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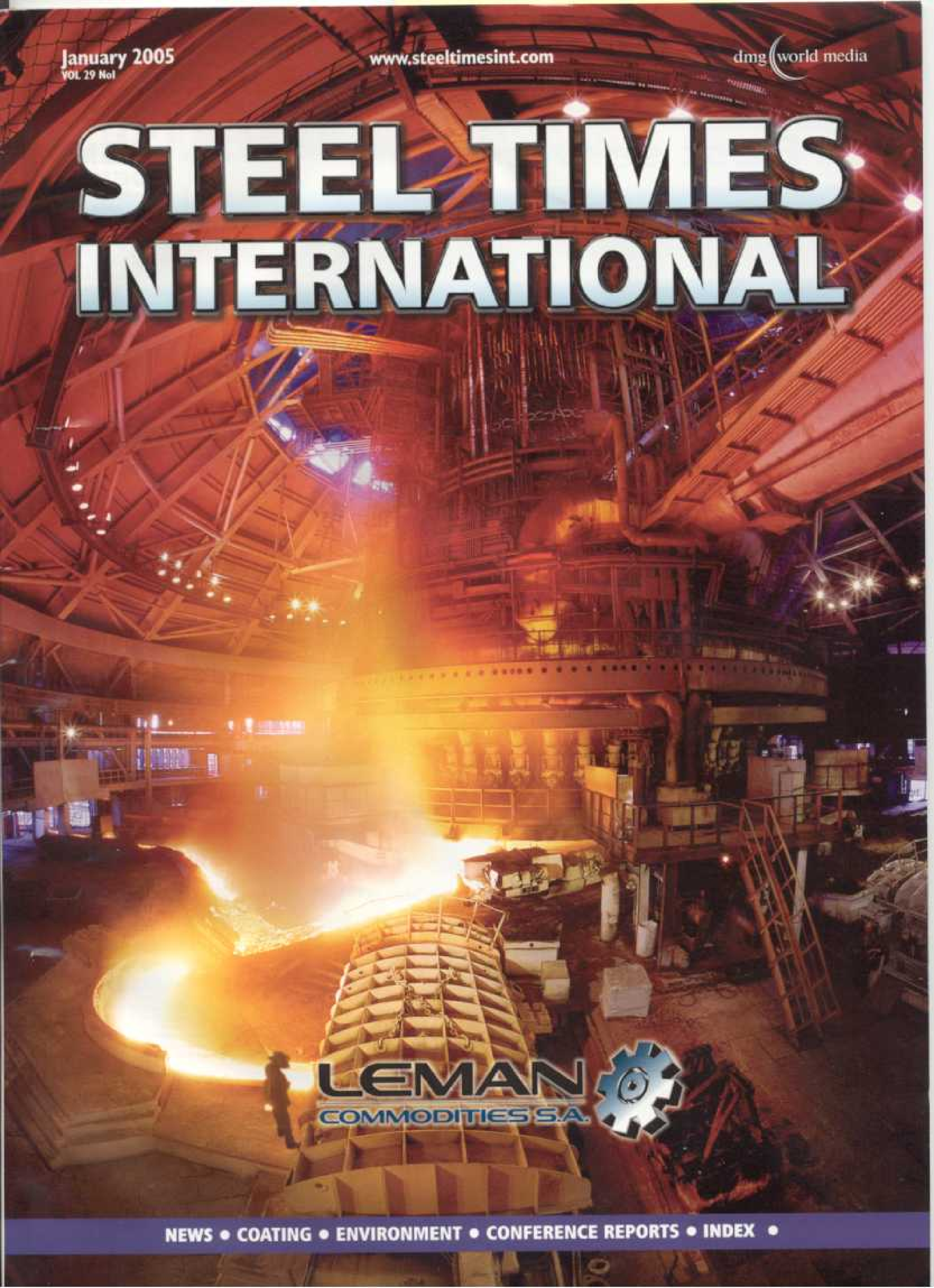

NEWS • COATING • ENVIRONMENT • CONFERENCE REPORTS • INDEX •

The new Techint electrolytic tinning line at Aceralia Aviles

Aceralia is successfully completing a major phase in the modernisation of its tinplate facilities at its plant in Aviles, Spain. Modernisation has included the construction of a new 250kt/y electrolytic tinning line, which has achieved its design parameters in a relatively short period of commercial operation.

