Technical Paper

# Research and Development of Technology for Use of Trivalent Chromating as Substitution Aimed at Abolition of Hexavalent Chromium

Yoichiro Hanada
Shinji Higo
Hideaki Ohkubo
Takuji Okumura
Kazuyuki Nabeoka

*Hexavalent chromium is widely used in rust preventive surface treatment. However, a reduction of substances hazardous to environment has been demanded socially and the use of hexavalent chromium in electric home appliances and automotive parts is already prohibited by the RoHS Directive (Restriction of the Use of Certain Hazardous Substance in Electrical and Electronic Equipment, 2006) and ELV (End-of-Life Vehicles Directive, 2007) of the EU.(1), (2) Following the designation of hexavalent chromium as an SVHC (substances of very high concern) by the REACH (Registration, Evaluation, Authorization and Restriction of Chemical substances) Regulation of the EU covering general industrial machines including construction machines, an early reduction in the usage of hexavalent chromium is desired.*

*With the aim of abolishing the use of hexavalent chromium, Komatsu has established trivalent chromating technology applicable to construction machinery parts that require high rust preventive performance and stable fastening performance. This paper reports an evaluation of the corrosion resistance and fastening characteristics of the trivalent chromate substitution film as compared with the conventional hexavalent chromate film.*

***Key Words:*** *Construction machinery, Material, Environment, Corrosion, Hexavalent chromium, Surface treatment, Bolt, Nut, Fastener*

## 1. Introduction

Hexavalent chromium is widely used in rust preventive surface treatment. However, because of its strong oxidation action, hexavalent chromium is handled as a substance that is harmful on account of its carcinogenicity, mutagenicity and teratology.[3] A reduction of environmentally hazardous substances is required in order to reduce environmental problems. As summarized in **Table 1**, the use of hexavalent chromium in electric and electronic parts was prohibited in 2006 through the RoHS Directive of the EU. From July 2007, the use of hexavalent chromium in automotive parts has been prohibited by the End-of-Life Vehicle (ELV) Directive of the EU. Following the designation of hexavalent chromium as an SVHC by the REACH Regulation of the EU covering general industrial machines including construction machines, reporting of total consumption of hexavalent chromium may be required if hexavalent chromium in excess of 0.1% is contained in parts of construction machinery to be newly produced and sold in the EU from 2011. Hexavalent chromium may be added as a substance whose consumption needs to be limited and an early reduction in the use of hexavalent chromium is necessary.

**Table 1** Environmental Regulations, etc. on Hexavalent Chromium in Automotive and Electric and Electronic Parts

| Environmental Regulations, etc. on Hexavalent Chromium | | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012～ |
|---|---|---|---|---|---|---|---|---|
| European ELV (End-of-Life Vehicle) Directive | Regulated harmful substances | | July → | Passenger cars and buses 9 persons or less in capacity, trucks 3.5t or less in total weight, automobiles with three wheels → | → | → | → | → |
| Electric and electronic products (RoHS Directive) | Regulated harmful substances | July → | Electric home appliances, communication equipment, etc. → | → | → | → | → | → |
| Target of Japan Automobile Manufacturers Association | Regulated harmful substances | | (Already accomplished) | January → | Passenger cars, commercial vehicles, motorcycles → | → | → | → |
| Requirements and obligations of REACH regulation | <Formed components> Harmful substances (SVHC) | | ○ Enforced in July | SVHC list announced ○ Oct. → | Replies to queries by users, disclosure of contents to downstream users →; Addition to list ○ Dec. | Reporting (Initial portion) | (Possibilities of approval or designation of restriction); June ○ Deadline for reporting | Reporting (Additionally registered portion) → |

The following three surface treatment methods as rust preventive treatment use hexavalent chromium for parts in construction machinery.

(1) Painting (Undercoating, etc. Already abolished by internal regulation)

(2) Hexavalent chromating on zinc plated layer

(3) Zinc dust chromic acid chemical conversion coating (Trademark "Dacrotized Treatment"[(4)])

**Table 2** summarizes rust preventive treatments that are affected by the abolition of hexavalent chromate and examples of parts affected by the abolition. The undercoating for painting shown in (1) above has already been abolished. The treatment by a zinc dust chromic acid chemical conversion coating shown in (3) is used by Komatsu only in limited cases and a substitution technology for it is already in use. Therefore, a substitution technology of hexavalent chromating used in surface treatment by zinc plating in (2) above was studied.

As substitution treatment for hexavalent chromating, trivalent chromating was selected and used as treatment featuring the high rust preventive performance and stable fastening performance that are required by parts used in construction machinery. This paper reports an evaluation of the corrosion resistance and fastening characteristics of the trivalent chromate substitution film as compared with the conventional hexavalent chromate film.

**Table 2** Rust preventive treatments free of hexavalent chromium for parts used in construction machinery

| Classification | Material containing hexavalent chromium | Hexavalent chromium rust preventive treatment | Rust preventive treatment free of hexavalent chromium | Example of affected parts |
|---|---|---|---|---|
| Zinc plating | Electrogalvanizing | Hexavalent chromate | Trivalent chromate | Fasteners, hydraulic hose fittings, hydraulic pipe connectors |
| | Electric zinc-iron alloy plating | | | |
| Zinc dust powder treatment | Zinc dust chromic acid chemical conversion coating acid | Dacrotized treatment | GEOMET treatment<br>Delta protect treatment | Fasteners, hydraulic pipe connectors, pin lock pins |
| Tube | Single-ply steel tube | Hexavalent chromate + (Fluorine resin coating) | Trivalent chromate + Fluorine resin coating | Grease pipe |
| | Double-ply steel tube | | | Brake pipe |
| Steel sheet | Electrogalvanized steel sheet | Coating-type chromate | Chromium-free steel sheet and cationic coating | Fuel tanks, hydraulic oil tanks |
| | Zinc hot dip galvanizing | | | Brackets, etc. |

## 2. Selection of Rust Preventive Treatment Film Free of Hexavalent Chromium and Technical Problems

### 2.1 Current Status of Chromating on Zinc Plating

Hexavalent chromating on zinc plating is widely used as rust preventive treatment of bolts, nuts and washers (**Fig. 1**), hydrauric hose fitting (**Fig. 2**), hydraulic pipe connectors (**Fig. 3**) and pipes of construction machinery (**Fig. 4**). At present, substitution of trivalent chromating is making good progress. The technical problems facing the substitution are described below.

