

High-Performance, Eco-Friendly Alternative Coating Process for Fasteners

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New nano-ceramic coating technology brings zinc plating to a new generation of fasteners that are totally free of chromate and heavy metal ions.

For many years galvanic zinc plating with hexavalent chromate passivation has been widely used as the primary means of surface finishing for fasteners. But environmental concerns have forced the industry to look for alternatives. In particular, the automotive industry has adopted zinc-rich and zinc alloy plating with trivalent chromate passivation as a substitute. But higher cost and greater coating thickness makes for a less-than-perfect replacement for traditional zinc plating technology. In this article, a nano-ceramic coating technology (NanoMate) on zinc-plated fasteners is introduced. In combination with trivalent chromate passivation, this nano-material technology can yield extremely high performance. It can even replace some of the fasteners from high-end materials such as stainless steel. We will also introduce a recent breakthrough process that brings zinc-plating to a new generation of fasteners that are totally free of chromate and heavy metal ions. A cost-effective, environmentally friendly coating system with excellent corrosion resistance properties has finally arrived.

Galvanic zinc plating has long been the primary means of finishing fasteners due process simplicity, cost and excellent appearance. Adding hexavalent chromate passivation, also simple, cost effective and attractive, has the added benefit of excellent corrosion resistance. As the concentration of hexavalent chromate is increased to improve the corrosion resistance, the fastener color ranges from iridescent to olive and black. **Table 1** compares the chromate concentration in the surface. The more hexavalent chromate, the better the corrosion resistance and the darker color.

Table 1. Comparison of Conversion Coatings from Trivalent and Hexavalent Chromium.

Type	Film Thickness (nm)	Cr+6 (mg/m ²)	Total Cr (mg/m ²)
Clear (Cr3+)	25-80	<0.1	30-40
Iridescent (Cr3+)	250-500	<0.1	100-180
Iridescent (Cr6+)	250-500	80-220	200-460
Green (Cr6+)	250-1000	80-400	1000-1800
Black (Cr6+)	250-1000	80-400	1000-1800

Clear or blue zinc can provide only very basic corrosion resistance. To have a metal-like glossy appearance with better corrosion resistance, fasteners will need to have Ni, Cd, or Cr plating. The other metal plating processes shown in **Table 1** are much more expensive, less efficient and more environmentally damaging due to the heavy metals that must be used and the waste stream they create.

In 2000, the EU community released the "End of Life Vehicles Directive" (*ELV, Directive 2000/53/EC*), which, after July 2003, allows for only 2 g of hexavalent chromium per vehicle for corrosion resistance purposes only. The directive requires the elimination of hexavalent chromium by July 2007. In 2002, new directives were issued: "Restriction of the use of certain hazardous substances in electrical and electronic equipment" (*RoHS, Directive 2002/95/EC*), and "Waste Electrical

and Electronic Equipment" (*WEEE, Directive 2002/96/EC*) dictating that all electronic components used in the EU shall not contain any hexavalent chrome by the end of 2006. Due to these regulations from Europe, the USA, Japan, China and many other countries followed suit. Hexavalent chromium that had been widely accepted for its anti-corrosive properties was to be replaced due to its carcinogenic and hazardous nature. Unfortunately, given the unique advantages of this process there does not seem to be an equivalent replacement.

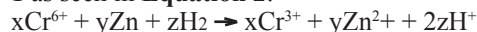
Trivalent chromium conversion and other nonchromium alternatives have received much attention in the past few years. Particularly for the automotive industry, trivalent chromium passivation has been used as the replacement for the hexavalent process. However, due to reduced performance, unstable reliability and much higher cost, trivalent chromate processes are still not fully accepted by the industry. The relatively poor performance of trivalent chromate on zinc plating, especially the black or olive green colors has forced auto manufacturers to introduce zinc-nickel, zinc-iron plating, or zinc-rich coating processes further complicating production cost models.