BY G ASTENGO, P COMELLI & L CORONEL

To address increased market demand and also to improve product quality, Aceralia (Arcelor Group) decided to install a new Electrolytic Tinning Line (ETL) at its plant in Aviles, Spain.

The new ETL can process strip up to 1250mm wide and has a capacity of 250kt/y. The line is mainly destined to produce very high quality materials in wide format to supply stamping lines for beverage cans. The line uses Phenol sulphonic acid (PSA) electrolyte but sufficient space has been left to convert to Methane Sulphonic Acid (MSA) and for inserting Tin Free Steel (TFS) coating tanks with relevant circuits, should the demand arise.

The contract was signed in December 2001 with a consortium consisting of Techint Compagnia Tecnica Internazionale SpA (Techint Technologies, Italy) and the locally based companies UTE Linea de Hojalata N3 composed of Duro Felguera Plantas Industriales SA, PHB Weserhütte SA, Ingemas SA and Daorje SA. A separate contract was signed with two electrical companies, TSK and Ingelectric.

Erection works started in October 2002 and shipment of equipment commenced at the close of 2002. After completion of individual running tests of each part of the line, the cold run and hot run stages were performed and the first trial plating realised in October 2003. The plant is now in full commercial operation and is producing first quality tinplate (**Fig 1**).

DESIGN PARAMETERS

The basic design parameters of the line are summarised in **Table 1**.

The ETL is capable of depositing coatings from $1.00g/m^2$ to $11.2g/m^2$. All combinations of differential coatings from $1.12/2.24g/m^2$ to $8.4/11.2g/m^2$ can be produced. The most common product of the equal coating per side is $2.8/2.8g/m^2$, and for differential coating is $2.8/8.4g/m^2$.

LAYOUT & FEATURES

The overall line length from the axis of Payoff Reel No 1 to the axis of Tension Reel No 2 is 140m.

The main features of the tinning line are:

Entry Section
- Double Payoff Reel system
- Two Thickness Gauges
- Double Cut Shear
- Narrow Lap Seam Welder with Preloader
- Notcher
- Turret Type Side Trimmer
- Scrap Bailer
- Double Entry Loop Towers (24 strands each)

Process Section
- Electrolytic Cleaning section
- Tension Leveller
- Electrolytic Pickle section
- TFS Plating section (space prevision)
- Tin Coating Weight Gauge
- Differential Markers
- Induction Reflow and Quench section
- Chemical Treatment section

Exit Section
- Exit Loop Tower (24 strand)
- Inspection Stand
- Instrument Stand with Laser Pinhole Detector & Thickness Gauge
- Flying Shear
- Dual Tension Reels

DESIGN FEATURES

ENTRY SECTION

The entry section features a dual Pay-off Reel. This arrangement, along with the thickness gauges, shear and welder preloader, allows the coil to be loaded and the entry section to reach process speed in a very short time (**Fig 2**).

Parameter	
Electrolyte*	Phenol sulphonic acid (PSA)
Production Capacity	
Tinplate	250kt/y
Tin Free Steel	Space provision
Line Reference Length	200m approx.
Material Specification	
Thickness	0.10 to 0.50mm
Width	600 to 1250mm
Coil Weight	25 000kg max
Coil OD	up to 2100mm
Line Speeds	
Entry & Exit Sections	650m/min max
Process Section	500m/min max
Threading Speed	30m/min
Exit Section Shear Speed	80m/min max
Coating Thickness (per side)	
Tin Coating	$11.2g/m^2$ max
	$1.00g/m^2$ min
Oil coating Type	DOS and ATBC
	$2.5\text{-}20mg/m^2/side$