**Fig. 1** Fasteners

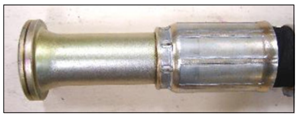


**Fig. 2** Hydraulic hose fitting

**Fig. 3** Hydraulic pipe connector

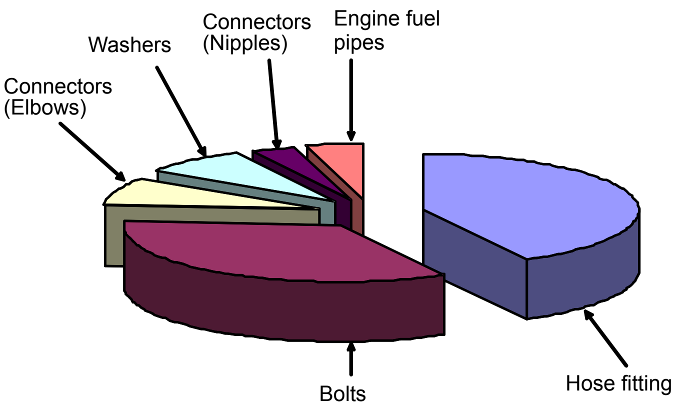



**Fig. 4** Ratios of parts at Komatsu to be free of hexavalent chromate

Fasteners are now also used in large construction machinery at Komatsu and large bolts (nominal diameter M16 or larger) that are generally not used by manufacturers of automobiles and electric home appliances account for more than half of all fasteners used at Komatsu. (**Fig. 5**) For this reason, it is important to substitute hexavalent chromating that can be used with these parts. However, in-house technology on trivalent chromating of large bolts and other fasteners is almost non-existent and technology development and evaluation technology are required.

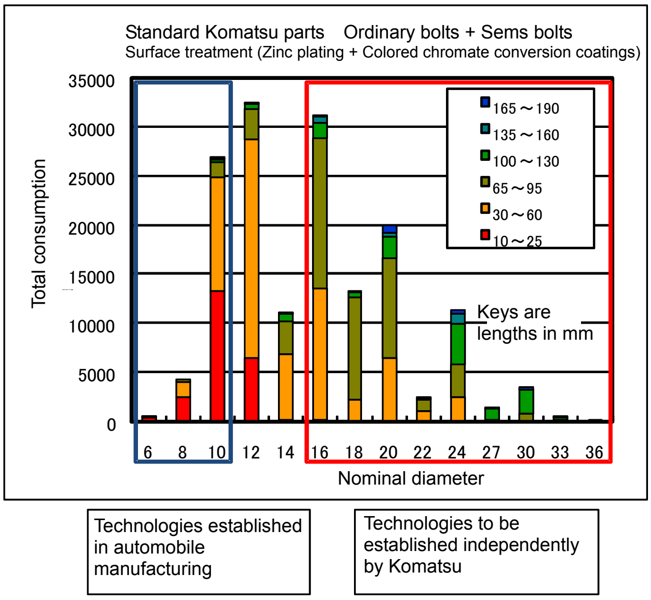



**Fig. 5** Use of affected bolts at Komatsu by size (Weight ratio)

In many cases, surface treatment of bolts in parts used in construction machinery is outsourced by manufacturers of fasteners. It is therefore indispensable to satisfy problems encountered by the procurement department such as when the trivalent chromium films in question are rich in versatility, substitution can be easily distinguished from the appearance and cost fluctuations occur less frequently. Because construction machinery is often used in harsh environments, the following challenges must be addressed in developing substitution technologies for hexavalent chromate.

1) Rust preventing capacity equal to that of hexavalent chromate films.
2) Friction coefficient equal to that of hexavalent chromate films.

### 2.2 Selection of Technology to Substitute Hexavalent Chromate

Trivalent chromating is now widely used in automobiles and electric home appliances as a substitute for hexavalent chromating [5] because trivalent chromating equipment can be additionally installed in the same production lines as those for hexavalent chromating and hexavalent chromate and trivalent chromate can be easily distinguished on product appearances. The color changes from yellow to white when hexavalent chromate is substituted by trivalent chromate.

To further enhance the anti-corrosion performance of trivalent chromate on electrogalvanizing, the zinc plated layer, which is a substrate under the chromate layer, is alloyed such as trivalent chromate of zinc-iron plating and trivalent chromate of zinc-nickel plating. (**Fig. 6**) As an example, trivalent chromate on zinc alloy plating is used such as in automotive parts (brake pipes) that especially require high resistance to corrosion. However, few manufacturers can treat trivalent chromate on zinc alloy plating while procurement problems are not as easy as in hexavalent chromate and trivalent chromating is costly. Therefore, serious obstacles remain to entirely switching from hexavalent chromating on zinc plating to trivalent chromating.


**Fig. 6:** Trivalent chromating of various types of zinc alloy plating

For these reasons, it was decided to exclude trivalent chromating of zinc alloy plating as a substitution technology for parts used in construction machines of Komatsu and selected trivalent chromating of zinc plating, whose technology is already established with parts for electric home appliances and automobiles proven with a high level of productivity and supply capability, as a candidate for substitute hexavalent chromating.

### 2.3 Composition of Substitute Material (Trivalent Chromate).

**Fig. 7** compares a hexavalent chromate layer and a trivalent chromate layer. The hexavalent chromate layer is an inorganic film composed of composite salts of hydrates of soluble hexavalent chromium and trivalent chromium.

