measured with the widely-used simplified viscometer (Iwata Cup made by ANEST IWATA Corporation). The ambient temperature at the time of measurement was 35°C, and the paint temperature was 25°C.

It has been clarified from the test results that the film thickness is counter-proportional to the spinning speed nearly as per Eq. (6). If the working speed of 500 rpm of the centrifuge used in this project is deemed as a precondition,

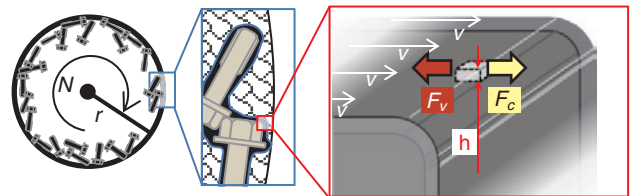


Fig. 18 Image of excess paint flinging off by centrifugal force

the paint viscosity should be 9.3 s to achieve the target film thickness of 2 μm .

Next, in an attempt to clarify how the seasonal factors such as the ambient temperature affect the film thickness, tests were conducted after changing the ambient temperature to 10°C under the earlier-mentioned test conditions. In that test, the film thickness was 1.5 μm when the paint viscosity was 9.3 s. A difference of about 0.5 μm to the film thickness of the target occurred. Accordingly, in order to get closer to the target, further processing conditions were considered.

The reason why the paint film thickness becomes thin when painting is performed at an ambient air temperature of 10°C is as follows. When the paint is flung off, the diluent also evaporates at the same time. At that time, if the ambient air temperature is low, less solvent evaporates and the viscosity increase of the paint slows down.

To back up the said principle, the difference of viscosity increase was measured when agitating 20 mL of the paint in a beaker of 65 mm diameter at various ambient temperatures. Figure 20 shows the test data.

It has been clarified from these findings that the viscosity increase is slow when the ambient temperature is low, and fast when high. It is therefore necessary to maintain increase of viscosity at a constant rate irrespective of the season. Another possible cause is that the amount of diluting solvent may differ even when the paint viscosity is rated the same when the ambient temperature is different. As this paint is an organic matter, the viscosity of paint itself changes along with a change of temperature. Hence the amount of diluting solvent to add to the paint differs to control the viscosity at a constant rate. Consequently, even when the paint film thickness just after flinging is the same, the thickness of paint film is not the same after the solvent evaporated and the paint hardened. To analyze difference from the amount of paint ingredient that produces actual paint film, the remaining component of the

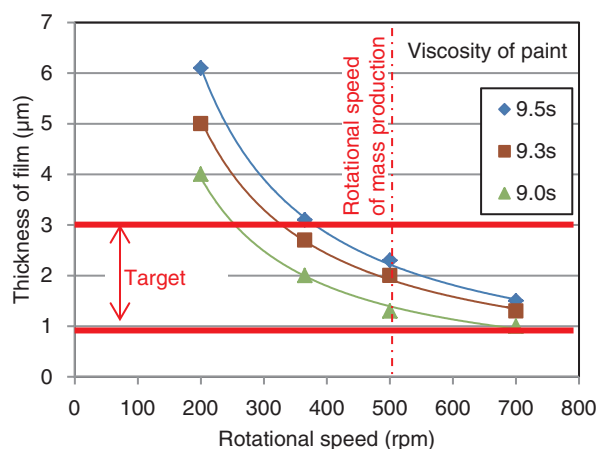


Fig. 19 Relationship between rotational speed of centrifuge and thickness of film for different paint viscosities

paint after heating was measured after adjusting in such a manner that the viscosity becomes the same under various ambient temperatures. The measurement was taken as per JIS K5601-1-2. The test data is shown in Fig. 21. A 3% difference was found in the amount of paint component remaining after heating between the viscosity adjustment at 15°C and at 25°C.

It has been clarified from the findings that the target film thickness is unattainable if only the spinning speed of the centrifuge and the viscosity of the paint are specified when the ambient temperature changes.