Space provision for Methane Sulphonic Acid (MSA)

Table 1 Basic design parameters

1 The new 250kt/y tinning line at Aceralia Aviles

2 Pay off reel

The thickness gauges are located on each pass line of the entry section. These gauges monitor the strip thickness of each coil. The double cut shear will then cut out the off-gauge material and this is deposited into the scrap bins located alongside the line. The welder is a Mieback horizontal narrow lap welder with preloader. The strip is fed into the welder while a coil is running. This coil head end is ready to be welded when the running coil is completed. The weld time is generally 17 to 18 seconds, depending on the width and thickness of the strip. The notcher, used to identify the weld position, is located immediately after the welder to allow the side trimmer to be adjusted for width or knife changes.

A turret type side trimmer is also located in the entry section of the line. This trimmer trims the strip to the desired width and reduces the possibility of strip breaks in the loop tower and leveller due to bad strip edges. This machine consists of two movable housings each containing two pairs of knife arbors (one pair operating, one pair standby). Each movable housing is adjustable for width changes. The housings also rotate 180 degrees for placing a new set of knives online and a worn set offline. Adjustments are also provided for radial and axial knife clearance. Radial adjustments of the knives are achieved via servo drives through a special eccentric arrange-ment of the knife cartridge. This

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eccentric adjustment is accomplished without reducing the drive gearing mesh (**Fig 3**).

There are two knife drives for the side trimmer. Each drive is mounted on an hydraulic shifting base so that the drives can be disengaged when the knife housings are rotated for changing cutters. Variable speed AC motors drive the knives.

3 Rotating turret edgetrimmer

The scrap from the side trimmer is sent to a bailer hopper located below the trimmer in the basement. The bailer takes these edge trimmings and compresses them into a bail measuring about 200 x 400mm, which is conveyed into a scrap bucket for easy handling and removal by overhead crane.

A double loop vertical accumulator tower is located between the entry section and process section. This can contain sufficient stored strip to maintain the process section at full speed during coil loading operations. Each tower has its own drive, which operate in unison with each other. Each tower contains 24 strands and has a total carriage travel of 21.6m. Eight helper roll drives are included to reduce tension build-up within the towers (**Fig 4**).

PROCESS SECTION

The process section starts with a cleaning section to remove the surface dirt and oils that have collected during prior processing operations. This cleaning section employs electrolytic cleaning for efficient removal of these soils from the strip. To increase the cleaning efficiency, necessary especially in the case of Double Reduced strip, a brushing machine is installed downstream of the electrolytic cleaning tank. Following cleaning, the strip is rinsed and dried and then enters the tension leveller to ensure flatness.

Following the tension leveller the strip enters the Pickling Unit. The purpose of this unit is to remove oxides and rust from the strip and to lightly etch the strip to present a clean and active steel surface to the plating section. This process is also performed using electrolytic action, similar to the cleaning step. The strip is rinsed and enters the Tin Plating section following the pickling step.

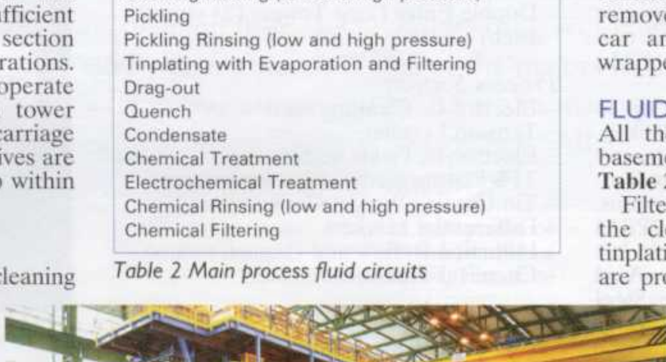
The tinning process uses Phenol Sulphonic Acid (PSA) as the plating medium. Eleven plating tanks are installed and two drag-out tanks. One half of the final cell in the plating section is equipped with insoluble anodes to control the tin concentration build up in the bath. The high speed of the line made it necessary to place splashguards around the strip as it leaves the plating bath. The function of the first drag-out tank is to reduce the loss of electrolyte as it adheres to the strip on leaving the last plating tank. The second drag-out tank adds the correct concentration of flux on to the strip surface for subsequent flash melting of the coating to a bright finish.