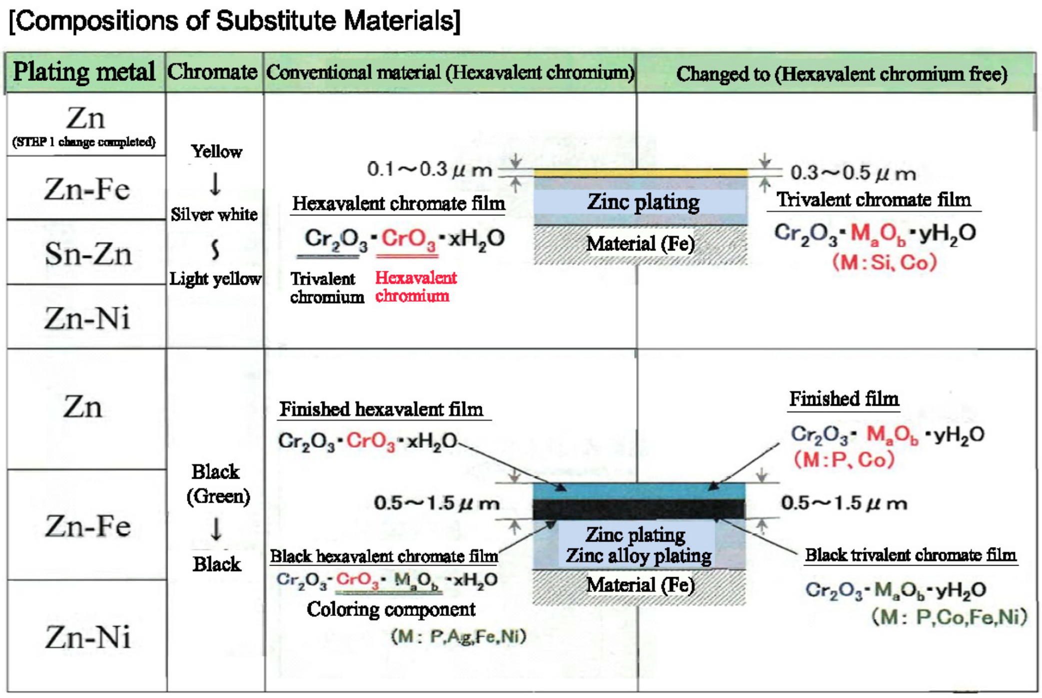



**Fig. 7** Structures of chromating films [6]

The trivalent chromate layer is composed of an upper layer that has colloidal silica as a main component and a lower layer of zinc. These two layers hold metal salts such as film cobalt of a trivalent chromium salt in the interface between them. Takigawa et al. performed an element analysis of the trivalent chromate layer on various zinc plated layers in the depth direction by the glow discharge mass spectrometry (GDS) method. Takigawa et al. reported that silicon of a silica component existed at a depth of 100 to 150 μm from the surface layer, that chromium and a metal element derived from a chelated metal salt in the thickness of 50 nm could be found on the interface of the plated layer and that the whole structure had two layers as shown in **Fig. 8**. [(7), (8), (9)]

Trivalent chromate is believed to attain a resistance to corrosion by having this dense silica layer. The corrosion resistance and fastening performance of a trivalent chromate layer were compared with those of a hexavalent chromate layer and trivalent chromating was confirmed appropriate as a substitution technology as follows.

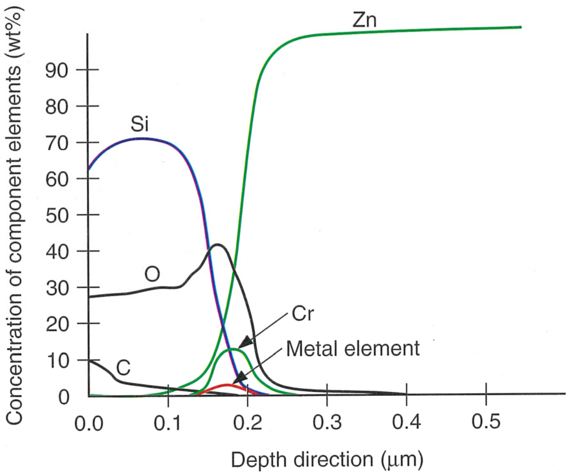



**Fig. 8** Concentration distribution of elements in a trivalent chromate layer on a zinc plated layer [(8)]

## 3. Rust Preventive Capacity of Trivalent Chromate

### 3.1 Sample Fabrication of Trivalent Chromate

Parts were test-treated in an actual electrogalvanizing line and trivalent chromating line in the same lot sizes as those for high volume production to evaluate resistance to corrosion and friction coefficient. Parts treated by test treatment equipment at the laboratory of a chemical solution manufacturer were also tested for comparison. A comparative study of parts that were trivalent chromated and hexavalent chromated was performed to compare evaluations of anti-corrosion tests including scars and press marks inflicted in the process.

### 3.2 Anti-Corrosion Test Method

One prominent difference between chromated parts used in construction machinery on one hand and in automobiles and electric home appliances on the other hand is that parts for construction machines are used as machine cover parts in many cases. In construction machines, hexavalent chromate layers without any painting on bolts are often exposed to the outside whereas automotive parts are mostly used inside the engine hood and other interior zones. As a result, the level of rust preventive performance required for parts in construction machinery is significantly higher than that for automobiles and electric home appliances. For this reason, the anti-corrosion evaluation criteria of Komatsu are much higher than the levels required for parts in automobiles and electric home appliances.

Neutral salt spray tests in corrosion resistance tests are mainly conducted by continuously spraying salt fog in accordance with Japanese Industrial Standard (JIS) Z 2371 (Methods of salt spray testing). The test method employed by Komatsu is for ambience tests in accordance with an in-house standard for evaluation of corrosion resistance that easily generates white rust by intermittently spraying salt water and setting an interval for stopping of salt spraying to enrich salt water. Results of in-house tests by Komatsu have shown that this test method accelerates the generation of white rust faster than by tests in accordance with the JIS method so that decisions on tests can be made early. Additionally, as an advantage, tests can be conducted using normal salt spray test apparatuses. All the tests reported in this paper were conducted in accordance with the corrosion resistance test method of Komatsu specified in **Table 3**.

