Commercial performance of non-chromium (VI) passivates

The European Union directives have dictated a switch by galvanised steel sheet producers to remove hexavalent chromium compounds from their products. Henkel have responded by providing two alternative sheet passivates, one totally chromium free, and one using only trivalent chromium. Corrosion performance of all the new products are very comparable to the hexavalent product and are in commercial use.

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Passivates are applied on Zn and AlZn coated steel to prevent corrosion. To build up such protective layers, traditionally hexavalent chromium compounds have been used which act as base for numerous subsequent operations like adhesive bonding, forming or painting. With the advent of the European Union directive prohibiting the use of certain chromium compounds, interest in hexavalent chromium-free coatings by the coil and steel industry has changed from an academic interest to an urgent commercial issue. Chemical suppliers are meeting this challenge by bringing new hexavalent chromium-free products to market.

There are two new regulations causing the concerted effort to remove hexavalent compounds from steel passivate coatings. First is the European Union `Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment Regulations`(RoHS). This regulation specifies the elimination of hexavalent chromium, and several other chemicals on new electrical and electronic equipment by July 1, 2006. This equipment includes items such as appliances, air conditioners, IT and telecommunications equipment, television sets and video recorders. Second, the European Union has a directive concerning `End of Vehicle Life` which is to ensure that any vehicle sold in the European Union does not contain hexavalent chromium after July 1, 2007. Consequently, in order to be used in the construction of items regulated by this new legislation, flat rolled steel parts must be hexavalent chromium-free by July 1, 2007.

In these regulations, the use of the provision `hexavalent chromium-free` is significant since the European Union regulations do not prohibit the use of chromium; rather they prohibit the use of chromium in the +6 valence state. This specification does not regulate the use of chromium(III) compounds. To comply with the regulation a passivation product may be comprised of only Cr(III) or chromium-free materials.

Henkel has developed both, a completely Cr-free passivation product range as well as passivates based on Cr(III) compounds.

CHROMIUM-FREE PASSIVATES

The elimination of hexavalent chromium from the traditional passivates has performance consequences, as compounds containing Cr(VI) have proven over the years to be good corrosion preventatives at a reasonable price. The chromium in the coatings formed is generally a mix of Cr(VI) and Cr(III) species and the solutions are usually applied by a `flood squeegee` method at a chromium coating weight of 10-20 mg/m^2. They are applied at ambient temperatures and are dried by a hot air dryer. Typical corrosion performance for these coatings is 96+ hours to < 5% white rust in the neutral salt spray test (NSS), and similar good performance in stack corrosion tests (1008 + hrs). They also dramatically outperform rust preventative oils in these tests.

Using the above performance as a benchmark, various ionic species have been tested to replace these traditional chromium based passivates including, but not limited to, salts or complexes of molybdenum, vanadium, titanium, manganese, zirconium or cobalt, as well as silane additives. Passerite® 5004 passivate was developed by Henkel and it contains phosphates and fluorides of manganese, molybdenum, and titanium along with a small quantity of organic polymer. The recommended application parameters for this passivate are as follows:
Passerite 5004 can be applied in existing lines provided ▷

Concentration of bath: Bulk Density BD [g/cm^3]

Bath pH: 2.5 - 3.5

Bath temperature: < 40°C

Strip PMT: 50 - 60°C min, 120°C max. (PMT = peak metal temperature)

Drying time: < 10 seconds

Coating weights: 0.3 - 0.8 g/m^2, 0.5 is typical

Application method: Flood/squeegee or roll coater

they are made from stainless steel and if application conditions are very similar to those of chromate passivates.

Using the parameters above, typical corrosion performance of treated hot-dip galvanised sheet is as follows:

The above results compare favourably with those of hexavalent chromium passivates, except for the NSS test, where performance is lower than that found for the traditional Cr(VI) containing passivates. The cyclic test results, however, are better than that typically found for hexavalent chromium passivates. In outside weathering, panels showed no corrosion after nearly two years.

Neutral salt spray (NSS): 36 - 72 hrs, < 5% white rust for HDG steel, 192 hrs - 20% white rust

Wet stack test: 1008 hrs, 5 - 15% white rust

KTW cyclic test: 20 - 30 cycles (DIN 50017), < 5% white rust

Based on the good performance of the Passerite 5004 passivate on hot dipped galvanised (HDG) steel substrate *(see Fig. 1)*, various other substrates were also tested. These included, Galvalume®, galvanneal and electro-galvanised steels, as well as aluminised substrates - all with good results. In particular, laboratory testing on Galvalume gave the following corrosion test results:

NSS: 72hrs - 1% white rust, 192 hrs - 20% white rust

Stack tests: 1008 hrs - 0.0 - 0.1 % white rust

C level and condensing humidity: 1008 hrs - 5% white rust

CHROMIUM (III) (TRIVALENT CHROMIUM) PASSIVATES

As the RoHS directive does not specify the elimination of chromium from the passivate coatings, but rather the elimination of hexavalent chromium, there has also been interest in using trivalent chromium products. This allows the retention of some of the advantages of the chromium-based passivates while still complying with the regulation regarding the elimination of hexavalent chromium. Cr(III) products have been in use for several decades and are typically somewhat less expensive to apply than non-chromium based passivates.