Following the plating section there is a tin coating weight gauge to measure and control the coating thickness.

The electrolytically deposited tin coating has a dull matte appearance. To form the continuous surface layer of tin and create the tin-iron alloy required for good corrosion resistance, the strip is heated to above 232°C, the melting point of tin, by passing it through high frequency induction coils. The tin melts within seconds and is then quenched to produce a bright lustrous finish free of stains or films caused by plating solution drying on the strip. For the best set up of the quench, both in terms of temperature and in terms of fluid dynamic, regulators for the spray headers are provided. The quench liquid is recirculated by three pumps (3+1 standby) from a tank placed in the basement. The quench control system can adjust the flow-rate on each strip face so as to control surface temperature.

Alkaline Cleaning
Electrolytic Cleaning
Brush Cleaning
Ultra filtering
Cleaning Rinsing (low and high pressure)
Pickling
Pickling Rinsing (low and high pressure)
Tinplating with Evaporation and Filtering
Drag-out
Quench
Condensate
Chemical Treatment
Electrochemical Treatment
Chemical Rinsing (low and high pressure)
Chemical Filtering

Table 2 Main process fluid circuits



4 Double loop accumulator tower at Aceralia

The pre-treatment and chemical treatment step is used to chemically or electrochemically stabi-lise the tinplate surface. This is to minimise oxidation, which can occur on the surface of tinplate during storage.

EXIT SECTION

The exit loop tower separates the exit and the process sections. A loop accumulator tower provides storage of strip at periods when the exit section slows down for coil terminations. The total travel of this 24-strand tower is 21.6m.

A vertical inspection station is located on the down pass exiting the loop tower (**Fig 5**). This station is equipped with mirrors and strobe lighting to view both sides of the strip. Manual inspection and a camera based inspection system are both used by Aceralia. The instrument stand consisting of a pinhole detector and a thickness gauge located in the exit section to monitor strip quality as it is recoiled.

Several exit section components help reduce the capacity needed in the exit loop tower by minimising slowdown in this section. A flying shear is provided to shear the strip at speeds of up to 80m/min. As the strip is sheared, the shear transfers the strip from one pass line to the other, directing the strip to the next tension reel group. The shear can also be used to cut strip for up to three samples. These are separated from the passing strip and brought into the reach of the operator by an elevator device.

The tension reel ramps up to line speed as soon as there are several wraps on the tension reel drum. The completed coil is removed from the tension reel by the coil car and the tension reel and the belt wrapper are prepared for the next coil.

FLUIDS RECIRCULATION

All the fluid circuits are located in the basement. The main circuits are listed in **Table 2**.

Filtering units to remove oil residues from the cleaning solutions and sludge from tinplating and chemical treatment solutions are provided to ensure lower consumption, reduced waste fluid disposal and better strip quality.

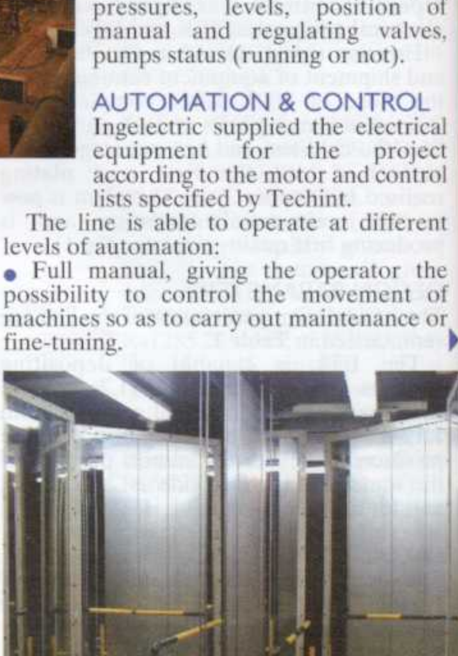
All circuits use acid-proof pumps (operating and stand-by), coolers and/or heat exchangers and proper instrumentation to permit complete control and operation from the main pulpit. User-friendly real-time screen pages present information on tempera-tures, flow-rates, conductivity, pH, pressures, levels, position of manual and regulating valves, pumps status (running or not).