**Table 3** Differences between the corrosion resistance evaluation method of Komatsu and JIS test method in substitute treatment (trivalent chromate)

| | Komatsu test standard (Test unique to Komatsu) | JIS test standard (JIS Z 2371) |
|---|---|---|
| Spraying chamber temperature | 35±2℃ | |
| Salt water concentration | 5±1% NaCl solution | |
| pH of spray solution | Neutral (pH 6.5 to 7.2) | |
| Salt spraying method | Intermittent spraying (Salt water sprayed for 8 hours and salt water spraying paused for 16 hours) This cycle is repeated for a specified duration of time. | Continuous spraying |

### 3.3 Results of Anti-Corrosion Test

**Figure 9** shows the results of the anti-corrosion test by presence or non-presence of scars on trivalent chromated bolts in the beginning of 2006 when the development project was started. It was found that scars and press marks on the chromate layer had to be reduced to curb white rust in the corrosion resistance test according to the Komatsu method. As mentioned earlier, anti-corrosion test according to the Komatsu's standard appears to accelerate corrosion (white rust) of zinc plating beneath the chromate layer due to attack by enriched salt water caused by intermittent spraying and by enriched salt water attacking scars.

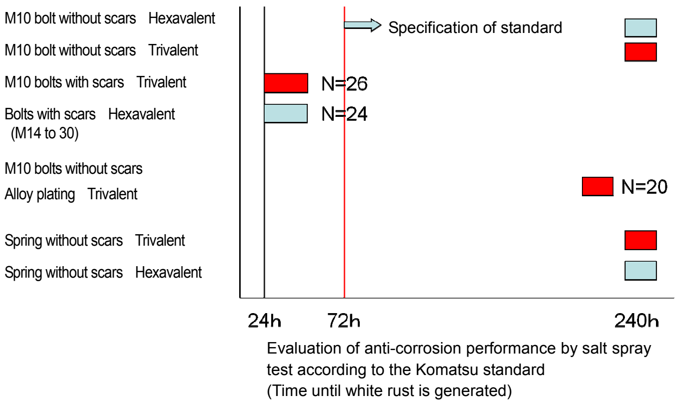



**Fig. 9** Results of anti-corrosion test

### 3.4 Surface Texture of Trivalent Chromating of High Corrosion Resistance

The test results described in 3.3 show that the surface conditions of the chromate layer were important for improving corrosion resistance. As mentioned in 2, passive state films are formed in hexavalent chromating due to reductive reaction of soluble hexavalent chromium to trivalent chromate in the case when defects are inflicted on films by scars. This is the so-called self-healing function by which high anti-corrosion performance is gained. Compared with this, trivalent chromate has a colloidal silica layer as a surface layer and a lower layer that contains metal salts such as cobalt in a trivalent chromium film. To increase corrosion resistance, defects in the colloidal silica layer as the surface layer had to be eliminated and films needed to have high toughness. To satisfy these requirements, optimization of the surface texture was attempted and achieved.

**Figure 10** shows the results of SEM observation of surfaces of chromated bolts to observe modified trivalent chromating films. Many cracks are observed in the hexavalent chromate films. The surfaces of modified trivalent chromate films had hardly any cracks on the surfaces.

