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## Recent Advances in Coil Coating Technology

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### Background

The application of coatings to continuous coils has been in existence as an industrial process for more than 50 years. The developments made over that period have led to an increase in both scale and speed. Coil coating has thus become the most efficient method of coating materials, allowing end users to displace this important practice from their plants as a fixed cost and into suppliers as a variable cost.

The future competitiveness of coil coating within Europe has the following drivers:

- product quality and differentiation
- cost and line versatility
- environmental compliance

Achieving these technical, economic and legislative challenges is paramount for an industry seeking to maintain and expand in a world where globalisation pressures exist.

Internationally, the coil coating process is the application of thousands of tons of chemicals, paints and lacquers to millions of square metres of surface. The fact that most of these coating materials have been solvent based immediately highlights the environmental compliance challenges facing the industry. Current and emerging legislation, such as the Solvent Emission Directive (SED) [1999/13/EC] <sup>in</sup> Europe, mean that coil coaters are continuously seeking “cleaner” technologies

Additionally, the End of Life Vehicle (ELV) Directive demands that the coatings used in automotive applications are free of heavy metals, which then impacts on the metal pretreatment (the chemical layer between substrate and paint/lacquer) chemicals that must be chromium free. Although the primary concerns with chromium focus on its hexavalent form, many packaging end-users are also demanding the withdrawal of its trivalent form which has historically been used as a pretreatment in canning and other sheet packaging.

In addition to these challenges coil coaters are always looking to increase their volume through the line. The overall line speed is in general limited by the time spent in the paint/lacquer curing ovens. Time at temperature is required to cure the organic film and also extreme care must be taken in balancing the coating line's fume exhaust system with the coating's solvent emission volume. Advances have been made in waterborne systems and higher solid coatings and these will be discussed further, as will alternative cure technology processes. It should also be stressed that probably in excess of 95% of all coated products will be post-formed, so all alloys and coatings that are specified must be tolerant to controlled deformation.

In coil coating for can end stock relatively thin lacquers are applied to aluminium: utilising advances in line design and lacquer formulations, some lines are now reported to be operating at speeds above 250m/min. This is close to the limit of speed that can be achieved by conventional roll coat application technology. Any potential speed increases beyond this limit will require alternative application technologies or processes.

## Cleaning

The bare aluminium strip surface presented to the first process step of cleaning has residual rolling oil from the cold rolling process, oxide films generated during the high temperature rolling passes (most evident on magnesium-containing alloys where MgO segregates to the surface) and deformed or surface active layers.

For painted products, corrosion susceptibility, in most instances, has been found to be controlled by surface active layers. This has only been studied in detail during the past decade [1, 2], initially through an industry-wide Brite-Euram programme focussing on filiform corrosion. These surface active layers arise from the high level of surface shear induced during rolling that transforms the near surface microstructure (Fig 1).