However, it is not easy to control conditions accordingly to various ambient temperatures, and it is not also easy to maintain a constant ambient temperature unlike in an ordinary spray painting. The measurement of remaining amount after heating takes a long time, and lowers production efficiency. It was therefore considered to maintain the temperature of the paint and the temperature of the object to paint at a constant level to exclude the influence of ambient temperature, aiming at a constant evaporation speed of the diluting solvent by equalizing the temperatures of the paint and the object to paint in order to eliminate influence of temperature. Also, when the paint temperature is constant, the amount of remaining component after heating can be controlled at a constant level only by adjusting the paint viscosity, allowing simplification of control of processing conditions. Figure

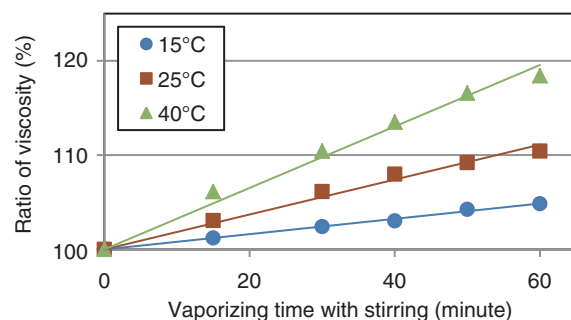


Fig. 20 Change viscosity of each temperature

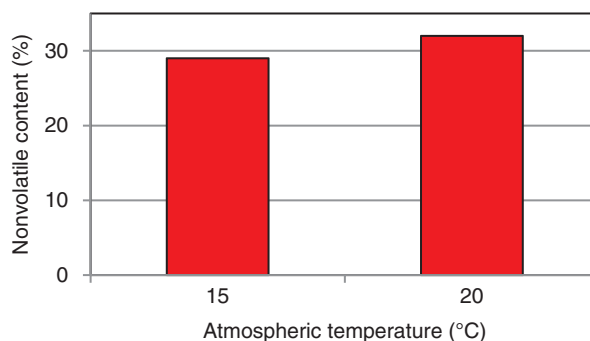


Fig. 21 Nonvolatile content of same viscosity paint under each room temperature

22 shows the film thickness when painted after increasing the temperatures of the paint and the object to paint up to 28°C from the ambient temperature of 10°C.

Even when the ambient temperature is 10°C, almost the same film thickness as at 35°C is attained by warming up the paint and the object to paint. As obvious from the findings, it has been confirmed that a constant film thickness is attainable by adjustment of temperatures of the paint and the object to paint to cope with the inconsistent film thickness caused by ambient temperature differences.

3.4.2. Conditions of baking for dip coating

Next, studies were conducted to determine the temperature conditions necessary for hardening of the polysiloxane paint selected as the paint matrix. As mentioned earlier, the cross-link density of this material is high, which means a high corrosion resistance is attainable. However, the bridging of this paint is by the dehydration condensation in which H_2O separates from the OH radical when the two siloxanes are heated, which means that the chemical reactions are advanced only by the heat. An appropriate amount of heat therefore must be applied at the time of the dehydration condensation to have the paint hardened.

For validation, baking was conducted under the heating conditions recommended for the selected polysiloxane paint. When the bolt was painted to a film thickness of 3 μm so that the chemical reactions take the longest time, and baked at 140°C for 20 min. as per the recommendation, an adequate corrosion resistance was confirmed.

However, it should be noted that in motorcycles, black bolts are often used in the hydraulic brake system. The bolt may be wetted with the brake fluid. As the brake fluid can damage paint film, the film on a black bolt should be resistant to the brake fluid. Accordingly, the brake fluid was heated up to 200°C, and the bolt was immersed in it. 200°C is the highest allowable working temperature of the brake

fluid. The paint film was found damaged in the test. It was therefore concluded that the paint film baked at 140°C for 20 min. was not applicable to the brake system. The cause was presumed in some areas where chemical reactions were incomplete. In the general painting, appearance faults tend to occur from the dust, etc. in the atmosphere sticking on the paint surface before hardening⁽¹⁶⁾. In such a case, the repair referred to as recoat, in which only the faulty part is ground and repainted, is conducted. In the recoating, the adhesion of paint between the first painting and the second painting sometimes causes an issue. When the bridging is incomplete in some part of the first paint film, it is easy to maintain good adhesion with the second paint film. Accordingly, such conditions that leave some incomplete bridging are often recommended. The temperature condition recommended in this case can be considered as based on the presumption of recoating. However, in order to satisfy the thread precision, dip coating in this development, the coating film is designed with one layer. It is therefore easily presumable that the upper limit of the film thickness target value will be exceeded if the coating film has two layers by recoating. That is, external appearance repair by recoating cannot be tolerated. From the above, it is considered that there is no need to leave the incomplete bridging portion for the purpose of securing the adhesion between the first layer and the second layer, and the baking conditions are changed.

