Pretreatment of Aluminium – An Overview

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Approximately 40% or 17 million tonnes of the total world aluminium shipment is in the form of rolled products and used in major markets including packaging (cans, foil), building/engineering (panels, roofing, appliances) and transportation (automotive, aerospace, trains). To ensure satisfactory performance all these products require modification of the surface which can be carried out after the material has been formed to final shape or more easily by coil surface processing which usually takes place on dedicated lines.

Aluminium strip in either sheet or coil form can be surface treated and coated to provide a wide variety of protective, decorative, or special-property finishes making it an ideal material for a wide range of applications.

The different surface treatments and coatings can be applied on individual sheets or formed components where process stage times can be relatively long, i.e. measured in minutes. Since many of the applications have now developed into high-volume markets, the modern tendency is to produce material, wherever feasible, on continuous strip process lines and so achieve the level of productivity required while minimising costs.

The process stages for paint and lacquer coating have been developed to be effective in a matter of seconds enabling speeds of 200 m/min. to be achieved and even 300m/min. for pretreatment-only lines.

In addition to high productivity, the continuous strip treatment enables strict process control, can be modified to specific customer product properties and provides a consistently high standard of quality across the strip width, throughout the coil length and on both top and bottom surfaces.

The surface finishing of aluminium involves the following stages:

Cleaning to remove residual oil, oxide films and mechanically disturbed layers

Pretreatment to provide corrosion protection and modify the surface for enhanced adhesion of organic coatings

Coating of a protective, decorative or special function finish

Cleaning

Aluminium may be cleaned to

Remove surface contaminants: residual mill oil and smut

Diminish, in a controlled fashion, or remove surface oxide

Etch the metal to remove near surface active layers

Provide a uniform surface to receive pretreatment

There are three general approaches to cleaning

Alkaline spray or immersion

Acid spray or immersion

Acid electrolytic cleaning

Pretreatment

The pretreatment process is often integrated with a preceding strip cleaning process, and usually a subsequent coating process.

An exception is the provision of pretreated-only coil which is cut into sheets for the packaging industry (e.g. food cans, metal closures) where the individual sheets are lacquered and printed on sheet coating lines. This is because it is not practical to print or decorate coils due to the wide range of designs required, and the relatively small runs per design.

Pretreated-only strip is coated with 5 to 10 mg/m2 dioctyl sebacate (DOS) to ensure the cut sheets destack and feed smoothly into the sheet coater/decorators.

The pretreatment can be either a chemical or an electrolytic process, to replace the natural oxide film. The chemical process is more usual, with different versions for food packaging applications (to satisfy regulations) and for architectural or transport applications.

Historically pretreatments for coil coated aluminium were chromium VI based formulations which provided excellent performance.

Theses chromate conversion coatings relied on a film forming mechanism based on acidified chromate with fluoride providing a source of CrVI ions which were released in service giving a “self-healing” mechanism in defect/damaged areas.

Formulations based on CrVI are still used for architectural applications while CrIII systems have been developed for food contact products.

The most commonly used pre-treatment for coil coating is a thin chromate film (~ 200 nm) which provides both good adhesion and corrosion protection.

Solutions can be chromate (yellow chromating) or chromate-phosphate (green chromating) and can be applied by immersion, spray or chemcoater (no-rinse).

However, as chromium(VI) is toxic, there has been a considerable amount of effort to develop more environmentally friendly alternative pre-treatment systems.

Current alternatives include:

Metal ion analogues to Cr(VI) (Mn, Co) and inorganic molecules reacting with oxidised Al to form mixed oxides (Ti, Zr)