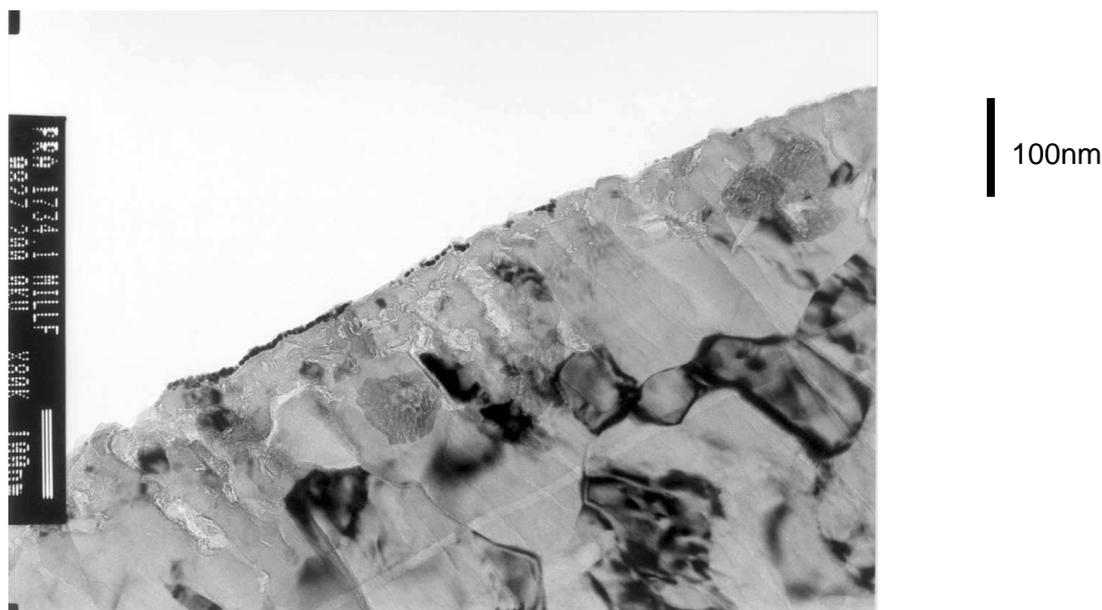


Fig 1. A 100 nm surface active layer on AA3105 cold rolled sheet.

Deformed surfaces are characterised by an ultra-fine grain size that can be stabilised by magnesium oxide pinning in magnesium-containing alloys [3]. However, it is not the fine grain size that is responsible for the enhanced corrosion susceptibility of the surface layer. This susceptibility is promoted by the preferential precipitation of manganese-rich dispersoids during annealing treatments, which is related to the manganese solid solution level and the temperature and time of annealing.

These deformed surface layers on aluminium alloys are produced most readily by hot rolling and, generally, the layer thickness of sheet and plate after hot rolling is of the order of a micron. The deformed layer thickness is progressively reduced by cold rolling so alloys that have been extensively cold rolled have thinner deformed layers that can more readily be removed by conventional etch cleaning operations. This means that resistance to corrosion can be improved by increasing the transfer gauge thickness so that after cold rolling the amount of surface to be removed at final gauge is 0.2 $\mu\text{m}$  or less.

The primary processes for cleaning aluminium are by spray or immersion in either acid or alkali solutions, although acid electrolytic processes are also used [4]. A line configuration may also include a mild pre-clean step to reduce the lubricant residues or any surface detritus.

Cleaning in alkaline solutions often produces a non-uniform surface in that aluminium and its oxide are soluble and magnesium oxide is relatively insoluble, hence a roughened surface can result. However, alkali cleaners are very effective in the removal of organics. On the other hand an acid cleaner will consistently attack both types of oxide, providing a more uniform surface.

For historical reasons alkali cleaning was initially the preferred cleaning option but gradually there has been a move to acid cleaners where proprietary cleaners are based on sulphuric acid and incorporate hydrofluoric acid and surfactants. The cleaners work by the sulphuric acid removing organics and oxides and the HF attacking both the oxides and the aluminium substrate: the degree of attack can be controlled by the amount of free fluoride in solution.

### **Pretreatment**

The key functions of pretreatments or conversion treatments after cleaning is both to provide good adhesion and to provide corrosion protection. Pretreatment application is either by a dip/spray process followed by rinsing (rinse pretreatment) or by roll coating (no-rinse pretreatment). The volume of chemicals used in both processes differs considerably, with the dip/spray process giving rise to a large volume of contaminated rinse water requiring treatment before disposal. On the other hand, roll coating requires a precise amount of solution to be applied uniformly across the strip which is then dried in place; the reaction with aluminium consumes all of the chemicals and no products requiring subsequent removal are formed, thus avoiding any potential environmental issues.

Historically chromium based pretreatments have been used based on chromate (Cr VI) and chrome-phosphate (Cr III) chemistries. Being highly acidic these pretreatments have often compensated for any inadequacies in the cleaning process. For architectural products both types of chromium pretreatments have been used but, with the major carcinogenic concerns surrounding the use of Cr VI compounds, Cr VI is not used for packaging products.

For rinse applications with Cr VI pretreatments the coating is formed by the reaction of solutions containing sodium dichromate and hydrofluoric acid. The HF attacks the residual surface oxides and aluminium, producing electrons which facilitate a redox reaction [5,6] resulting in the reduction of the hexavalent dichromate ion ( $\text{Cr}_2\text{O}_7$ ) to a trivalent chromium oxide ( $\text{Cr}_2\text{O}_3$ ). Importantly excess Cr VI is retained in such films and, in downstream product applications where these films could be damaged, the excess hexavalent chromium reacts with water and the aluminium to produce a new conversion coating i.e. the pre-treatment system is self-repairing. The no-rinse roll-coatable analogue of this system typically contains  $\text{CrO}_3$ , HF and amorphous  $\text{SiO}_2$  as a carrier.

