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High Performance Alternative to Hexavalent Chromium Passivation of Plated Zinc and Zinc Alloys

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ABSTRACT

Hexavalent chrome passivates have been used for improving the corrosion resistance of sacrificial zinc and zinc alloy coatings on ferrous substrates for many years. However, forthcoming legislation and corporate policies are beginning to curtail the use of hexavalent chrome compounds and replacements are actively being sought.

Comparative corrosion resistance data is presented here. The data shows that the corrosion resistance of the trivalent passivates do not significantly diminish after thermal shock, as is the case with hexavalent chromates. This makes it particularly suitable for components that are subjected to high ambient temperatures.

No changes to the dimensional characteristics of the components occur. Recommended application areas include the engine compartment, brake components, fasteners of all sizes and fluid system components.

When used in conjunction with certain final finishes, these hexavalent chrome free passivates have the potential to replace more expensive alloy or dip spin type coatings.

INTRODUCTION

Zinc and zinc alloy plated coatings are applied to ferrous metals in order to give sacrificial corrosion protection to the base metal. However these sacrificial coatings are very susceptible to corrosion themselves particularly in conditions of high humidity. Corrosion products formed on zinc type deposits are generally referred to as 'white rust'. Prevention of white rust is usually achieved by application of a conversion coating, traditionally based on hexavalent chromium compounds. These treatments convert the metal surface into a complex mixture of chromium compounds giving excellent corrosion resistance.

However, hexavalent chromium compounds have long been recognized as carcinogenic. This, included with the need to increase the recyclability of vehicles has led to research for reliable alternatives that will achieve at least similar corrosion protection (to hexavalent types). The preferred alternatives to hexavalent chromium compounds are those based on less toxic trivalent chromium compounds. Table 1 shows the relative concentrations contained within some passivate films of differing colors and thickness'.

Table 1 Comparison between films containing hexavalent and trivalent chrome compounds*

Type	Cr^{+6} (mg/dm^2)	Cr^{+3} (mg/dm^2)	Total Cr (mg/dm^2)
Clear (trivalent)	**0**	**0.3**	**0.3**
Iridescent (trivalent)	**0**	**1.2**	**1.2**
Iridescent (hexavalent)	**0.7**	**2.0**	**2.7**
Green (hexavalent)	**0.4**	**9.6**	**10.0**
Black (hexavalent)	**0.7**	**9.3**	**10.0**

**See analytical methods I.*

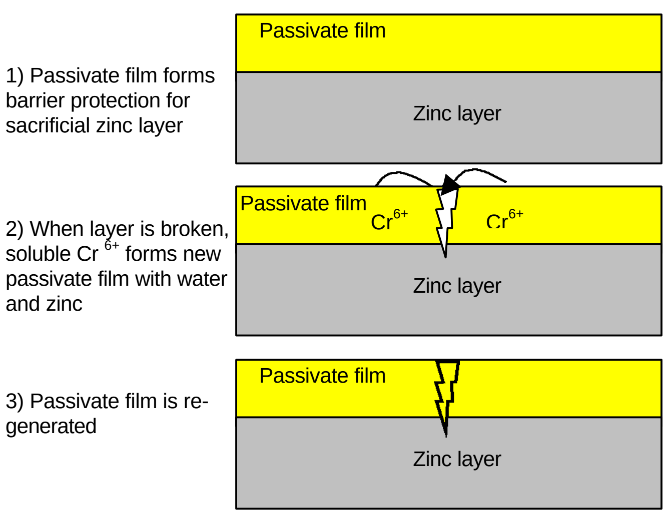
TRIVALENT PASSIVATES

Although trivalent passivates have actually been in use for some 20 years, their corrosion performance was always inferior to that of hexavalent chromates. Generally, only 'blue-bright' systems (with relatively low corrosion performance) for zinc plate had been available. However, new technologies mean that trivalent systems can now compete with and outperform the hexavalent types.

The new technologies discussed in this paper are suitable for zinc, zinc-iron, zinc-cobalt and zinc-nickel. The finishes obtained range from clear, to light iridescent, to gray depending on which deposit it is applied to. Particular attention is drawn to the success of trivalent passivated zinc-iron deposits.

Compared corrosion protection – When the new generation of trivalent passivates are compared against traditional zinc and yellow passivate we find that the results are very similar when tested in ASTM B117 neutral salt spray. Test results are given in the sections of this paper detailing application onto various plated deposits. These results confirm that the new trivalent passivates perform well even though they do not appear to exhibit the self healing properties of the scratched hexavalent chrome containing films (see Figure 1). Importance is placed on building a thick trivalent film to maximize the corrosion resistance, particularly in bulk (i.e. barrel) plating operations. For correct application a minimum application of one minute is recommended. This will give a coating film thickness of between 200 and 400 nanometers.