Preparing bolts coated with the newly-developed paint, test pieces were produced by baking at various temperatures for 20 min. each. The test pieces were immersed in the brake fluid, and after that the appearance was checked. It has been confirmed from the tests that no deterioration of paint film such as melting occurs even when immersed in the heated brake fluid if the paint film is baked at 180°C for 20 min. as shown by Fig. 23. Accordingly the baking temperature was set at 180°C × 20 min. or more.

In the meantime, an excessively high baking temperature or long period of baking can cause oxidation of the plating, making the presumed corrosion resistance unattainable. It was therefore decided to seek conditions causing no deterioration of paint film even when baked for a long time at a high temperature. As the time period from loading up to

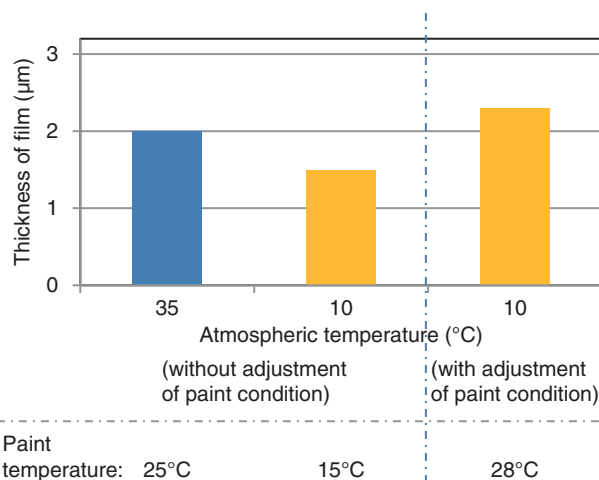


Fig. 22 Thickness of film under various seasons

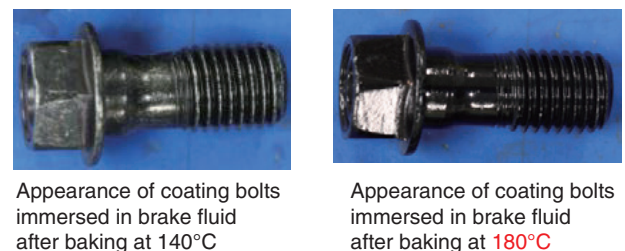


Fig. 23 Appearance of coating bolts immersed in brake fluid after baking at different temperatures

unloading is 60 min. in the baking oven used in this project, the baking period cannot be longer than that. As well as setting conditions within that range, confirmation tests were conducted up to 120 min., presuming an irregular stopping of the production line.

Increasing the temperature from 180°C by a 20°C increment, the paint film on the samples was baked at each temperature for various time periods, and corrosion resistance was measured. The test data are shown in Fig. 24.

It has been clarified from the tests that when baked at 240°C for 60 min., the corrosion resistance lowers significantly. Accordingly, the baking condition has been set at the temperature between 180°C and 220°C, and the time period between 20 min. and 60 min.

It should also be noted that in that temperature range, no immediate failure will occur even in the case of an unexpected line stopping.

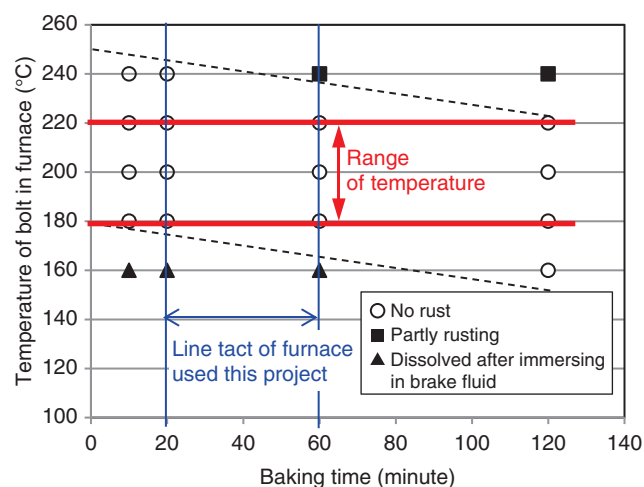


Fig. 24 Corrosion resistant confirmation result of baking temperature distinctiveness

4. Applications to Motorcycle Bolts and Benefits

4.1. Appearance

Figure 25 shows appearance of bolts having the newly-developed surface treatment actually applied.