AUTOMATION & CONTROL

Ingelectric supplied the electrical equipment for the project according to the motor and control lists specified by Techint.

The line is able to operate at different levels of automation:

- Full manual, giving the operator the possibility to control the movement of machines so as to carry out maintenance or fine-tuning.



5 Vertical Inspection Station

I The Bohus Malmön exposure site in Sweden, which has been used since 1997 to compare chrome-free coated panels with chrome containing systems (conventional 45° test orientation shown)

Accelerated exposure tests favour chromate containing coating systems but in practice there is little correlation between laboratory-based testing and natural conditions where seven years of testing chrome-free coatings have shown some to perform equally as well as chrome based systems.

Assessing the weathering performance of chromate-free coil coatings

BY P HEFFER* & B LEE**

Chromate ions, most often in the form of zinc and strontium chromate pigments, have been the mainstay of high performance anti-corrosive coatings for many years. In various forms they are used in a wide range of industries including aircraft, construction, marine and oil. Chromate compounds are used in pre-treatments, etch primers and a variety of other substrate-specific primers.

However, environmental legislation around the world is moving to restrict the use of chromate pigments. As a result there is a general agreement to work towards the elimination of hexavalent chromium (Cr^{VI}) compounds for corrosion protection – whilst coil coaters, naturally, are looking for maintained or improved anti-corrosion properties and continuing economy in use.

The urgency of the problem has raised demands for fast answers through accelerated corrosion tests but there are real doubts about their value. The faster the test, the higher the acceleration factor, the lower the chances for good correlation with natural conditions. In the late 1990s the European Coil Coating Association (ECCA) carried out an exhaustive study comparing natural and laboratory-based weathering. Tests included the established ASTM B-117 salt spray test; the more recent 'Prohesion' test – with and without combinations with the QUV accelerated weathering test and specific industry protocols. Studies were made on the face of the panel, the edges, scribes, fastenings, etc in a very detailed study. No usable correlations were found for any systems on galvanised steel.

Natural weathering is not a controlled process. We can record rainfall, temperature extremes and average hours of sunlight and panel temperatures and we can attempt to incorporate this data into our laboratory testing but we cannot incorporate the element of disorder, of natural chaos. In the foreseeable future we will need the support of real-time natural exposures at aggressive locations over extended periods of time. Becker has exposed thousands of panels at Bohus Malmön on the west coast of Sweden, a severe marine exposure site (**Fig 1**) and, more recently, at Hainan Island in China where the higher temperatures should make the conditions even more severe. Bohus Malmön provides aggressive corrosion testing, more likely to show up primer weaknesses than, for example, one of Becker's industrial test sites. Only one external site has been used at this stage to keep the number of variables in the test down to a manageable level.

CORROSION CHEMISTRY

Anti-corrosive pre-treatments and primers aim to passivate sites susceptible to attack, inhibiting the rate of electrochemical corrosion.

For steel the corrosion reaction is:

$$Fe + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2$$

forming red rust.

With zinc coated steels the zinc coating is sacrificially consumed in preference to the steel due to its greater reactivity. The reaction involved is:

$$2Zn + 2H_2O + O_2 \rightarrow 2Zn^{2+} + 4OH^-$$

and 'white rust' is produced.