Theoretical Aspects

The first reaction when a conversion coating is applied on Zn-plated surface is the acidic conversion solution dissolving the zinc as in **Equation 1**: $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

Due to the consumption of acid, the pH-value in front of the zinc layer will increase in the conversion solution.

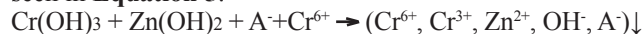
For the hexavalent chromium conversion, Cr⁶⁺ is reduced to Cr³⁺ by zinc and hydrogen produced in reaction to **Equation 1** as seen in **Equation 2**:



Part of the Cr³⁺ intermediate will form chrome hydroxide and precipitate on the top of the zinc surface as a result of the pH-shift as seen in **Equation 3**: $Cr^{3+} + 3(OH)^- \rightarrow Cr(OH)_3 \downarrow$

This thick, gelatinous trivalent chromium layer is known as Cr-O-Cr olation polymer. At the same time, the Zn cation will form zinc hydroxide on the surface as indicated in **Equation 4**: $Zn^{2+} + 2(OH)^- \rightarrow Zn(OH)_2$

During precipitation of the chrome hydroxide (olation polymer) and zinc hydroxide, many cations and anions, especially hexavalent chrome, are incorporated in the layer as seen in **Equation 5**:



For all these reactions, the Cr³⁺ ion is of a low concentration after precipitation, while the hexavalent chromium plays the most important role for corrosion resistance. However, even in a hexavalent chromium conversion, the reaction takes place via trivalent chrome and the Cr⁶⁺ is actually incorporated into the precipitate. The anions in the thick precipitate (olation polymer) control color, thickness, and the "self-healing" ability of the film. The ratio of Cr⁶⁺ and Cr³⁺ in the solution is very important. Once the Cr³⁺ concentration becomes too high the solution must be adjusted or even replaced.

Trivalent Chromium Conversion Coating Chemistry

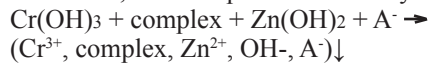
The alternative to the hexavalent chromium conversion where a noncomplex trivalent intermediate is created, an aqueous Cr(III) complex is formed in a hexavalent free conversion coating, **Equation 6:** $\text{Cr}(\text{NO}_3)_3 + 6\text{H}_2\text{O} \rightarrow \text{Cr}(\text{H}_2\text{O})_6(\text{NO}_3)_3$

The mechanism by which the Cr(III)-complex precipitates on the zinc surface to build a conversion coating layer is due to the pH-shift, **Equation 7:**



Similar to the hexavalent chromium conversion, the Zn cation will form zinc hydroxide on the surface as seen in **Equation 8:** $\text{Zn}^{2+} + 2(\text{OH})^- \rightarrow \text{Zn}(\text{OH})_2$

During precipitation of the chromium (III) hydroxide and zinc hydroxide, many cations and anions, especially trivalent chromium, are incorporated in the layer, **Equation 9:**



In the hexavalent chromium conversion coating, the reaction speed limiting step is the creation of the Cr(III)-intermediate (**Equation 2**), whereas in the trivalent chromium conversion it is the reaction of the complex (**Equation 7**). If the complex is water, the reaction speed is high due to the weak complex, and the conversion coating will be powdery with bad adhesion.

For the strong complex such as fluoride, the reaction speed is low and the layer is thin, which is usually used for Cr(III) blue conversion. For other complexes that are stronger than water, but weaker than fluoride, the trivalent chromium conversion coating can be thicker. Based on the research of Dr. Klos, **Klaus Peter** in the late 90s, a cobalt complex and co-precipitation has become an efficient way to build up the passivation thickness as the “thick trivalent chromate” on zinc plating. This process has actually become the basic building block for most of the commercial trivalent chromate chemistries. Although the corrosion resistance can be significantly improved, the brittle structure of the thick oxide layer has been known to negatively influence reliability. Sealing with a topcoat or chemical sealer can significantly improve the reliability performance. Some of the drawbacks of this process are the difficulties in controlling the chemical bath and the hazardous nature of cobalt compounds in production waste. Many auto makers view the trivalent chromate process as a temporary solution to be employed while waiting for new processes which will eliminate chromates and other heavy metals altogether.

