Chromium-free pre-treatment for coil coating

Chromium-free coil pre-treatment provides equivalent or better performance to conventional coatings, but with significantly reduced environmental impact. Henkel's Granodine 1455 can be used with a wide range of paint systems and substrates using all of the current coil coating application methods.

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Chromium-free pre-treatments for the coil coating industry have been commercially available for many years; products for aluminium have been available for more than 20 years, although these have been limited mainly to non-sterilised packaging applications such as can end stock, and for steel-based substrates, products based on titanium have been available for more than 10 years. Until recently, there has been a low demand for these pre-treatments in the automotive, appliance or architectural markets. This was due to the excellent performance and track record of chromium-based products, whether they were based on no-rinse or reaction/rinse technology.

With the introduction of new environmental legislation such as the End of Life Vehicle directive (ELV), the Waste Electrical and Electronics Equipment directive (WEEE) and the Registration Evaluation Authorisation and restriction of Chemicals (REACH), demand for chromium-free pre-treatments has increased in both the automotive and appliance markets. A similar demand for such pre-treatments in the architectural market has not yet materialised, but is envisaged in the near future.

Granodine 1455 is Henkel's solution to this demand; it is flexible in application method, and substrate and end-use applications, while giving performance that is as good as the chromium-based products currently in use today.

PRODUCT CHARACTERISTICS

Granodine 1455 is a no-rinse, single pack, chromium-free pre-treatment for coil coating that produces a uniform, virtually colourless, clear coating that improves the adhesion and corrosion properties of painted materials. It is suitable for a wide range of end use applications such as architectural, appliance, automotive, general industry uses and adhesive bonding.

Composition Granodine 1455 is based on titanium technology combined with a water-soluble organic polymer. ESCA (Electron Spectroscopy for Chemical Analysis) depth profile of a sample of hot dipped galvanised steel (HDG) pre-treated with Granodine 1455 is shown in *Figure 1*, and shows an atomic percentage distribution of the surface coating. The zinc originates from the substrate and its distribution through the whole coating confirms a conversion-type coating. The carbon is significant for the polymer; enrichment on the surface can be seen.

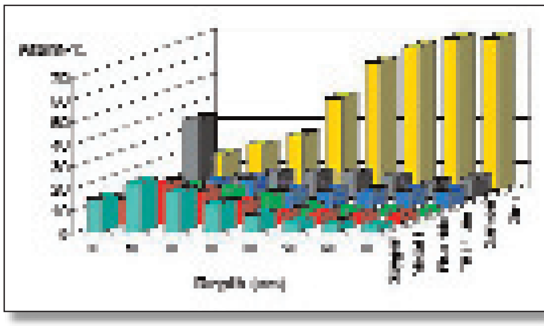

Fig.1 ESCA depth profile of HDG pre-treated with Granodine 1455

Substrate compatibility Granodine 1455 is currently used today, with exceptional performance, on a wide range of substrates such as:

- Hot dipped galvanised steel (HDG)
- Electrozinc
- Galfan
- Galvalume
- Galvanneal
- Cold rolled steel (CRS)
- Stainless steel
- Aluminium
- Aluminised steel

APPLICATION METHODS

It is applied on coil coating lines using all of the methods currently available, namely Chemcoater, the Coiltech system and conventional dip or spray followed

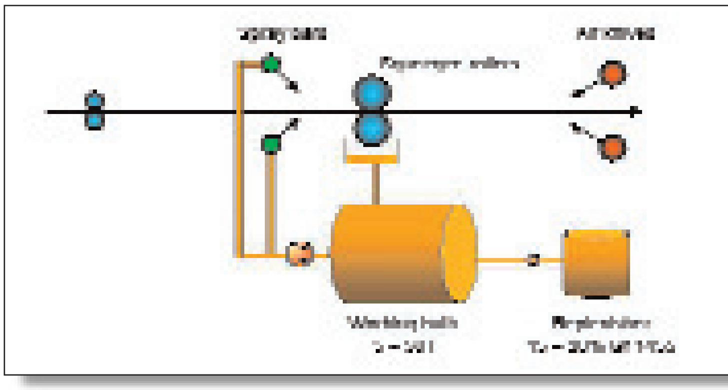

Fig.2 **Coiltech application schematic**

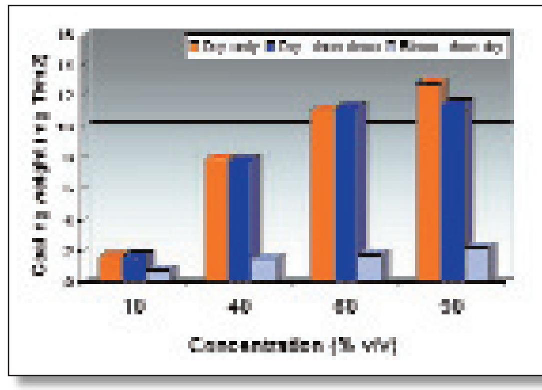

Fig.3 **Granodine 1455 coating stability**

by squeegee. The Coiltech application method has been in use in the coil coating industry for more than 17 years. In its simplest form, it consists of a pump that applies the product to the strip (by low pressure sprays) just prior to a set of squeegee rollers. As these rollers are not 100% efficient, a wet film of product measuring one to three microns is left on the strip and subsequently dried. Excess product is returned to the product reservoir via a catch tray situated under the strip (see *Figure 2*). As seen, the application method has a considerable influence on both the operating and control parameters of the working bath.