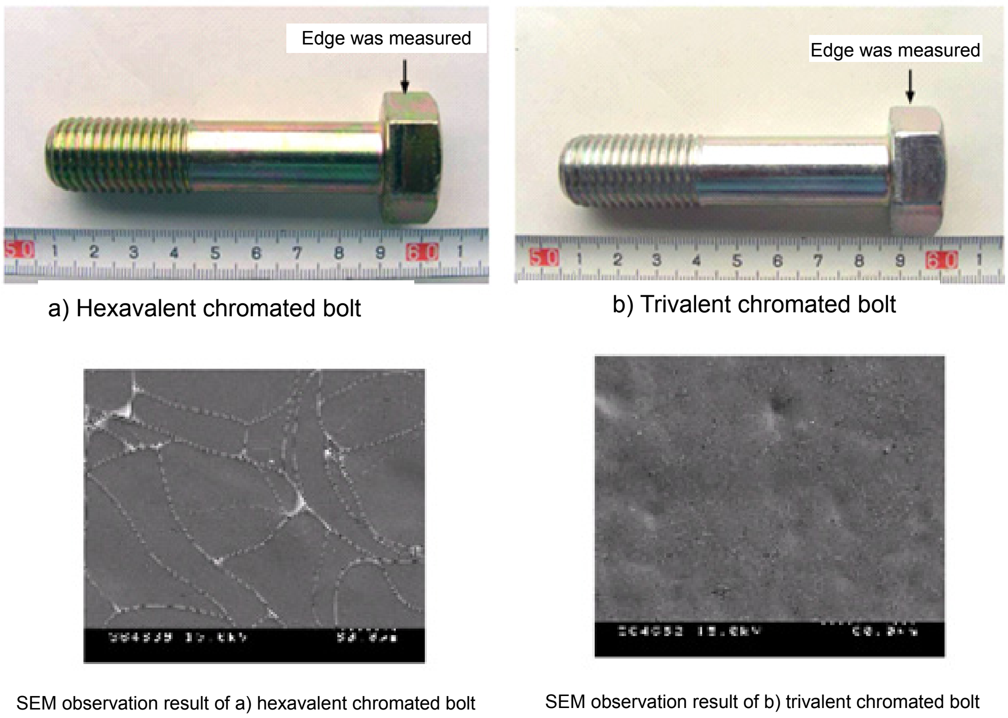
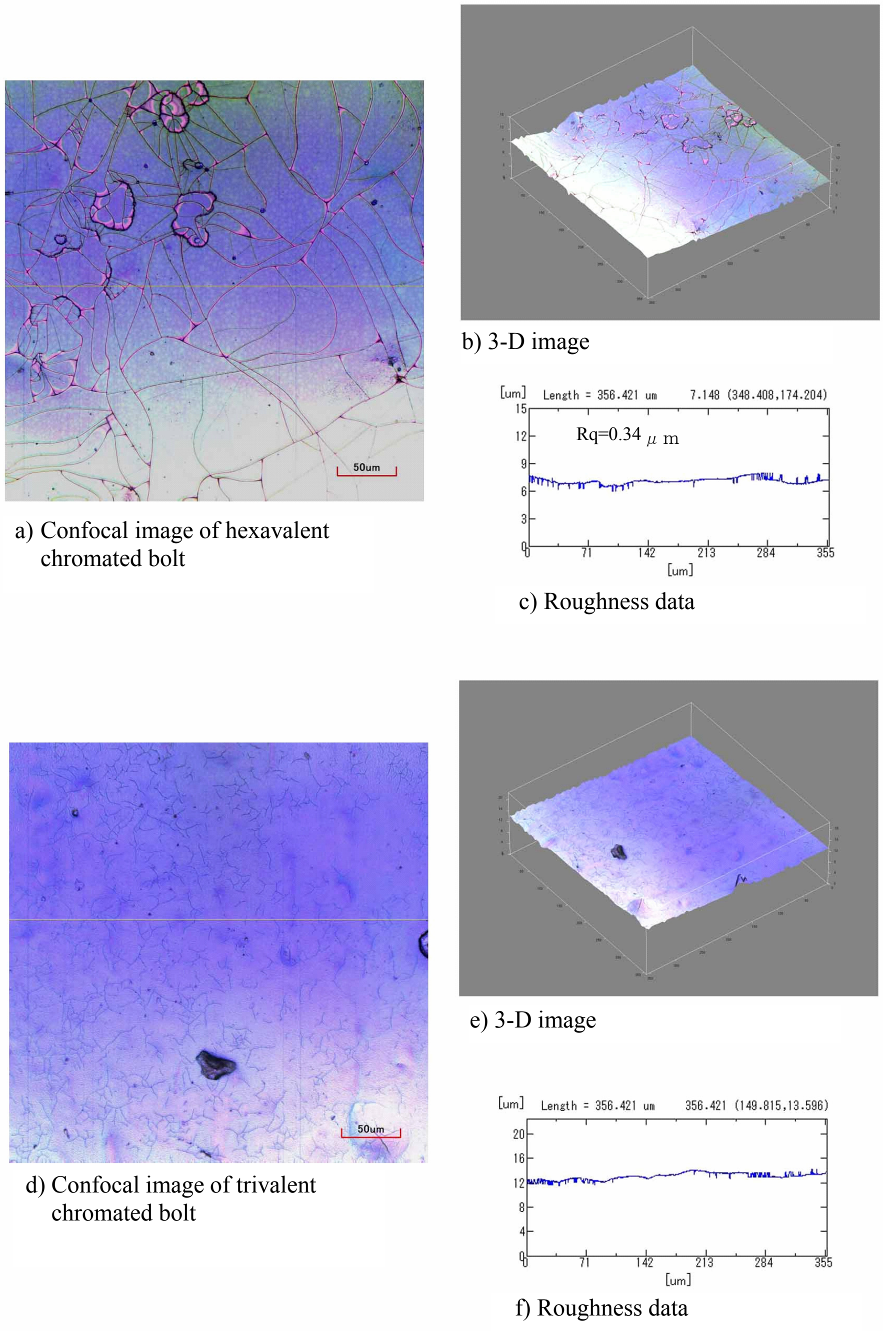



**Fig. 10** Surface observation results of high corrosion resistance trivalent chromated film

Additionally, observation results of confocal images are shown in **Fig. 11**. Whereas many cracks were observed in hexavalent chromate with surface roughness of about 0.34 µm, the surface roughness of the trivalent chromate layer was 0.54 µm with a considerable difference in surface roughness even though a dense silica layer was formed.




a) Confocal image of hexavalent chromated bolt

b) 3-D image

c) Roughness data

d) Confocal image of trivalent chromated bolt

e) 3-D image

f) Roughness data

**Fig. 11** Observation results of surfaces of bolts (hexavalent chromated and trivalent chromated bolts) by confocal microscope

### 3.5 Cross Section of High Corrosion Resistance Trivalent Chromating

**Figure 12** shows observation results of cross section of a hexavalent chromate layer and trivalent chromate layer by SEM. The hexavalent chromate layer consists of one layer whereas a high corrosion resistance trivalent chromate layer has two layers. Judging from the result of the EPMA analysis shown in **Fig. 13**, the surface layer of the trivalent chromate layer seems to be a colloidal silica layer.

### 3.6 Anti-Corrosion Test Results of High Corrosion Resistance Trivalent Chromate

The results of an anti-corrosion test of the trivalent chromate layer described in 3.5 are shown in **Fig. 14**. The results of a 240 hours salt spray test show almost identical corrosion resistance to that for hexavalent chromated bolts.