With the black chemical layer provided as an undercoat, there is no unevenness of color. The L^* number of initial appearance is under 28, which means the appearance is as good or better than the black chromium plating.

The appearance after tightening was checked. The appearance of M6 bolt after being tightened to the specified torque is shown in Fig. 26.

4.2. Corrosion Resistance

Figure 27 shows the result of corrosion acceleration

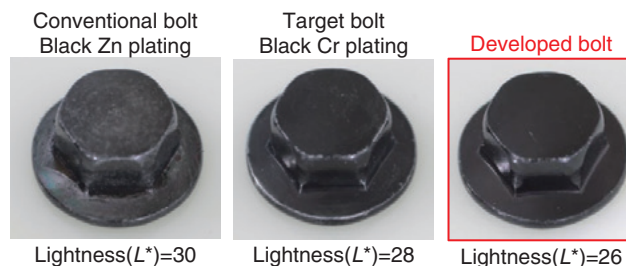


Fig. 25 Appearance of bolts

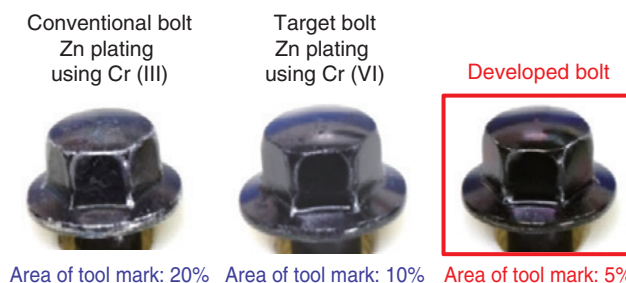


Fig. 26 Appearance of bolts after tightening

Count of test cycles		4	12
Bolt of handle holder	Appearance		
	Developed (Upper)	No rust	No rust
	Conventional (Lower)	WR: 3%	WR: 50%
Screw of master cylinder	Appearance		
	Developed (Right)	No rust	No rust
	Conventional (Left)	WR: 3%	WR: 100% RR: 5%
Oil bolt of caliper	Appearance		
	Developed (Upper)	No rust	WR: 1%
	Conventional (Lower)	WR: 1%	WR: 100%

WR: Area ratio of white rust
RR: Area ratio of red rust

Fig. 27 Appearance of bolt after corrosion test

test in the test mode assuming the actual use environment by attaching the bolts of the conventional product and the developed product to the test motorcycle. From these findings, an adequate corrosion resistance has been confirmed.

4.3. Weather Test

The color fade was measured after exposing in the outdoor environment basically as per JIS K5600-7-6 for 1.5 years. The color difference ΔE^*ab analyzed as per JIS Z8729 is shown in Fig. 28.

With the proper pigment selected for coloring, no apparent color fade is seen. Note that the discoloration of the conventional bolt was unmeasurable because of corrosion. It was concluded from these findings that substitution from current bolts was allowable because the discoloration including corrosion was less than that of current surface treatment.

4.4. Tightening Tests

Figure 29 shows comparison of friction coefficient on seating surfaces made of SP, A6061 and painted aluminum. In any seating surface material, the deviation of friction coefficient is smaller in the newly-developed surface treatment, falls within the range of conventional treatment.

While the large deviation in the conventional surface treatment can be considered attributable to the friction coefficient not intensively adjusted in the conventional surface treatment, we consider the deviation is small in the newly-developed surface treatment because the friction coefficient is intensively controlled by the friction modifier.

4.5. Film Thickness

Among the preset conditions, those under which the film thickness becomes the maximum are when

the spinning speed of the centrifuge is the lowest and the paint viscosity is the highest. In the meantime, the thickness becomes smallest when the spinning speed is the highest and the paint viscosity is the lowest. The thickness of paint film was measured from 10 pcs of the bolts treated under each of the above-mentioned two conditions. The average, maximum and minimum are shown in Fig. 30. Under either condition, the thickness falls within the target of 1 - 3 μm . It has thus been proven that the newly-developed surface treatment has no negatively effect on the fit of thread when tightening while maintaining an adequate blackness.