For rinse applications of Cr III pretreatments, the reacting solutions contain  $\text{CrO}_3$ , phosphoric acid and hydrofluoric acid. Similar oxidation/ reduction reactions take place to the above, resulting in the deposition of a trivalent chromium phosphate film. The no-rinse roll-coatable analogue of this system contains chromium phosphate, HF and a polymer, typically polyacrylic acid, which can act both as an adhesion promoter and corrosion inhibitor.

As the market moves away from chromium pretreatments, the technical challenges are greater, not only because of the inherent corrosion resistance demanded from pretreatments but also because of the less reactive nature of the Cr-free systems with the aluminium strip, thereby placing a greater emphasis on the efficiency and quality of the precursor cleaning step. Thus there is a greater demand on non-Cr pretreatments to act as adhesion promoters with good uniform barrier properties

These adhesion and barrier aspects can be achieved by using a treatment to enhance the natural oxide layer, such as anodising or hydrothermal treatment in water or steam. Anodising pretreatments have been used very effectively for many years although they are not in widespread use as coil line treatments. Coil line treatments are based on fast anodising in either sulphuric acid or phosphoric acid and these types of pretreatment have the advantages of speed, control and uniformity compared to most chemical conversion treatments (Fig 2); they rely on a balance between anodic film formation and chemical dissolution of the anodic film and are much under-utilised as chrome-free pretreatments.

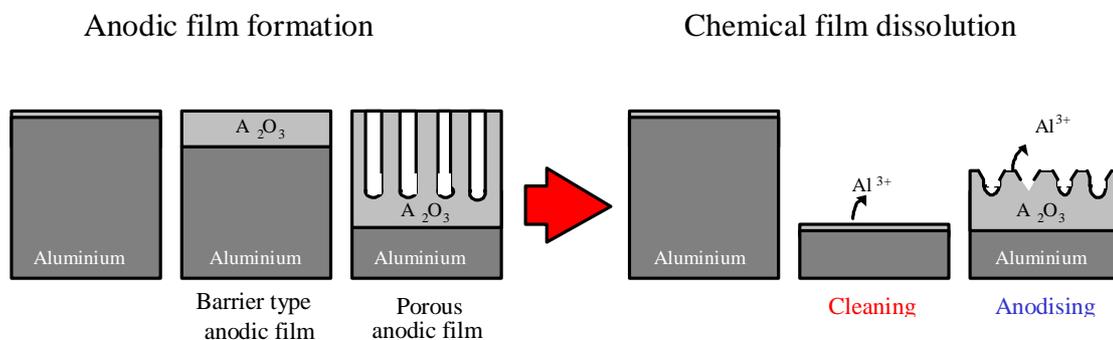


Fig 2 Schematic of electrolytic cleaning and continuous anodising film formation

Fluorotitanic and fluorozirconic acid based pretreatments [7] are in fairly widespread use as chrome-free alternatives. Such pretreatments can certainly be effective but are more difficult to monitor in production compared to traditional chrome-based systems. This is particularly an issue where polymeric additions are made to the formulation to improve performance. For such systems good adhesion is achieved through good surface coverage of a uniform film of either zirconium and/or titanium oxide. However, adhesion is severely compromised if the film is too thick and this can lead to in-service coating failures that are unrelated to corrosion sensitivity.

Pretreatment systems based on the use of adhesion promoters such as silanes [8], phosphonates and polyacrylic acids have been extensively researched. These pretreatments can certainly be very effective especially when applied as monolayers rather than thick films. They are probably most useful when used in combination with a thin anodising treatment (as a post-anodising step) or similar treatment to increase the barrier film thickness and to develop a micro-surface roughness to enhance adhesion.

## Paints & Lacquers

### *Architectural*

The choice of a paint system depends on a number of key factors including aesthetic appearance (shade, gloss, roughness), mechanical properties (abrasion resistance, scratch resistance, impact resistance, formability), durability (colour and gloss retention, weathering resistance, corrosion resistance), environmental impact and cost.

