Cirrus Paint-free Colour™: Robust Coloured Coatings on Aluminium Alloys

Ian J Mardon*, Fengyan Hou*, and Chris Goode*

* Cirrus Materials Science Ltd, Auckland, New Zealand
chris.goode@cirrusmaterials.com

ABSTRACT

Cirrus Hybrid™ technology offers a means to deposit thin, corrosion resistant coatings on light metal alloys. Cirrus recently developed a novel evolution of this coating technology, Cirrus Paint-free Colour™, to directly deposit a range of coloured coatings on these same alloys without the necessity for dyes, paints, or other toxic materials. Cirrus Paint-free Colour™ is a patented novel coating technology that delivers greater energy efficiency, environmental friendliness, and surface protection while offering a weight advantage over organic-based and paint coatings.

Light alloys such as aluminium are often the first choice of material for applications in architecture, automotive and aerospace, due to a high strength-to-weight ratio and corrosion resistant oxide layers. Typically, these industries use paint or organic coatings which are not only highly energy intensive, but also use toxic chemicals that are increasingly challenged by sustainability concerns.

Cirrus Paint-free Colour™ leverages a combination of anodisation and electro-deposition to create a nano-pore structure that interferes with the wavelengths of light on aluminium. The result is a uniformly coloured surface that is exceptionally scratch resistant – providing a paint-free solution to manufacturing.

The colours are produced by novel manipulation of the novel structure of the anodising tube arrays during the process to create a combination of plasmonic absorption and surface interference, allowing for a wide colour selection. Cirrus Hybrid™ coatings are between 3 and 15 microns thick and can be highly corrosion resistant. This offers a disruptive new sustainable coating system for light metal alloys, well suited to 3D-printed components. Cirrus Paint-free Colour™ for aluminium is 75% thinner, lighter and 5x more energy efficient to apply than paint.

Keywords: structural colour, corrosion resistance, waterborne coatings, nanotechnology, materials science

1 INTRODUCTION

Many traditional colour coatings involve paints or other organic-based formulations designed to be applied to steel substrates. In recent years, steel has begun to be replaced with lighter materials to improve overall performance in automotive and aerospace industries. In addition, the use of organic formulations and solvents is receiving more legislative restriction due to environmental and health concerns [1].

Aluminium alloys are a common choice of material in such applications due to their desirable strength-to-weight ratio and their corrosion resistant oxide layers. Previously, various combinations of anodised surfaces with deposited organics or metal salts have been used to create coloured surfaces on light metal substrates [2]. These coating technologies have seen little-to-no adoption outside of architectural and other decorative applications. This is due to strict performance standards which such coatings do not meet. These approaches, have typically adopted sulphuric acid anodising with AC electrolysis of metal salts, resulting in colour generation that is purely dependent on light interference behaviour of the deposited oxides/hydroxides. Similarly, these porous anodised surfaces are instead treated with organic dyes to be later sealed into the oxide [3].

Aerospace and automotive coatings are organic-based coloured coatings, which are energy intensive, produce environmentally damaging toxic wastes and other by-products, such as Volatile Organic Compounds (VOCs). It is clear that new technologies are required to allow for adoption of aluminium alloys as suitable materials in high performance industries while also reducing reliance on organic paint coatings to meet legislative requirements and address environmental concerns.

2 CIRRUS PAINT-FREE COLOUR™ PROCESS DEVELOPMENT

Cirrus Paint-free Colour™ is a patented technology that combines anodised light metal surfaces with functional metal and/or polymer materials deposited into the porous anodised oxide. The Cirrus Hybrid™ process overview is shown in Figure 1. In the first step, an aluminium part is subject to proprietary, principally phosphoric acid, anodising (PAA). This is followed by a controlled metal deposition where the metal grows from the bottom of and seals the pores. Advantageously, one of several functional coatings may be deposited which strongly interlocks with the pore structure and completes the coating system.