Trivalent Chromium—Other Factors

Although trivalent chromium conversion processes have been accepted by manufacturers worldwide it is not without regrets. The cost of trivalent conversion is already higher than hexavalent but yields rather poor performance and reliability. To meet or exceed hexavalent chrome manufacturers must rely on more costly plating and expensive top coats and sealers.

Let's consider the problem of color. Light iridescent colors can be realized from trivalent chromium compounds, but these are visually different than those obtained from hexavalent chromium processes. Hexavalent yellow is another good example. It is possible to produce a yellow trivalent coating but it is quite different than the yellow we are used to seeing. The addition of dyes and other metal ions yields coatings that are somewhat color compatible, but with a negative impact on

performance and reliability. In order to meet manufacturer's specifications, there is going to be more upward pressure on the price curve as Zn-Ni or other alloys are required to mitigate the problems introduced by coloration.

The trivalent chromium conversion process, although extraordinarily useful when the performance vacuum was created by necessary regulation, is in need of an upgrade. In fact, a totally different corrosion resistance mechanism should be developed instead of relying entirely on electrochemical methods such as hexavalent chromate.

NanoMate for Zinc-Plated Parts: New Corrosion Resistance Mechanism for Metal by Nano-Material Technology

Theoretically, metal corrosion comes from penetration of moisture and some ionic substances. Blocking this should be the only remaining alternative other than some electrochemical mechanism. Painting and sealing, when combined with hexavalent chromate passivation, has been commonly used to improve the corrosive resistance for metals. Both blocking and strong electrochemical reactions can provide extremely high corrosion resistance. However, the lack of bonding of the topcoat to the base conversion oxide makes the performance drop significantly if not using hexavalent chromate. More precisely stated, all existing corrosion resistance mechanisms for metal work well only with hexavalent chromate.

A proprietary nano-material technology, NanoMate Process, has been developed by **Nanmat Technology** (Kaohsiung, Taiwan). This revolutionary technology has been proven to be effective for improving the corrosion resistance of almost all types of metals in an environmental friendly process. The NanoMate process is also a possible alternative for the non-chromium replacement for hexavalent chromium conversion. Recently, this new technology has been modified for use as a corrosion resistance mechanism of zinc-plated parts, especially fasteners, and achieves outstanding performance as compared to other technologies. Commercial production of NanoMate treated fasteners has already begun.

The NanoMate process for fasteners starts with a solution that is made from nano organo-ceramic material. This solution can be either aqueous or solvent based, depending on the application. The solution can be applied on zinc-plated or alloy-plated fasteners by dip-spin immediately after electroplating with trivalent chromium or non-chromate conversion. A post cure at an elevated temperature (normally 150°C to 180°C) for about 10 minutes is necessary to form a thin, dense nano-material coating on the zinc surface.

Due to the active oxide surface, an oxidation reaction between the organo-ceramic nano-particles and the conversion oxide or native oxide of the metal surface forms a strong chemical bond. During the thermal curing process, the nano-ceramic particles crosslink to form an ultra dense film on top of the metal. The strong chemical bonding between the organo-ceramic and the conversion oxide all the way to the zinc surface coupled with the ultra dense structure of the organo-ceramic improves the corrosion resistance significantly. Multiple coatings can be applied to provide better uniformity and higher performance. This new corrosion resistance mechanism provides a blocking mechanism for moisture and corrosion substances thereby significantly improving corrosion resistance.

The New Process on Trivalent Chromate Conversion

By combining NanoMate with trivalent chromate passivation, one can provide not only high performance, but also facilitate a wide variety of colors for the plated surface.