HOW CHROMATES PREVENT CORROSION

Passivation or inhibition reduces the galvanic current between the zinc and iron. Partially soluble hexavalent chromate salts passivate the anodic areas of metals although there is little agreement as to the mechanism involved. One explanation is that the CrO_4^{2-} ion is an anodic precipitation inhibitor and oxidising agent but there is evidence that its reduction product Cr^{3+} may also act as a cathodic inhibitor. Research carried out at the University of Surrey in England in conjunction with Becker has demonstrated that effectively all the hexavalent chrome in a 'chrome-rinsed' pre-treatment such as *Bonderite 1303* is effectively converted to Cr^{3+} prior to the application of the primer.

The delivery of chromate from the primer to the substrate relies on moisture permeating the coating, dissolving traces of pigment. The active compound is then precipitated at the primer/substrate interface. At a cut edge or scribe chromate is leached out of the exposed primer and deposited on the anodic and cathodic areas. The solubility of strontium chromate in water can reach 0.6g/l although it has been shown that just 10ppm can provide effective protection against cut edge corrosion of coil-coated steel. **Table 1** shows the solubility of various chromates in water.

If the solubility is high it can lead to excessive leaching of the pigment and even cause osmotic blistering of the film. Conversely low solubility will result in insufficient CrO_4^{2-} being present at the metal surface to give inhibition.

Unfortunately the chromates used in these systems have been classified as toxic, due to the toxic and carcinogenic properties of the hexavalent Cr^{VI} species. Animal studies have confirmed the carcinogenic activity of calcium, zinc, strontium and lead chromates. There is, however, inadequate evidence of carcinogenicity from metallic chromium, barium chromate and trivalent chromium III compounds.

CHROMATE ALTERNATIVES & TESTS

Several factors limit the choice of alternative anti-corrosives. Some cannot be dispersed sufficiently finely to be incorporated into conventional thin film primer systems. Some interfere with the curing mechanism or cause rapid increases in viscosity during storage. Another problem is that much of the work carried out by suppliers has been aimed at air-drying or low-stoving coatings that are applied to mild steel, rather than pre-treated galvanised steel. Less effort has been directed towards the coil-coating sector with its special requirements and specialist resin systems.

Early attempts to replace chromates centred on zinc phosphate but these proved inadequate. Orthophosphate hydrates have been modified with metals such as aluminium, calcium, magnesium and molybdenum. Polyphosphates have been developed from these. Molybdates and metaborates have been proposed, as well as the addition of organo-metallics and even ion-exchange pigments.

The basic idea behind all these pigments is to provide a source of salts of limited solubility which will partially dissolve to *(a)* form a very thin coating on the metal to be protected, *(b)* act as anodic or

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Chromate	Solubility in water (moles $Cr0_4^{2-}$ per litre)	Comment
$NaCr_2O_7.2H_2O$	3.3	Too soluble for a pigment
$3ZnCrO_4.K_2CrO_4.Zn(OH)_2.2H_2O$	$1.5x10^{-2}$	
$SrCrO_4$	$7.0x10^{-3}$	Anticorrosive pigments
$ZnCrO_4.4Zn(OH)_2$	$3x10^{-4}$	
$PbCrO_4$	$7x10^{-7}$	Colour pigment – no anticorrosive activity

Table 1 Solubility of chromates in water

cathodic inhibitors and *(c)* provide a renewable source of these salts as they are washed away or used up.

Alternative chrome-free pigments for coil primers are only part of the overall coating system. The metal pre-treatment, which forms part of the cleaning and degreasing process, is traditionally chrome-based and this also must be modified. Substrate manufacturers have also been looking at improvements to their products: In galvanised steel the removal of lead from the zinc coating has improved corrosion resistance significantly.

Becker has worked closely with major pre-treatment suppliers for many years to provide a fully chrome-free package and systems have been used commercially and in line trials across Europe over the past six years (**Table 2**). In all cases, panels were exposed in both accelerated test cabinets and natural external environments.