Most aluminium sheet will be roll-coated (Fig 3) with a thin backing coat and a two-coat topcoat, although products with up to 4 layers of topcoat are available for specific applications. The initial coat is the primer, its dry thickness usually in the range of 5 to 15 microns, to provide adhesion to the pretreated metal and it may contain anti-corrosive pigments. The second coat, or topcoat, is usually in the range of 10 to 25 microns and it provides the colour and appearance to the final coated system along with the other key properties required to meet the product's performance specification. An alternative approach is to produce a product with a basecoat (colour) with a clear topcoat (gloss).

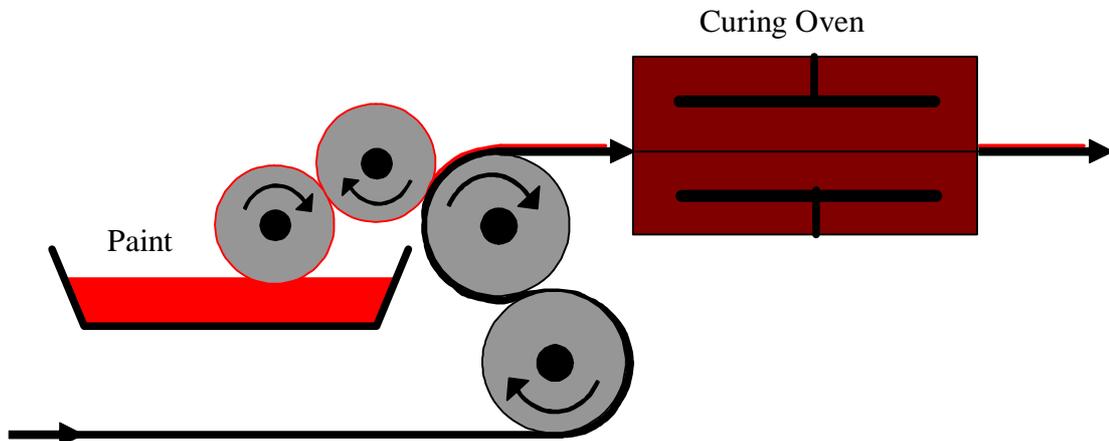


Fig3 Schematic of roll coat application of paint to the strip

There are two types of resins used in developing liquid paints for coil coating, thermosetting and thermoplastic. The thermosets include acrylics, polyurethanes, polyesters and silicon polyesters. The polyesters are also used in powder spray applications. The thermoplastics include PVC-plastisols, PVDFs (polyvinylidene fluoride) and polyamide-nylons. Each resin type can provide a different balance of properties:

- Polyesters provide good all round properties including very good colour matching capability and colour retention combined with good flexibility, hardness, resistance to weathering and chemicals.
- Vinyls provide the best resistance to acid, alkalis and many solvents. The most common building block is polyvinyl chloride (PVC). Fluorinated versions (PVDF) offer the best protection against weathering including UV resistance and for this reason they are mostly used in critical applications and prestige buildings.
- Acrylics provide high gloss plus yellowing and mar resistance.
- Urethanes combine hardness and abrasion resistance coupled to good weathering performance.

## **Packaging**

Coil coating for packaging is dominated by the market for easy-open ends for beverage cans. Can end lacquers are normally applied at around 1-2.5g/m<sup>2</sup> on the external surface and 7-10g/m<sup>2</sup> on the internal. The internal coating, in particular, must withstand the high speed forming process of the end (above all the tab rivet) whilst protecting the beverage from the container (and vice versa). Historically this application was dominated by the highly ductile vinyl organosols (vinyl chloride-vinyl acetate copolymers dispersed in solvent) but recently a combination of environmental pressures and consumer health concerns has led to replacement of solvent based vinyls with variants including:

- Water based
- Vinyl (chlorine) free
- Low BADGE (BADGE-free)
- Bisphenol A-free

These developments are based on epoxy-ester or polyesters with enhanced flexibility.

## **Alternative Technologies**

In the challenges that face the coil coater, he/she is consistently examining alternative technologies.