Table 2 summarizes the salt spray test data for a typical NanoMate coating plus Nanmat's proprietary trivalent chromate passivation. The most significant factor affecting corrosion resistance is the thickness of the nano-ceramic coating. For the clear NanoMate coating on blue trivalent passivation, (C500 and C1000) seen in **Table 2**, the trivalent chemical is only in the range of 2% to 4%, which is much lower than the normal thick trivalent chromate chemical that is generally about 10% to 15%. The standalone performance for the trivalent chromate passivation is very poor. However, the performance after the NanoMate coating is superior to most other treatments. Zn plating with a NanoMate coating can even meet the automotive requirements for Zn-Ni alloy plating with sealant (such as *GMW4205*) or the requirement for zinc-rich coatings (*GMW3359*). Using the NanoMate solution means a lower cost and lower thickness that will meet most of the high performance requirements of many industries.

Fasteners Made Using this New Process

Nanmat's StainlessZ fastener process is produced by zinc plating with light trivalent chromate conversion and a thin NanoMate coating (<1µm), the NanoMate StainlessZ fasteners can outperform the fasteners made of 410 and 302 stainless steel (**Figure 1**). Not only the corrosion resistance, but also the mechanical strength and hardness for these NanoMate StainlessZ coated fasteners can exceed the stainless steel fastener requirements.



Fig. 1 — Nanmat's StainlessZ coated fasteners have corrosion resistance as good as stainless steel.

Black Diamond Fasteners by the New Process

Black hexavalent chromate passivation performance has been very difficult to duplicate until Nanmat's Black Diamond NanoMate fastener process. Black trivalent chromate conversion normally creates significant damage to the galvanic zinc layer which is very hard to improve even by adding a topcoat or chemical sealant. **Figure 2** shows the trivalent black passivation before and after the NanoMate coating. One can easily see, the porous structure of the black passivation is fully covered by the dense NanoMate coating. The performance for the "Black Diamond by NanoMate" easily outperforms other trivalent chromate processes, but also the black hexavalent chromate process as well. With only 2-3 µm of black NanoMate coating on black passivation, the performance meets not only black zinc (such as *GMW3044X*), but also black zinc-nickel's requirement (such as *GMW4700B*).

Table 2. Salt Spray Test Results (ASTM B117) for Different Fasteners in Production from Hexavalent, Trivalent Chromium and NanoMate Processes.

Product	Thickness (Plating)	Thickness (Coating)	Salt Spray Test	
			Hr. to White	Hr. to Red
Yellow Zinc (Cr6+)	3-5 µm	Cr 6+	48	150
Blue Zinc (Cr6+)	3-5 µm	Cr 6+	24	48
Blue Zinc (Cr3+) + Sealant (<i>GMW3044X</i>)	8 µm	2-5 µm	>120	>240
Black ZnNi (Cr3+) + Sealant (<i>GMW4700B</i>)	8 µm	2-5 µm	>196 (>72 hr. gray shadow)	>480
NanoMate Clear C500(Cr3+)	3-5 µm	0.5-1 µm	>200	>500
NanoMate clear C1000(Cr3+)	8 µm	1-2 µm	>500	>1000
NanoMate Yellow (Y1000(Cr3+)	8 µm	1-2 µm	>500	>1000
NanoMate black B240(Cr3+)	5 µm	1-2 µm	>120 (no gray shadow)	>300
NanoMate black B1000(Cr3+)	8 µm	2-3 µm	>300 (no gray shadow)	>1000
NanMate Cr-free	5 µm	1-2 µm	>120	>360

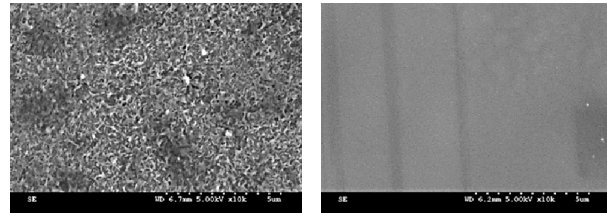


Fig. 2 — Surface microstructure for the trivalent black passivation before (l); after the NanoMate coating (r).