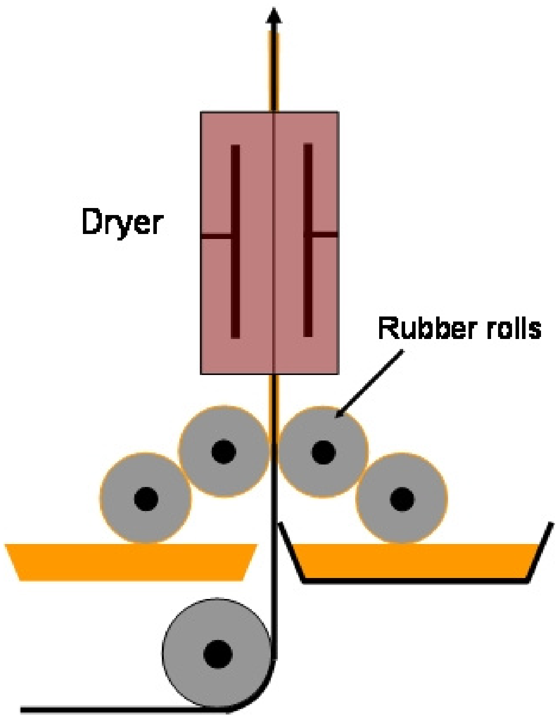
Inorganic film-forming oxides which cover the surface and promote adhesion (silicates, molybdates, vanadates)

Organic polymers with high complexing capacity.

In excess of 50% of global packaging products and 25% of European architectural products use Cr-free pretreatment systems.

Earlier conversion coatings required excess solution to be washed off the metal surface giving rise to considerable volumes of contaminated rinse water requiring treatment before disposal. However in the case of no-rinse application a precise amount of pretreatment solution is applied uniformly across the strip and then dried in place. These ‘no-rinse’ aqueous chemicals have been formulated to remain on the aluminium surface. Their reaction with the aluminium means that no products are formed which will subsequently require removal, so avoiding most of the potential environmental problems.

The pretreatment, typically a no-rinse chrome chemical type, is applied to each side of the strip by roller coating. A typical pretreatment is 120 mg/m2 dry coating weight.

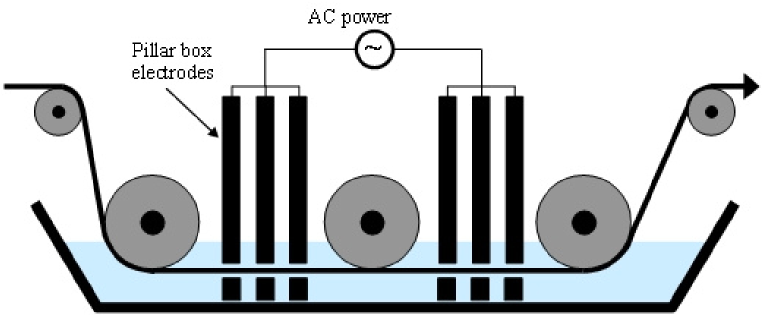


No-rinse chemcoater application

The pretreatment is dried, typically by passing the strip through a hot air oven to achieve a metal temperature of approximately 40 to 60℃. The strip is then air and water cooled to around ambient temperature and squeegee rolls and an air knife dry the strip before it passes to the next paint coating stage.

An alternative electrolytic pretreatment process is effectively anodizing in a hot electrolyte using liquid contacts. The power supply can be either d.c (direct current) or a.c. (alternating current) with the latter either single or 3-phase.

A cell containing an electrolyte (e.g. 20% sulphuric acid) is divided into 2 or more compartments, with electrodes in each compartment. Current passes between the electrodes and the strip via the electrolyte - there is no mechanical contact with the strip.



Electrolytic Cell

By using a.c., graphite electrodes, with slots through which the strip passes, can be used, pretreating each side of the strip simultaneously. The pretreatment film is produced whilst the strip is subjected to the anodic half-cycle, and the film is modified by chemical attack during the cathodic half-cycle. Full pretreatment can be effected in aproximately 3 seconds. When using d.c., either lead, or lead covered, electrodes must be used in the cathodic section.

If a preceding acid degrease/clean is used, it can employ the same chemical composition as that in the pretreatment cell (e.g. 20% sulphuric acid) thus avoiding the necessity of rinsing the cleaned strip prior to entering the pretreatment cell.