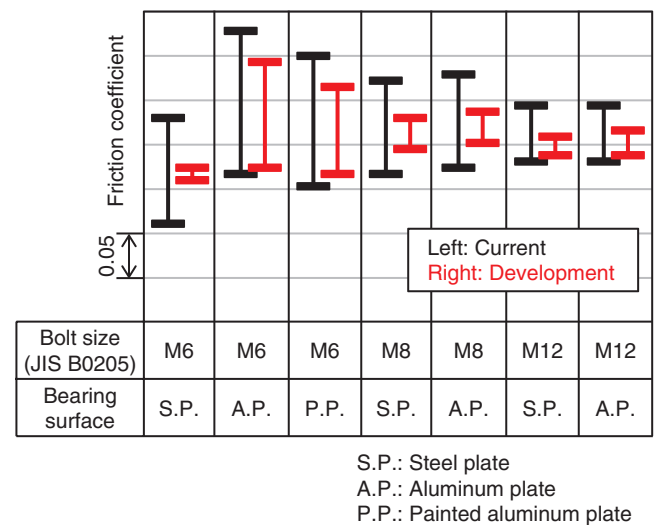


Fig. 29 Comparison of friction coefficient on various seating surfaces

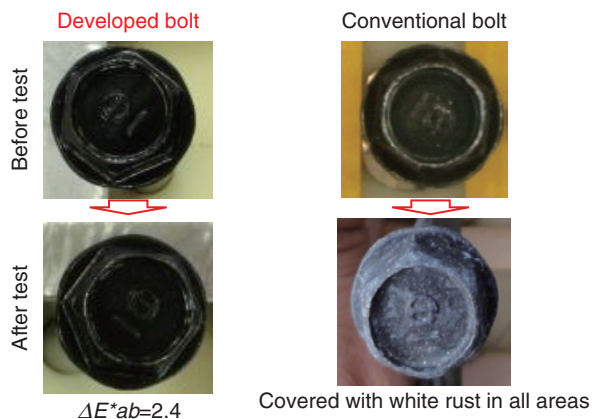


Fig. 28 Appearance before and after outdoor exposure test

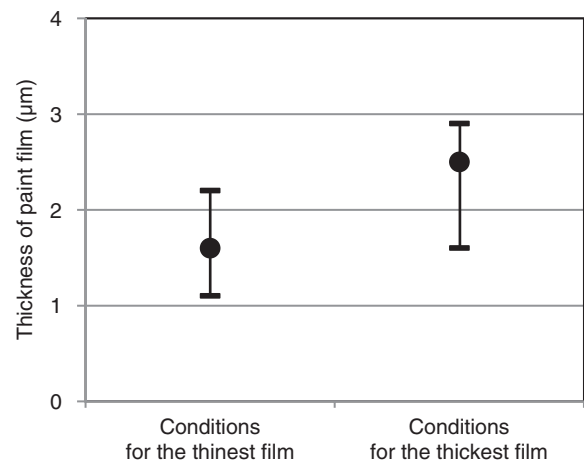


Fig. 30 Verification of film thickness deviations

5. Conclusion

The new surface treatment has been developed for black bolts that satisfy appearance and functional requirements of motorcycles by combining the black chemical coating and the dip coating. Given below is a summary of findings from this project.

- (1) The two-step coloring, i.e., the black painting overlaid on the chemically-produced black undercoat using the trivalent chromium, ensures uniform blackness of the bolt while maintaining thread precision.
- (2) With the clarification of how the chemical treatment solution containing the trivalent chromium deteriorates along with its limits, it is now possible to define the color of chemical conversion treatment film that serves as an undercoat of painting. Simultaneously, frequent changes of treatment solution requiring stopping of production equipment are no longer necessary, thus contributing to an enhancement of production efficiency.
- (3) The elimination of concealing treatment on the chemically-produced coating using the trivalent chromium contributes to the enhancement of adhesion and corrosion resistance. Also, the specifying of environmental conditions before the painting permits prevention of early corrosion of the chemically-produced undercoat using the trivalent chromium.
- (4) The addition of the friction modifier dispersible in the black paint permits a paint film having a required friction coefficient.
- (5) The clarification of the factors that affect paint film thickness in the dip coating helps to ensure consistent film thickness regardless of season.
- (6) The exclusion of recoat from the preconditions allows setting of paint baking conditions applicable to surfaces subjected to brake fluids.

The newly-developed surface treatment ensures blackness that can satisfy the requirements from motorcycles without using the environmentally hazardous material, and allows application of high-quality black bolts to motorcycles.

Note that the newly-developed surface treatment is referred to as HyD-Coat (BLK), which is a made word from Hybrid to mean the use of two kinds of material, Dual to mean the realization of appearance by two layers, Coat to mean a surface treatment, and BLK to mean a black color.

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