Nonchromate Conversion with the New Process

For the past few years, Nanmat has been working to develop chromate-free technology based on our NanoMate template. Ideally, the NanoMate coating would be applied directly over zinc plating. However, the white rust performance data for production lots was somewhat less than expectation. Recently a proprietary conversion process has been developed that will act as a base for the NanoMate coating.

The resulting SST data for this process can meet typical automotive industry requirement for zinc plating with sealant at >120 hours for white rust and >360 hours for red rust (*GMW3044X*, *Ford S437*, *VW TL217*, etc). By increasing the coating thickness and adjusting the conversion process, preliminary data has shown the possibility of exceeding the specification for Zn-Ni and Zn-Fe plating at >240 hour WR and >720 hour RR.

Figure 3 shows the surface microstructure for zinc plating, the chrome-free green conversion and the very dense surface after application of the NanoMate coating. One can easily see the crystal structure right after the plating may not be able to provide a good surface for NanoMate; but after the chrome-free green conversion, the nano-porous microstructure provides an excellent surface for the NanoMate coating to bond with. The extremely dense structure for the image in lower left of **Figure 3** can explain the high corrosion resistance performance perfectly.

This is the first time in history of zinc plating technology that a totally green technology chromate free, cobalt free, and heavy metal ion free, can meet or even exceed the performance of hexavalent or trivalent chromate. It can fulfill the all time goal for automobile and many other industries for environmental regulations. This technology represents a new

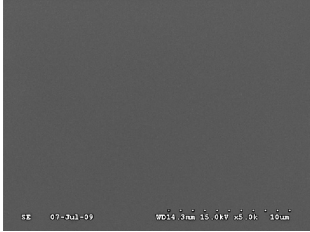
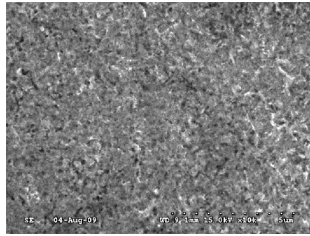
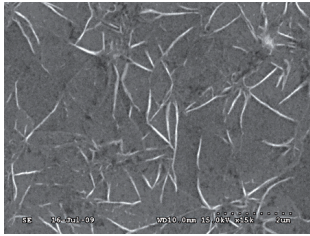


Fig. 3 — Microstructure for zinc plating (upper left), after chrome-free conversion (upper right) and after NanMate coating (left).

paradigm for zinc plating that will begin the next generation for surface finishing.

Conclusions

There is a growing realization that trivalent chromium conversion as an intermediate stage is the most commercially acceptable alternative. Certain drawbacks of trivalent chromium conversion such as high cost, poor color selections, etc., create opportunities for nonchromate alternatives on zinc-plated parts. By reviewing many nonchromium alterna-

tives, NanoMate process by organo-ceramic nano-material technology shows the most promising outcome even when compared with the many variants of trivalent or hexavalent chromium conversion processes.

For the replacement of conversion coatings on fasteners, the NanoMate process provides high performance, compatible appearance, low cost and lower operational and capital cost. This NanoMate process has not only created a totally new and effective mechanism of corrosion protection, but also brings in the most promising non-chromium alternative for hexavalent chromium on zinc-plated fasteners. Through the recent production and popularization of these NanoMate coated fasteners, a revolutionary and environmental friendly change of the fastener industry could be in a very near future.

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Company Profile:

Nanmat Technology Co. Ltd. was founded as a joint-venture between Nantex Industry Co., Ltd. and Chemat Electronic Materials, LLC, with the purpose of introducing world leading technologies. Nanmat has been focusing on advanced materials with strong R&D and technical service effort, combined with serious manufacturing and quality control systems. Nanmat offers CVD precursors, nano solution and surface treatment of fasteners. www.nanmat.com