The initial introduction of Henkel's Passerite 6001, a trivalent chromium passivate, was very successful. Further refinement of the coating bath was made to improve some application issues found on some lines, resulting in introduction of Passerite 6003. Both products are used commercially in Europe and North America.

The application parameters for Passerite 6001 and 6003 are similar:

Bath concentration: 10 - 100% dependent on the flow to the line, 20 - 50% is typical

Bath pH: < 3.5

Zn dissolution in bath: < 1.8% by weight

Bath temperature: < 50°C

Strip PMT: 45 - 100°C

Drying time: < 10 seconds

Application method: Flood/squeegee, roll coater

Coating weight: 175 - 300 mg/m^2

Cr coating weight: 30 - 60 mg Cr/m^2

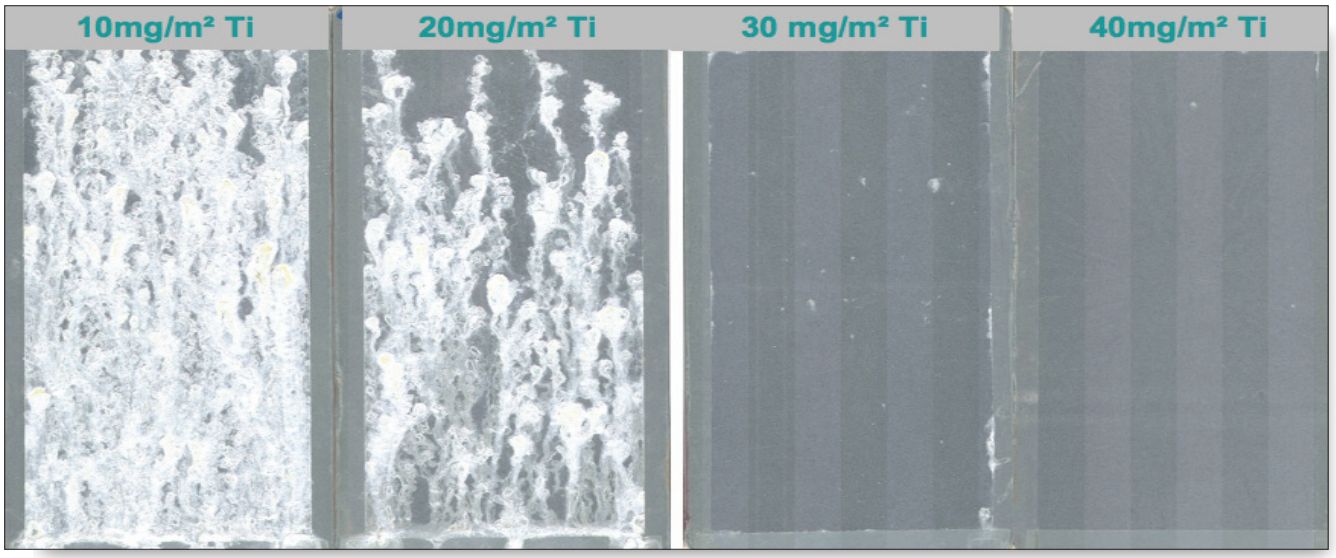

Fig.1 **Passerite® 5004: Bare metal corrosion protection after 72 hours neutral salt spray test on HDG steel**

The typical corrosion results for Passerite 6001 and 6003 are:

Neutral salt spray: 36 - 72 hrs, < 5% white rust

Stack test: 1008 + hrs, < 5% white rust

KTW cyclic test (DIN 50017): 20+ cycles, < 5% white rust.

These results compare favourably with the traditional Cr(VI) passivates, and the Neutral Salt Spray results are somewhat better for both these products than for the non-chromium Passerite 5004. However, the KTW results are slightly better for Passerite 5004 than for Passerite 6001, 6003, or for the traditional passivates. Typically, Passerite 6001 and 6003 are coated in the range of 30 - 60 mg Cr/m^2 since lower coating weights can give lower passivation protection. Bare metal corrosion performance of Passerite 6001 is shown in *Fig 2*.

Passerite 6001 and 6003 have been tested on multiple substrates, including HDG steel, Galvalume, galvanneal, aluminised, and electrogalv (EG). The trivalent chromium products outperform Passerite 5004 on aluminised substrate and in de-ionised (DI) water immersion testing, but Passerite 5004 performs best in wet stack testing. A number of mills in Europe and North America have converted to Passerite 6001 and 6003 passivates, thereby complying with the various regulations limiting hexavalent chromium.