Figure 1 Diagram of self healing characteristic



THERMAL SHOCK RESISTANCE – Trivalent passivates were originally introduced to replace toxic hexavalent chrome compounds. Investigations have shown that the new trivalent systems show significant technical advantages over the hexavalent types. One of the most important advantages of these trivalent passivates is their resistance to thermal shock treatments. These tests involve subjecting components to high temperatures (300°F/150°C) for one hour before neutral salt spray testing to ASTM B117. This is to simulate the conditions 'underhood' where very high temperatures are encountered on components that are located near to the engine. Traditionally, hexavalent passivates perform poorly in this environment, losing in excess of 90% of their corrosion performance. This loss of performance is due to dehydration and 'cracking'[1] of the passivate film.

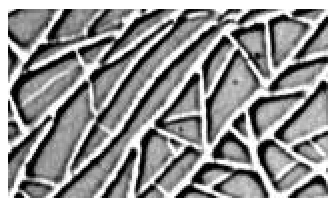
Scanning electron microscope images show the difference in the coatings after thermal shock (see Pictures 1 – 4). The thermal shock was for one hour at 300°F/150°C. The original SEM images were taken at 10,000 times magnification.

Pictures 1 to 4 Effect of thermal shock

(1) Hexavalent before thermal shock

(3) Trivalent before thermal shock

(2) Hexavalent after thermal shock



(4) Trivalent after thermal shock

The above pictures clearly show that hexavalent passivate films are micro-cracked. Generally, this is not a problem before the coating is subjected to heat, as the chromate can re-generate itself due to the presence of soluble hexavalent chrome products. Therefore as long as water and soluble hexavalent chrome remain present, self-regeneration is possible (see Figure 1). However, after being subjected to heat the film is dehydrated and self-regeneration can not occur[1]. As seen in Picture 2, the cracks also become very large. This process is generally assumed to begin at temperatures above 60ºC (140ºF).

In contrast the trivalent films show very little cracking even after heating, therefore the barrier coating protection stays relatively intact.

Dyeing of the passivate film – High corrosion resistant trivalent passivates produce a thick coating film. This film is thick enough to absorb a dye. This capability provides for color matching of components and/or bulk identification of plated parts.

Dimensional tolerance – The metallic coatings discussed in this paper are electrodeposited in rack or barrel applications. These methods of plating components have the distinct advantage of giving highly uniform deposits. This means that the problem of ‘thread fill’ commonly seen with other methods of coating fasteners is completely avoided. As passivation is carried out in aqueous solutions with a specific gravity close to water, there is no subsequent sticking together of components.

In line with traditional electroplated coatings, those passivated with trivalent passivates are able to withstand post plate deformation.

FURTHER IMPROVMENTS TO TRIVALENT PASSIVATES – It is very common today to apply a final finish to plated and chromated parts. This improves the corrosion resistance and/or the friction coefficient properties. Trivalent passivates also benefit from the application of a final finish. It has been found that the Organo-mineral type topcoats are particularly suitable. The term Organo-mineral is used to describe a coating containing a mixture of both organic and inorganic materials. These have the advantage of improving both corrosion resistance and modifying the friction coefficient. The improvement obtained for the friction coefficient[2] on passivated zinc is shown in Table 2.

Table 2 Comparison of zinc plated finish with and without torque-tension modification

Zinc & passivate finish +	**Under head friction coefficient***
No topcoat	0.41
Organo-mineral leach & seal type	0.10 – 0.15
Organo-mineral non leach	0.08 – 0.18
Dry film lubricant	0.10 – 0.15
Organic lacquer lubricant	0.10 – 0.15

**Actual friction value depends on specification requirements, type and concentration that the lubricants are applied.*

As most automotive specifications call for a torque-tension value (coefficient of friction) on fasteners between 0.10 – 0.15, data in Table 2 shows that unlubricated zinc is not acceptable. As passivates do not give improvements in torque-tension, a subsequent final finish or topcoat is usually required. The Organo-mineral types of finishes also have the advantage that they retain their lubricity after repeated fastening. Application of a final finish usually gives an attractive clear finish when applied over an iridescent trivalent passivate.