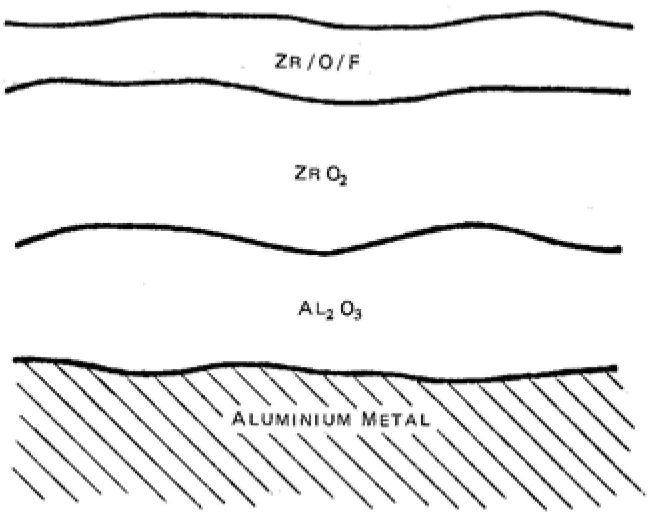
After the pretreatment and drying stages the strip is coated with a lacquer or paint depending on the final product application.

Mechanisms

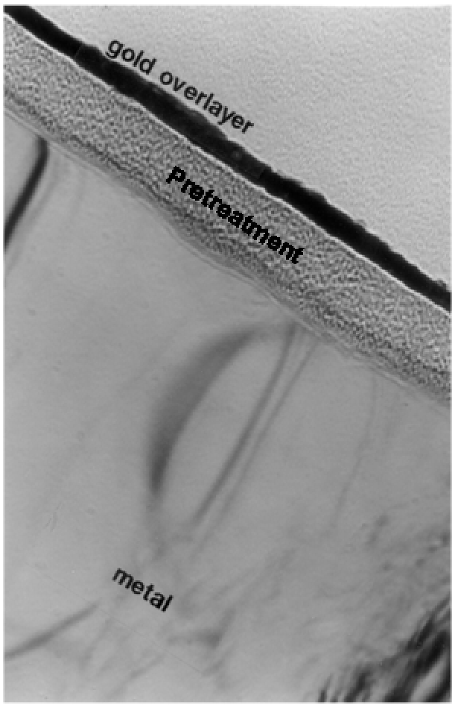
Pretreatment functionality is a combination of one or more attributes. These attributes are a result of the reactivity of the applied chemistry and the structure of the resulting film:

- Formation of a barrier layer restricting the flow of ions, water and oxygen to the substrate
- Chemical and mechanical stabilisation of the native oxide film
- Production of a surface with chemical bonding potential to subsequently applied organic materials
- Increase of surface area available for coating
- To give a mechanically rough surface to enhance interlocking
- Provision of electrochemically derived corrosion resistance

Each pretreatment system has at least two of these factors at the heart of its performance. The list above can be subdivided into those factors that act on or in conjunction with the substrate and those that improve interactions with coatings or adhesives. This subdivision is perhaps obvious however it demonstrates the importance of the pretreatment at the interface between metallic and organic materials. Furthermore it indicates the critical nature of this sub 100µm layer to the performance of a large percentage of aluminium used in a coated or bonded form. What is not obvious but is implied by the various factors is that the structure of the pretreatment layer plays a part in determining performance.



Structure of zirconium based pretreatment



TEM cross section through a pretreatment layer

Many pretreatment layers have a structure that varies from the substrate to the outer surface. This structure occurs as a direct result of the applied wet chemistry and the processing it undergoes. The reaction times, albeit short, are long enough to allow segregation of the film into layers. When the process is optimised, chemical groupings are found in the correct location to allow desirable interactions with substrate or coating. Of course the possibility exists for non optimised structure formation due to process or formulation variation. In these situations the structure may be mechanically weakened, compromised with regards to hydrolysis or lack the ability to maintain adhesion to either substrate or coating. Failure of the product during service will often result.

CONCLUSION

Pretreatment represents a small but important cog in a multibillion dollar industry.

However, in the twenty-first century, industry requirements for control and minimisation of failure coupled with increased competition and higher production speeds place ever increasing demands on pretreated surfaces.