Chemcoater and Coiltech systems The application of Granodine 1455 using either a Chemcoater or Coiltech system requires similar solution parameters and control methods. Normally a makeup solution of the correct strength is first prepared and this is then used to maintain the level of a working bath supplying the coater heads. Typical application conditions are detailed below:

- Make up: 6–20% v/v
- Temperature: 20–40°C
- Drying: >40°C

Various methods can be used to determine the concentration of Granodine 1455, the choice of which depends to some extent upon whether the makeup or working solution is monitored. Some examples are indicated below:

- Makeup bath: Free acid, polymer titration, conductivity, photometric (titanium)
- Working bath: Polymer titration, conductivity, photometric (titanium)

Generally, no other control methods are required due to the low volumes, short replenishment times and high concentrations used. Granodine 1455 is normally applied to the strip at coating weights of 2–10mg titanium/m^2. For some systems using CRS, where corrosion resistance is more critical, good results have been achieved with slightly higher coating weights of up to 15mg titanium/m^2. Coating weights can be determined either on-line or off-line using a number of methods. These include:

- On-line:
  - Wet film using Infra-red spectroscopy
  - Wet film using product consumption and surface area processed
  - X-ray fluorescence spectrometry (titanium)
- Off line:
  - X-ray fluorescence spectrometry (titanium)

The coating deposited using either a Chemcoater or Coiltech application method consists mainly of an unreacted, metered layer with a thin reacted layer at the metal pre-treatment interface. Prior to drying, rinsing with de-ionised water results in the removal of all but this small reacted portion of the coating. When the coating is dried prior to rinsing, experiments have shown that more that 95% of the coating remains on the surface. This is illustrated in *Figure 3*. HDG panels, pre-treated with Granodine 1455 at a number of different concentrations, were treated in a number of ways before the titanium coating weight was measured using X-ray fluorescence spectrometry. The panels were either dried after pre-treatment, dried and then rinsed with de-ionised water, or rinsed with de-ionised water while the pre-treatment was still wet and then dried.

Conventional dip or spray system The final application method is more conventional, involving a dip or spray process followed by squeegee rolls, a schematic of which can be seen in *Figure 4*. This requires a different set of operating conditions to those outlined above owing to a different deposition mechanism. In this case, the majority of the coating arises through a

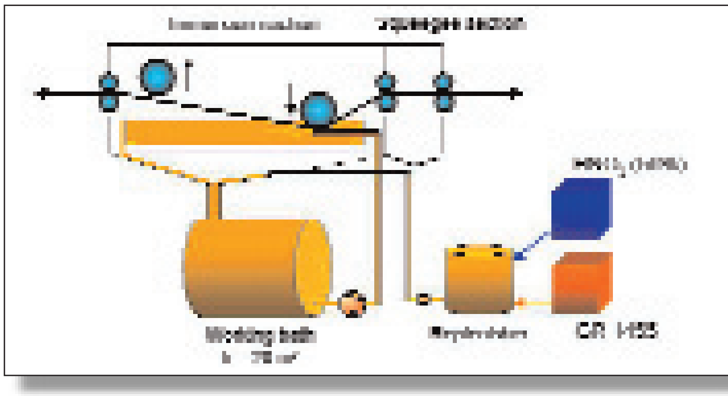

Fig.4 Conventional dip application schematic

reaction between the pre-treatment and the metal surface. Only a small proportion is metered onto the strip by the exit squeegee rollers. Typical application conditions are shown below:

- Make up: 1–5% v/v
- Temperature: 25–40°C
- Contact time: 1–5 seconds
- pH: 3–3.6
- Drying: >40°C

The coating weight deposited in this way is 2–6mg titanium/m² and is measured using X-ray fluorescence spectrometry. It is influenced by a number of factors including pH, time and temperature. Most working baths are controlled by pH, whose range must be kept between 3 and 3.6. Below pH3, the bath is too reactive and little coating is deposited, above pH3.6, the bath can become unstable. The pH is adjusted using either ammonia (usually during initial make up only) or nitric acid. The working solution is analysed photometrically or by inductively coupled plasma spectrometry (ICP) on a weekly basis for constituents and contaminants. The key control limits are indicated below:

- Titanium > 80ppm
- Zinc < 4,000ppm
- Aluminium < 100ppm
- Iron < 20ppm
- Sodium < 1,000ppm
- Nitrate < 8,000ppm
- Chromium < 5ppm