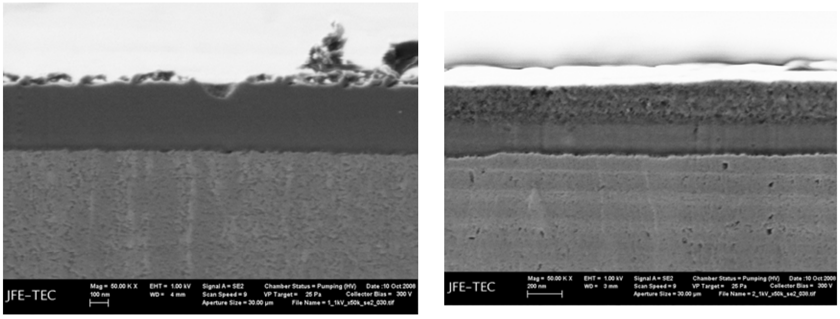



**Fig. 12** Observation results of sections of a hexavalent chromated bolt (left) and a trivalent chromated bolt (right)

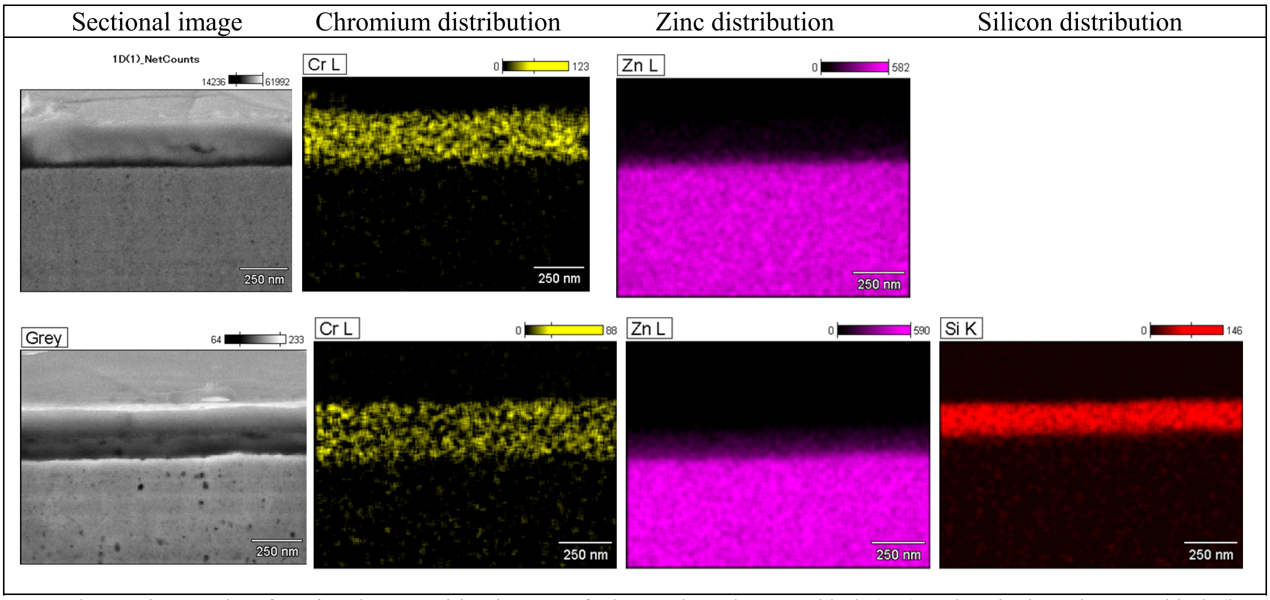



**Fig. 13** Observation results of sectional composition images of a hexavalent chromated bolt (top) and a trivalent chromated bolt (bottom)

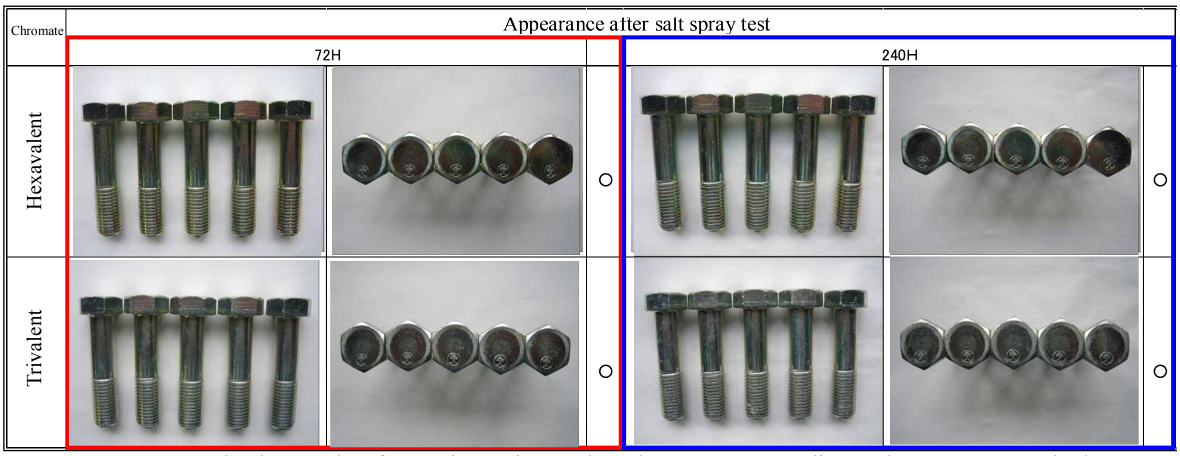



**Fig. 14** Evaluation results of corrosion resistance by salt spray test according to the Komatsu standard

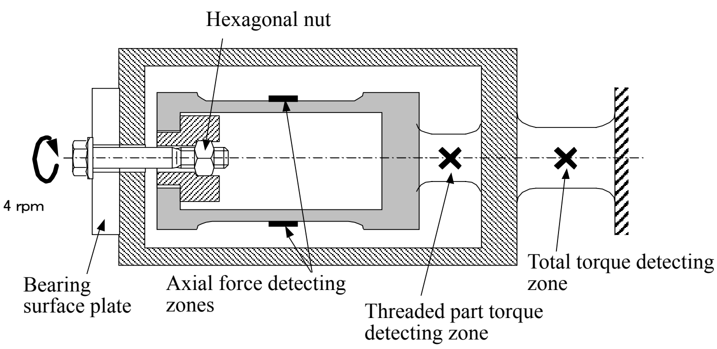
# 4. Fastening Performance of Trivalent Chromated Bolt

## 4.1 Fastening Performance of High Corrosion Resistance Trivalent Chromated Bolt

Friction coefficients of a hexavalent chromate layer and a trivalent chromate layer were compared and studied. The friction coefficient was evaluated based on the overall friction coefficient that is generally used by automobile manufacturers and others. The overall friction coefficient was calculated as shown in **Fig. 15**.