As part of continuous improvement exercises, coil coaters have worked closely with paint suppliers in the development of both high-solids coatings and water-borne coatings. **High solids coatings** as their name implies, have a higher content of solid components than conventional solvent-borne systems. Typically coating systems with a solids content of >85% fall into this category and, since they contain less solvent, they offer a significant reduction in VOC emissions compared to conventional systems. As well as reducing emissions, high-solids coatings can impart thicker application layers than conventional systems, leading to timesaving. The reduction in solvent however, means that such coatings are more sensitive to inadequate surface preparation of the substrate.

**Water-borne coatings** are systems that predominantly utilise water as the solvent to dissolve the binder. Typically up to 80% of the total solvent is water with the remainder being organic co-solvents such as glycol ethers. Such systems benefit from large reductions in VOC emissions and an associated reduction in both fire risk and worker exposure to organic vapours. However, due to the corrosive nature of the water in the formulation, special equipment can often be required for application. Control of humidity is also critical to achieving the desired film formation. Most resins have now been incorporated into water-borne coating formulations and they are finding widespread applications for packaging products. For architectural products the use of water-borne coatings has focused more on primers rather than the diverse range of paints used for topcoat functionality.

**Powder coating** is another alternative, utilising 100% resin in a dry, powdered form and working on the principle of attraction by oppositely charged species. The powder is delivered through a spray gun where it gains a low amperage, high-voltage positive charge.



The surface to be coated is electrically grounded so that the positively charged powder particles are attracted to it. The coated surface is then reacted in an oven where the powder melts and fuses into a smooth coating. This has been widely used in the post-painting of individual parts but has had less impact, to date, in coil coating. Within Europe Otefal Spa is the market leader for coil coating with line speeds typically operating at up to 20m/min. The speed has been limited by the array of electrostatic guns that must be synchronised to achieve uniform film coverage. However, powder coating has the attraction of being solvent-free and can be cured using infra-red or induction heating technologies.

Other application technologies for powder include the Powder Cloud technique developed by MSC of Illinois and the Electro Magnetic Brush (EMB) application technique developed by DSM resins in Europe. The Powder Cloud technology applies powder to the coil strip as it passes through a charged cloud of powder coating. The identically charged powder particles repel each other and deposit on to the earthed coil strip. The EMB approach is based on technology that it is used for laser copiers and photocopiers.

New developments in the formulation of powder coatings generally relate to their application in packaging products such as cans, where FDA approval is still pending. Significant advances have also been made in the development of powder coatings for architectural products that require superior long-term durability and also powders that can form thinner applied films.

Interesting developments in oven technology have come out of Adphos AG [9] who have developed nir®, **Near Infra-Red ovens** to be used as boosters to conventional ovens or as stand alone systems. These are small footprint modules that utilise high intensity heat emissions from the near infra-red wavelength spectrum and can cure 20micron coatings in less than 3 seconds as compared to say 20 seconds. Using lamp systems for curing also means that they are only switched on when needed as compared to the continuous power requirement of convection ovens. However, as the solvents will be rapidly driven off, the extraction system has to be extremely efficient such that the LEL (Lower Explosion Limit) is not exceeded.

Other forms of **Radiation Curing** using Ultraviolet (UV) or Electron Beam (EB) have been practised since the late 1960s. Although the growth rates of these technologies have been relatively slow, they have been continuous. Conceptually radiation curing could solve many of the coil coaters problems; they are liquid coatings applied to the substrate surface via roll coating and cured at room temperature in seconds without volatile materials being lost from the surface. However barriers to their use exist, including the capital equipment costs involved and the limited availability of formulations for particular applications.

Electron beam and ultraviolet curing have developed in parallel since the 1960's due to their similarities. Companies which produce UV curable formulations will generally also produce EB curables, the main difference being that UV requires a photoinitiator in the formulation whilst EB does not.

The absence of a photoinitiator is EB's main advantage over UV since photoinitiator residues remain in cured coatings and prompt worries over health, odour etc. Hence, UV coatings have not been used in coil coating for packaging applications. There are, however, currently initiatives to obtain FDA approval for the use of radcure coatings in direct food contact.

For steel coil lines a UV curing system is often incorporated at the end of galvanising lines whereas, for aluminium architectural lines, opportunities may exist for thin functional (e.g scratch resistance) coatings above the topcoat.

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