Becker's biggest project to date started in 1997. This compared the latest developments in pre-treatments and primers applied to the three main ferrous substrates: HDG (Hot Dip Galvanised) zinc coated steel, Galvalume 45/55 zinc/aluminium coated steel and Galfan 95/5 zinc/aluminium coated steel. **Table 2** shows the large number of primers evaluated, both chromated and chrome-free. Substrates from different steel producers were pre-treated with 15 different recipes. The most popular topcoats were then applied to the primed panels. The complete investigation of all permutations would have totalled 7965 systems, so an experimental design was used to whittle down the number to 770 combinations of substrate, pre-treatment, primer and topcoat. Panels were subjected to accelerated testing in ASTM B117 salt spray (continuous fog of 5% sodium chloride at 35°C) and ASTM G85-A5 Prohesion cabinets (cyclic fog of 0.05% sodium chloride and 0.35% ammonium sulphate with 1 hour fog unheated and 1 hour dry at 35°C). In addition, natural exposure was conducted at Bohus Malmön in two orientations – conventional 45° south facing (**Fig 1**) and vertical north facing 'under eaves' (**Fig 2**). (Paint facing north under the eaves is attacked more severely because drying takes longer with no sun to warm the surface).

ECCA's lack of success in finding accelerated tests to mimic natural exposure confirms Becker's long-held view that salt spray testing alone does not provide sufficient evidence to launch a new product. Unfortunately ASTM B117 salt spray is the most widely specified accelerated test for the evaluation of corrosion resistance and hence is the driving force behind the performance criteria of many protective coatings despite strong evidence of its unreliability. The initial findings from Becker's project confirm that there is little correlation between laboratory-based testing and natural conditions. Certain formulations, which perform well in salt spray, actually perform worse in the field.

Other panels that performed poorly in salt spray are still performing well at Bohus Malmön after six years' exposure, illustrating why some primers that perform poorly in salt spray have become commercially accepted on the basis of their exterior performance.

2 *Vertical north facing 'under eaves' testing at Bohus Malmön is a more severe natural test*

A selection of panels that are performing well on exterior exposure compared with their accelerated test counter-parts are illustrated in **Figs 3, 4 & 5 a, b, c**. Each series shows, from left to right, (a) hot salt spray, (b) Prohesion, (c) scribed north-facing and south-facing panels respectively.

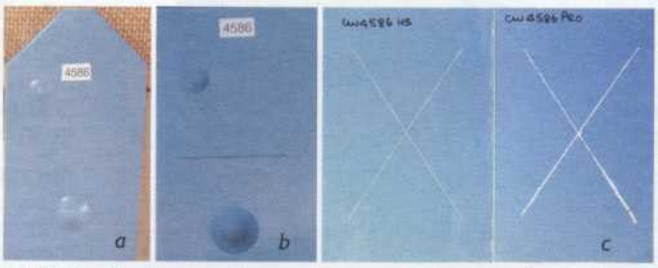
This extensive work shows that:

- It is unlikely a single pigment will replace strontium chromate. Combinations of two or three pigments are needed to give a synergistic effect.
- Higher loadings do not automatically lead to improved corrosion resistance. Levels need to be optimised. This is commercially important due to the higher cost of the new materials.
- A particular combination that works in one resin system over a particular pre-treatment may not work in a different resin/pre-treatment combination.
- This can lead to a self-perpetuating project in search of 'the best chrome-free primer' as 'new improved' raw materials are produced by suppliers. Hundreds of new permutations are currently being evaluated in this most recent phase of exposures.

Resin developments form a further piece of the jigsaw. High-build non-PVC systems are becoming more popular, generally using polyester or polyurethane primers that can be applied at higher film thickness, typically around 20-25 microns. This situation generates further formulation problems with differences in rates of release of the separate ions from the different anti-corrosives when combined in thicker resin films.