1. Fastening Performance Evaluation (Measurement of Friction Coefficient)

Configuration of Fastening Test




A block diagram of the test apparatus is shown on the left. The friction coefficient is calculated based on axial force and torque obtained when a load cell is clamped using a bearing surface plate and hexagonal nut.

◎ Calculation formula for overall friction coefficient (By TSB 0500)

$$\mu = \frac{\dfrac{2T}{F} - \dfrac{P}{\pi}}{\dfrac{d2}{\cos\alpha} + dw}$$

Where T: Tightening torque
F: Axial force
P: Screw thread pitch
d2: Effective diameter of screw (Reference size)
$\alpha$ : Half size of screw thread
dw: Bearing surface equivalent diameter

$$dw = \frac{2}{3} \cdot \frac{do^3 - di^3}{do^2 - di^2}$$

Where do: Outer diameter of contacting bearing surface
di: Inner diameter of contacting bearing surface

Provided $\mu s = \mu w$
($\mu s$: Friction coefficient of threaded part
$\mu w$: Friction coefficient of seat)

◎ Calculation formula for friction coefficient $\mu s$ of threaded part

$$\mu s = \frac{\cos\alpha}{d2} \cdot \left( \frac{2Ts}{F} - \frac{P}{\pi} \right)$$

Where $\mu s$: Friction coefficient of threaded part
Ts: Torque of threaded part

◎ Calculation formula for bearing surface friction coefficient $\mu w$

$$\mu w = \frac{2 \cdot Tw}{F \cdot dw}$$

Where $\mu w$: Friction coefficient of seat
Tw: Torque of seat

**Fig. 15** Block diagram of the bolt fastening test and the method for calculating overall friction coefficient

The tests were performed on surfaces of bolts with an anticorrosion oil. Normally, the friction coefficient is measured under dry conditions without the addition of oil. However, in actual usage, bolts are used with an oil component in many cases and measurement results under wet conditions are shown.

Friction coefficients of M20 and M22 bolts treated with high corrosion resistance hexavalent chromating and trivalent chromating are shown in **Fig. 16**. The friction coefficient of trivalent chromate is almost identical to that of hexavalent chromate.

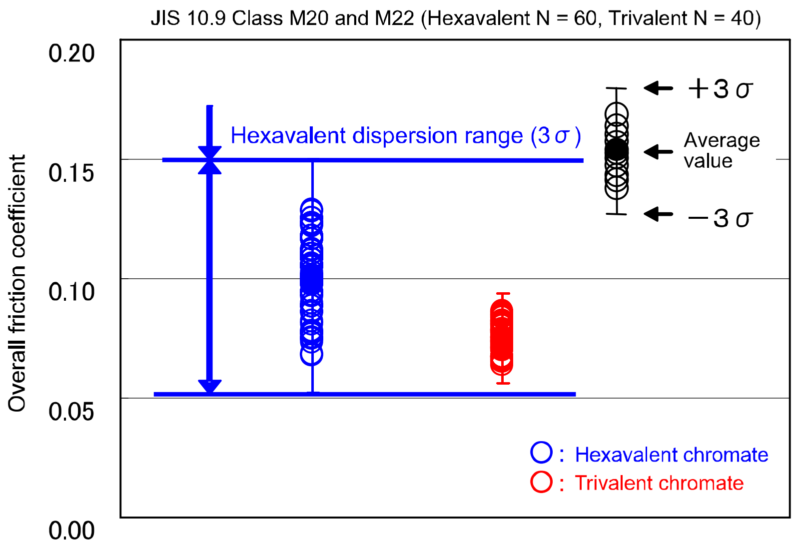



**Fig. 16** Comparison of the overall friction coefficients of hexavalent chromate and trivalent chromate in the fastening test

### 4.2 Observation of Bolt Surface after Fastening Test

An EPMA analysis of the surface conditions of bolts after the bolt fastening test was performed to examine differences in dispersions of hexavalent chromated and trivalent chromated bolts in the fastening test. **Figure 17** shows analytical results of elements on hexavalent chromated bolts after the fastening test. Iron and zinc were detected on sliding surfaces. In some zones, no chromium element was detected. It shows that the zinc plated layer was separated during the fastening test so that the chromate layer on it was also separated. The friction coefficient seemed to have dispersed as a result of the separation of the zinc plated layer.

Throughout the test, the same torque test conditions were used. The results of the EPMA analysis of trivalent chromated bolts after the fastening test are shown in **Fig. 18**. Because iron was not detected on the sliding surfaces and chromium and zinc were detected on the front side, separation of the zinc layer and chromate layer was not extensive.

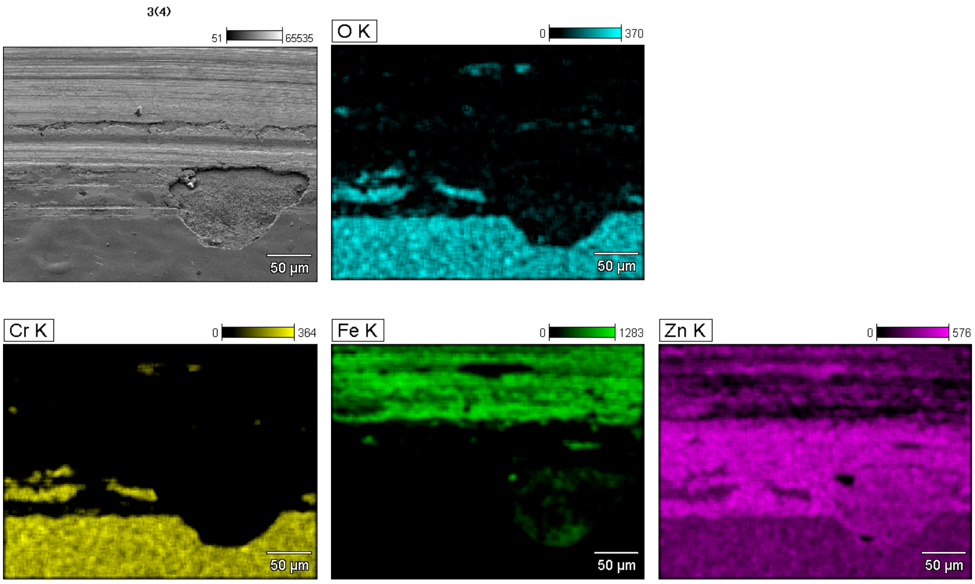



**Fig. 17** SEM-EDX mapping of bolt (M20, hexavalent chromate, after fastening test)
Data type: Net count, magnification 200, acceleration voltage 15.0kV