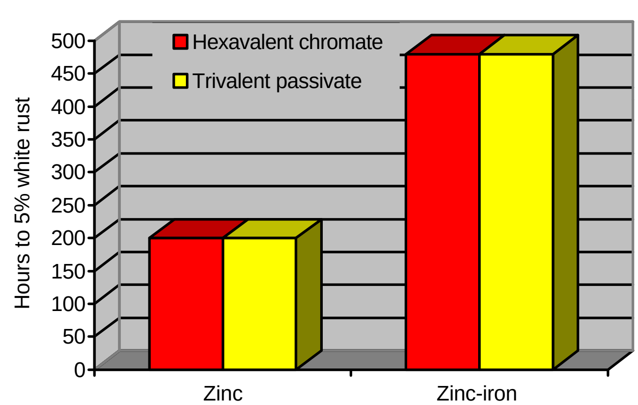
PASSIVATION OF VARIOUS PLATED DEPOSITS – The vast majority of sacrificial coating protection is applied by electroplating methods. Electroplating remains extremely economical, can be applied to bulk and larger items and gives a highly corrosion resistant finish. The new trivalent passivates have been successfully applied to pure zinc, zinc-iron, zinc-cobalt and zinc-nickel alloys.

ZINC – The majority of electroplated sacrificial coatings are still those of pure zinc. Although colors of blue, black and green are easily achieved, the majority of zinc plate is still post-treated in a ‘yellow’ or iridescent passivate. This coating remains popular because it provides a highly corrosion resistant deposit at very low cost and is globally available to high standards.

Therefore it is quite natural that research has been focused on finding an alternative to this passivate. The new trivalent based passivate to replace traditional yellow passivate is somewhat lighter in appearance and is iridescent. Comments have already been made by specifiers that this change in color is desirable as it gives end users an instant visual differential between components that are coated in hexavalent or trivalent finishes.

ZINC-IRON – The new generation of trivalent passivates work particularly well on plated zinc-iron. The film gives a clear to light coating with exceptionally good corrosion resistance. This coating has good potential as a lower cost replacement for the more expensive protective coatings. The corrosion resistance of zinc and zinc-iron coatings using the new passivate is shown in Chart 1.

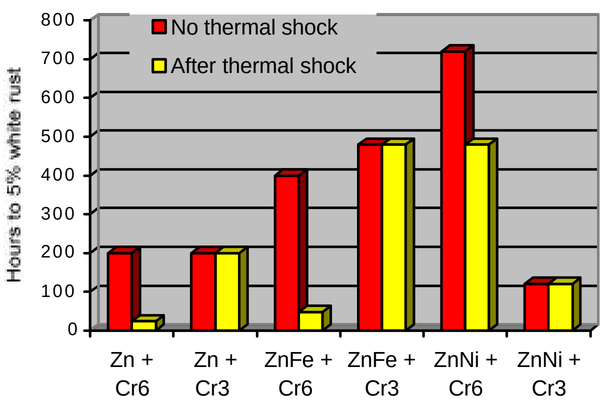
CHART 1
Comparing hexavalent and trivalent finishes on 8um zinc & zinc-iron plated steel panels



ZINC-NICKEL – Zinc-nickel coatings have been used for some years now, particularly for steel strip. The exceptional corrosion resistance of the deposit has led to developments for commercial electroplating of small components. The technology is now used extensively, especially on parts previously cadmium plated for the automotive industry. However, similar to other zinc coatings, the zinc-nickel deposit does require a conversion coating to give the excellent corrosion protection. Therefore continuing use of zinc-nickel in automotive applications requires an alternative to hexavalent chromate. The new generation of trivalent passivates has the ability to passivate zinc-nickel deposits. Finishes can give a blue-gray or iridescent film on high alloy deposits (12 – 15% Ni). Zinc-nickel differs to the alternative deposits outlined above when a trivalent passivate is applied. This is because hexavalent passivates appear to offer superior corrosion protection, even after thermal shock treatment. Therefore application of a final finish is advised when using a trivalent passivate on zinc-nickel.

Relative results to white rust can be seen in Chart 2. This chart also demonstrates the significant advantage to corrosion resistance of trivalent passivates after thermal shock treatment.

CHART 2
Thermal degradation of conversion coatings on Zn, ZnFe & ZnNi (12-15% Ni) plated steel panels



This resistance to thermal shock offers potential major cost savings in automotive applications. Zinc-nickel or metal filled organic coatings are often specified as an underhood treatment. As they show good resistance to thermal shock treatment processes. However, these coatings can be expensive. Therefore if a more economical deposit is used with a trivalent passivate, high performance can be achieved at significantly reduced cost. Given the data above, zinc-iron could be a good choice of deposit to meet today's needs for increased corrosion resistance after thermal shock.

USING THE NEW TRIVALENT PASSIVATES – The new type of trivalent passivate which gives this increased corrosion performance has been designed to fit in standard electroplating lines. Typical operating parameters are shown in Table 4. Attention is drawn to using the recommended operating parameters. In particular the makeup concentrations and immersion times.