Substrates	3 (HDG, Galfan, Galvalume)
Pre-treatments	15 (9 chromate free)
Primers	59 (30 chromate free)
Topcoats	3 (SDPE, PVDF, Plastisol)
Tests	1000hr hot salt spray & Prohesion
Location	Bohus Malmön, N & S facing
Orientation	North vertical South 45°
Total systems	**770**

Table 2 Becker's 1997 Primer Development project



3 *HDG with chromate-free pre-treatment, chromate-free polyester primer and polyester topcoat*

4 *Galfan with chromate-free pre-treatment, chromate-free polyester-polyurethane primer and PVDF topcoat*

5 *HDG with standard chromate pre-treatment, chromate acrylic primer and plastisol top coat*

UNDERSTANDING THE SCIENCE

Becker's primer evaluations have not been confined to exterior performance testing. Work is being done to better understand the mechanisms of adhesion and the physical and chemical interactions between paint, pre-treatment and metal surface, including the roles of the different formulation components. This work uses the surface analytical expertise of The University of Surrey with X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) analysis.

XPS interrogates the top five nanometers of a surface by exposing it to a beam of X-rays, which then eject electrons from the inner electron shells. The energy of the electrons is characteristic of the element and its oxidation state.

ToF-SIMS is even more surface-specific, analysing the top two nanometers of a surface. A beam of ions of an element such as gallium is directed on to the surface and the secondary ions ejected are categorised in a time of flight analyser. These techniques identify the chemistry of the surface and, using a combination of the two processes, we are better able to understand the adhesion mechanisms (and failures) at the pre-treatment/primer and primer/topcoat interfaces.

In conclusion, Polyurethane primers, both conventional and high build, are generally most successful when it comes to incorporating the new chrome-free pigments. Some systems perform at the same level as chromates.

Chrome-free epoxy primers can be produced but their inherently lower flexibility introduces points of weakness for corrosion initiation at micro cracks in severely formed areas.

If a chrome-free pre-treatment is to be used, the ongoing exposure series must be checked for compatibility and interactions. ▶20

16▶ Tinning line at Aceralia ...

- Semi-automatic, when the operator just has to start one of the sequences.
- Automatic, when the sequences are automatically started up by the process events.

Eighty sequences have been foreseen by Techint to control the automatic coil and strip handling, most of them are configurable so that the operator, via the HMI, can provide the link to more sequences to create powerful macro sequences.

The system that manages the recirculation tanks are organised in several subsystems, each consisting of more instrumentation loops.

The rectifiers to supply the DC for cleaning and electroplating are controlled through the automatic implementation of algorithms appropriate to the particular process (cleaning, plating, post treatment, etc). This provides a variable set (current reference) that satisfies as best as possible the preset values such as current or Coulomb density, while taking into account the actual status of the plant depending on variables such as strip width and process speed.

All these auxiliaries are managed by sequences that allow manual intervention but, more commonly, operation is automatic.

The automation system is complete with a multi level troubleshooting system able to signal-up faults and investigate their possible causes, sometimes deriving from incorrect operations or machine or system faults.

Coating Variation	
Across strip width	±10% of nominal weight ±15% for 1÷1.5g/m^2 coating weight
Along strip	±3% of nominal coating weight (tin coating)
Trimming & Coiling	
Trimmed width accuracy	+0.30/ -0.0mm
Coil winding	±0.5mm (lap to lap) <1.0mm (max cumulative)

Table 3 Product tolerances

OPERATING RESULTS

The operation at Aceralia has shown a steady increase in productivity since the initial commercial start-up of the new line in October 2003. The line has produced first quality coils within the design tolerances indicated in **Table 3** since the beginning of commercial operation.

Aceralia continues to gain experience with the operation of the new line and has a continuing programme of data collection and fine-tuning of operating practices to achieve optimal quality over the range of line speeds.

This facility has been designed and constructed in the modern environment of 'global' design, supply, construction and financing activities. The co-operative effort between several international companies and the close attention of a dedicated project management team were essential to the success of the project. STI