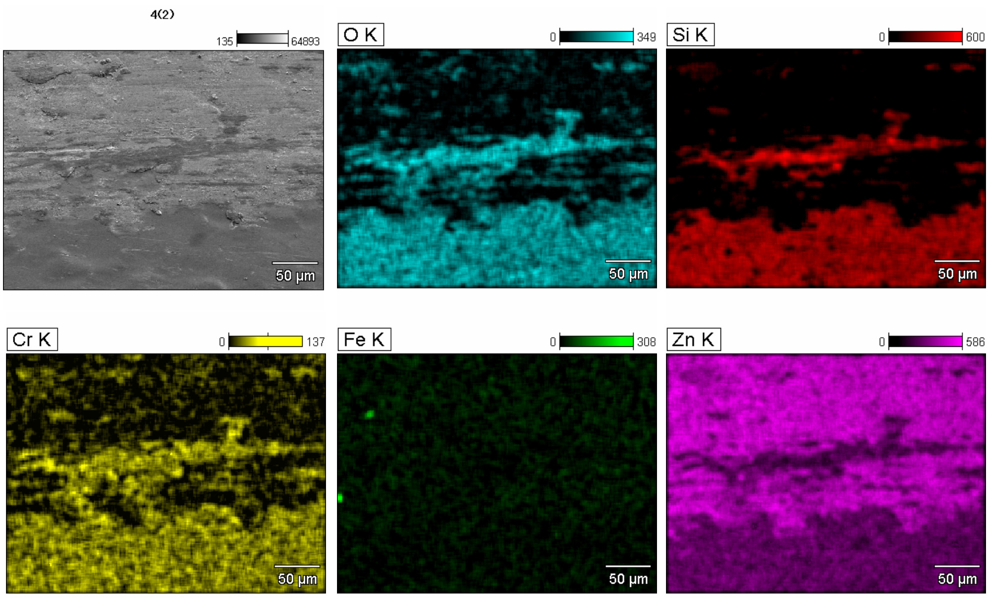



**Fig. 18** SEM-EDX mapping of bolt (M20, trivalent chromate, after fastening test)
Data type: Net count, magnification 200, acceleration voltage 15.0kV

### 4.3 Surface Hardness of Fasteners Tested in Fastening Test

**Fig. 19** plots the surface hardness of bolts, nuts and washers used in the fastening test measured by a microhardness testing machine.

The diagram shows that the hardness of trivalent chromate layers is slightly low compared with that of hexavalent chromate layers.

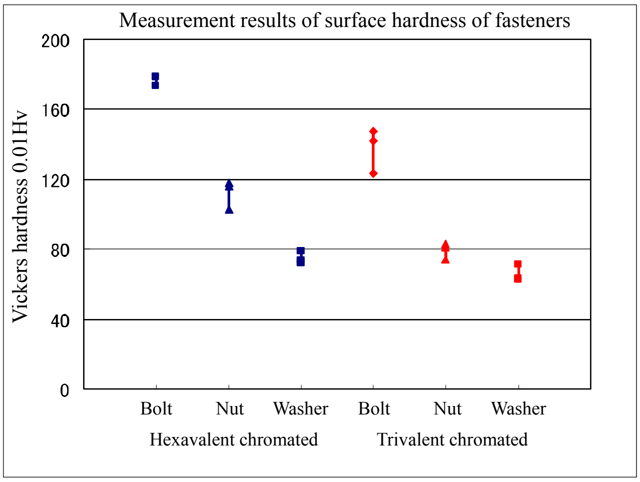



**Fig. 19** Measurement results of the surface hardness of fasteners tested in the fastening test

## 5. Conclusion

A comparison of structures of hexavalent chromated and trivalent chromated films indicates the following:

1) The high corrosion resistance trivalent chromate layer has two layers. The surface layer is formed by a dense colloidal silica layer, exhibiting an almost identical corrosion resistance to that of the hexavalent chromate layer.

2) The fastening performances of hexavalent chromated and trivalent chromated fasteners are similar. However, dispersions of friction coefficients of trivalent chromated fasteners are small compared with those of hexavalent chromated fasteners. This can be attributed to almost no separation experienced with trivalent chromated fasteners during fastener fastening while the hexavalent chromate layer peels off together with the zinc plated layer.

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**Introduction of the writers**


**Yoichiro Hanada**

Entered Komatsu in 1983.
Currently assigned to Research & Technical Group the Materials Technical Center, Development Division.

**Shinji Higo**

Entered Komatsu in 1985.
Currently assigned to the Planning & Administration Group, Materials Technical Center, Development Division.

**Hideaki Ohkubo**

Entered Komatsu in 1982.
Currently assigned to the Planning & Administration Group, Materials Technical Center, Development Division.

**Takuji Okumura**

Entered Komatsu in 1983.
Currently assigned to Research & Technical Group the Materials Technical Center, Development Division.

**Kazuyuki Nabeoka**

Entered Komatsu in 1982.
Currently assigned to the Regulations and Standards Group, Planning and Administration Department, Development Division.



**[A few words from writers]**

The range of usage of materials containing hexavalent chromium is wide and diverse and changing these materials while maintaining the same performance was not easy. Under the leadership of the Development Division, however, the purchasing divisions, production divisions and quality assurance departments of the entire Komatsu Group including its affiliates concertedly undertook activities to successfully accomplish the task. The parts suppliers also fully cooperated in these activities.

The writers are very grateful to those who participated in this development project for their cooperation. Continued efforts will be made to further reduce the use of environmentally hazardous substances.