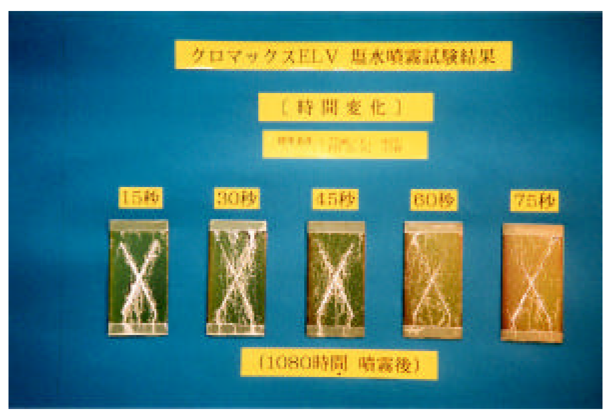
Equipment required is standard to most zinc and zinc alloy plating lines and consists of plastic tanks with titanium or Teflon heaters. As the solution will evaporate, solution dragout can be returned to reduce effluent treatment and chemical costs.

Table 4 Operating parameters of the new trivalent passivate systems

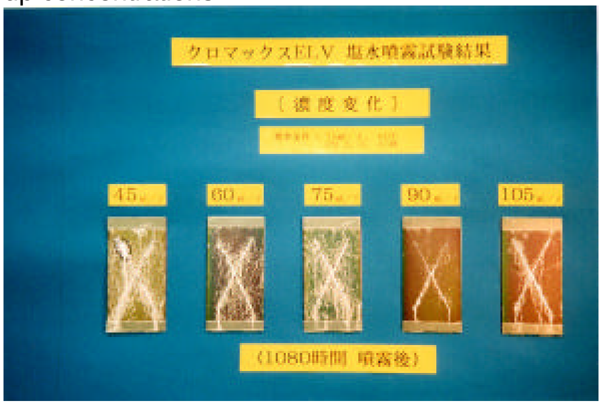
	RACK	BARREL
Concentration	9 - 12%	9 - 12%
Temperature	65°C (150°F)	65°C (150°F)
pH	1.9	1.9
Immersion time	45 sec	90 sec

Pictures 5 & 6 demonstrate the importance of maintaining the correct solution operating parameters. These pictures clearly show that full corrosion protection is not achieved until the operating parameters described in table 4 are applied.

Picture 5 This picture compares different immersion times.



Picture 6 This picture compares different make-up concentrations.



AREAS OF APPLICATION – The new generation of trivalent passivates now have the potential to replace the traditional hexavalent types in most applications. Parts can be treated in both rack and barrel.

With the application of a colorless final finish (see above) a clear finish is obtained. A black color can be achieved by application of a suitable organic film, usually directly on the passivate film. This means that the trivalent passivate is suitable for application on all automotive components currently sacrificially coated.

In common with most electroplated coatings, the finish will not change the dimensional characteristics of the component. This is particularly important when coating mass-produced items such as fasteners.

CONCLUSION

Trivalent passivates, originally introduced to replace hexavalent systems now show important technical and cost advantages over traditional hexavalent chrome passivated plated finishes and metallic flake dip-spin type coatings. Particular attention is drawn to the fact that the new range of trivalent passivates are able to withstand thermal shock treatments. They also have the advantage in being relatively simple to waste-treat and do not contain volatile organic compounds.

When used with inexpensive zinc or zinc-iron deposits, cost effective, high performance coatings can be obtained in a variety of colors, including black.

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2. Dave Crotty, MacDermid technical paper AD99-102 AUTOMOTIVE FINISHING'98
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   Detroit, Michigan
3. MacDermid inc. Table 2 references the following torque-tension modifying processes respectively: JS600, JS2000, Corrolub, T'n'T fluid and Maculube.

ANALYTICAL METHODS

I. Detection of chrome compounds –

The deposit and passivate layer is stripped in dilute mineral acid. The total chromium is then measured by Atomic Absorption. The chromate level is then determined by dionex chromatography. By subtracting the chromate concentration from the total chromium, a theoretical concentration of trivalent chromium can be calculated. However, this method can only be recommended for qualitative analyses as the method has some operational drawbacks:

a) Stripping zinc generates a reducing environment, and hexavalent chrome is readily reduced to trivalent chrome.
b) Leachability methods will extract some of the hexavalent chromium compounds into solution, which we can then measure. However, using this method it is difficult to know how much hexavalent chromium remains in the coating. Again the error is difficult to quantify.

II. Scanning Electron Microscope of Cr^{6+} and Cr^{3+} conversion films –

The SEM images were made under partial heat and vacuum.

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