Paintability and formability were also explored relative to the traditional passivates. Formability was improved over traditional chemical treatments for all three products. At coating weights greater than 300 mg/m^2, Passerite 5004 showed the best formability of these passivates (coefficient of friction COF < 0.10). As with traditional passivates, paintability of all three products is variable, dependent upon substrates, paints, preparation and performance criteria. Painted corrosion performance of different Cr (VI)-free passerites and two powder paints are shown in *figure 3*.

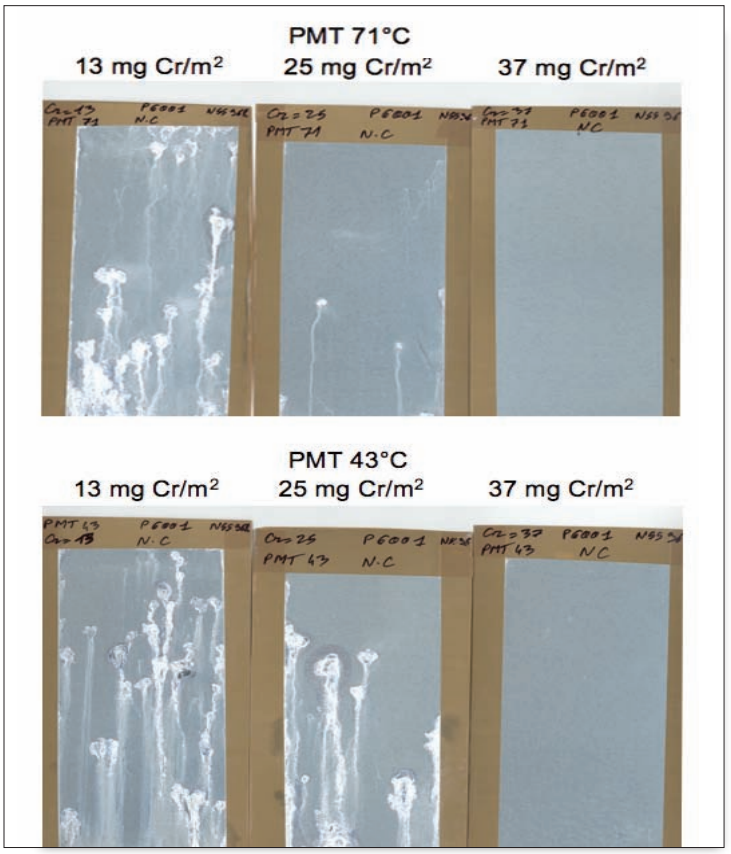

Fig.2 **Passerite 6001: Bare metal corrosion performance after 96 hours neutral salt spray test on HDG steel**

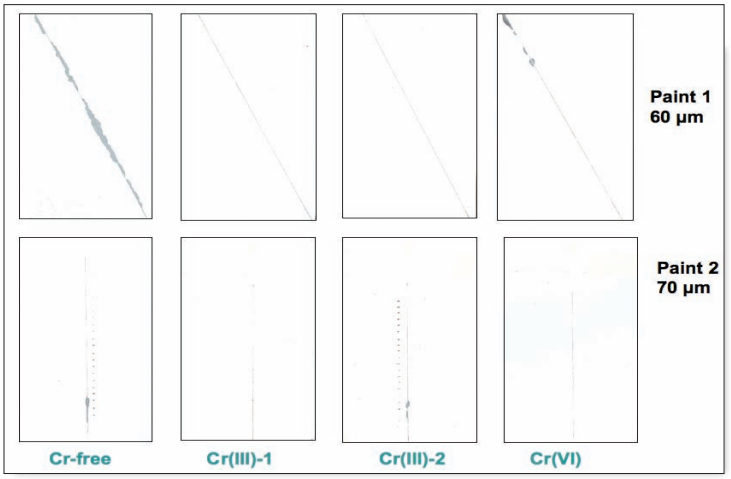

Fig.3 **Painted corrosion performance of different Cr(VI)-free passerites and two powder paints after 240 hours neutral salt spray test on HDG steel**

CONCLUSION

The European Union RoHS directive has dictated a switch by galvanised sheet producers to remove hexavalent chromium compounds from their products. Many other countries have already followed suit or have pending regulations similar to RoHS. In response, the worldwide steel industry has moved to comply with these regulations. Both Cr(III) and non-Cr products have been developed and commercialised to comply with these regulations; and have garnered great interest worldwide. Although some coaters find that these replacement products may require more attention to application than chromate passivates, these hexavalent chromium-free treatments comply with the new regulations and still provide good protection to metal sheet.

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