PERFORMANCE

Granodine 1455 has been found to give comparable performance to chromium-based pre-treatments on a wide range of substrates and paint systems. This is illustrated in *Figures 5* and *6* where the performance of Granodine 1455 has been compared in laboratory trials

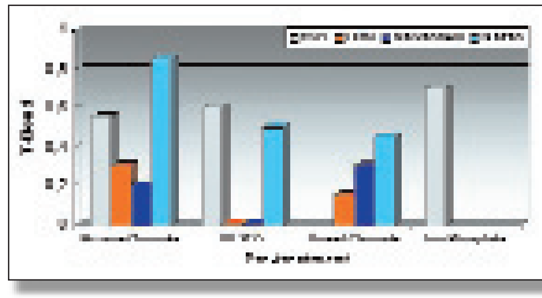

Fig.5 T bend adhesion performance with alternative pre-treatments and substrates

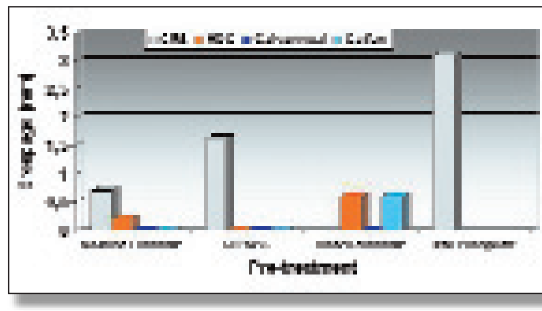

Fig.6 Corrosion performance

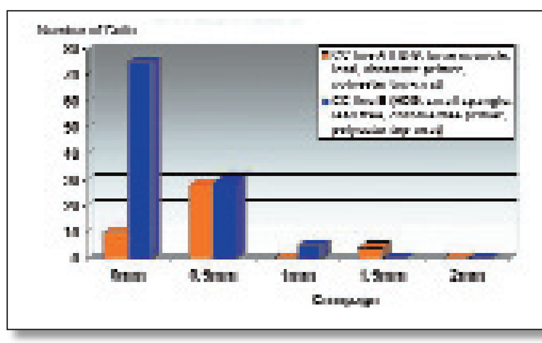

Fig.7 Neutral salt spray performance

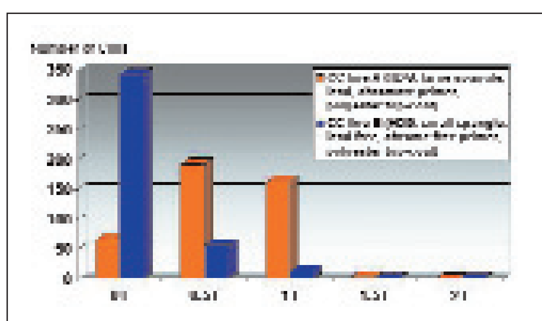

Fig.8 T bend adhesion performance, comparison of coating lines

to a no-rinse chromate, a conventional chromium rinsed product with a chromium post rinse, and an iron phosphate with a chromium post rinse on HDG, Galfan, Galvanneal and CRS. The paint system comprises a chromium-free primer (5 micron) under a polyester ▷

top-coat (20 micron). The performance of Granodine 1455 on galvanised material was found, in many cases, to be better than the chromium based pre-treatments.

The excellent performance of Granodine 1455 can best be appreciated by reviewing the test results of material actually processed on coil coating lines. Such an analysis is illustrated in *Figures 7* and *8* for two lines, designated line A and line B. In *Figure 7* creep is assessed after 360 hours for line A and 504 hours for line B. For line A, large spangle, lead-containing HDG was assessed with a chromium primer and polyester top-coat while for line B, small spangle, lead-free HDG was assessed with a chromium-free polyester universal primer under a polyester top-coat. The performance from both lines is very good with line B predictably giving better results than line A.

AUTOMATIC DOSING AND CONTROL

Automatic dosing and control can be readily achieved using Henkel's Lineguard range of equipment. These are tailor-made for each individual coil coating line and are especially suitable for Chemcoater or Coiltech applications. The equipment automatically pre-dilutes Granodine 1455 to the correct application strength and then delivers it to the line's application system via a recirculation reservoir. The Lineguard equipment continually and automatically maintains the volume in this reservoir. The system can be modified to provide on-line coating weight measurements if required. Using such equipment dramatically reduces the interaction between the line operator and the pre-treatment, thus improving safety while reducing time commitments.

CONCLUSIONS

Since its commercial introduction in Europe in 1998, 12 lines have converted to this chromium-free alternative coil coating pre-treatment, with more planned in the near future. Although the production on these lines is predominantly steel-based, many of them also process aluminium for a range of applications.

Granodine 1455 has demonstrated that it is a viable alternative to chromium-based pre-treatments under a wide range of paint systems and on a wide range of substrates using all of the application methods currently operating on coil coating lines. MS

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