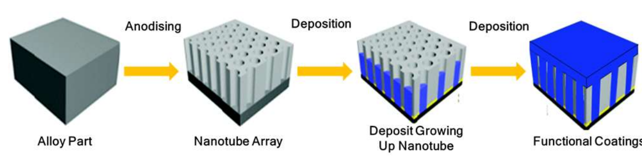

Figure 1: Cirrus Hybrid™ Process Overview

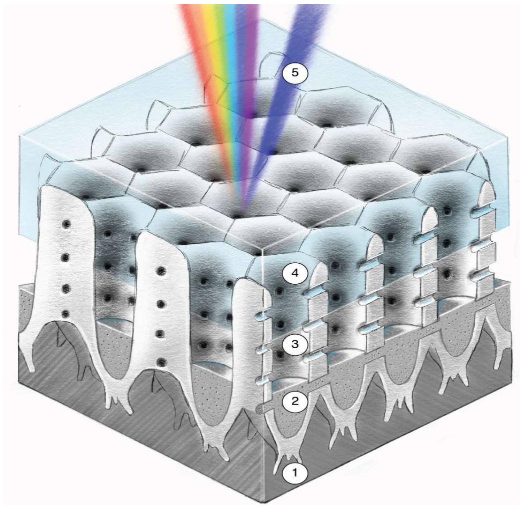

Figure 2: Paint-free Colour™ Surface

In this article, Cirrus Paint-free Colour™ coatings are presented, where nickel nanowires partially fill the PAA structure. This combination produces coloured coating, where the optical properties are developed as a result of the coating morphology. Figure 2 shows the structure of the Cirrus Paint-free Colour™ Surface. Here the anodising and initial metal pore filling (1 and 2 of Figure 2) are similar to the standard Cirrus Hybrid™ process, however the functional layer is replaced with an air gap and seal (3 and 4 of Figure 2). By selecting the appropriate process parameters, structural colouration can be produced as desired.

Here, we report both the novel combination of anodising and metallisation process with the ability to produce a full spectrum of coloured surfaces and mathematical modelling of the colour generation mechanism. Simulations and measurements of the coating colours showed good agreement. These results demonstrated that the critical colour determinant is the morphology of the as-anodised film, where the colour is revealed after the metallisation step. PAA allows for a large range of morphologies to be developed; however, to support the development of a consistent morphology the anodising process must be carefully controlled.

Cirrus Paint-free Colour™ technology is a candidate to replace paint in lightweight automotive and aerospace applications. We posit that the low energy Paint-free Colour™ process will decrease carbon emissions, reduce VOC emissions, provide a safer alternative to existing technologies in addition to cost savings, and improved end-of-life recycling options.

3 EXPERIMENTAL

3.1 *Substrate Preparation*

Aluminium Al-6061 alloy sheet, 2mm thick, was laser cut into 3cm x 5cm coupons which were cleaned in alkaline degrease solution, followed by chemical activation of the surface using an acid etch. A 50% nitric acid dip for several minutes was used to de-smut the substrates prior to anodising.

3.2 *Application of Cirrus Paint-free Colour™ coatings*

Multiple samples were prepared for each of the chosen parameters to allow for independent testing of various coating properties. A proprietary, phosphoric acid-based anodising bath was used to produce an anodised layer of between 5 and 10 microns on the aluminium coupons. Polyethylene glycol, included in the bath, allowed for higher voltage anodising. The coupons were anodised at 60, 70, 80, and 90 volts, to evaluate the effect of anodising voltage on the resultant coating colour. The anodising temperature was maintained at a set temperature (± 0.5 °C) using a both recirculating cooler, and air agitation of the anodising solution.

Anodised samples were rinsed with deionised water and immediately submerged into the electroplating bath to allow the solution to diffuse into the porous surface. Various commercial nickel-plating baths were used, including semi-bright nickel, bright-nickel, zinc-nickel, etc., with the colour produced being substantially independent of the bath selection. An initial very low current density was applied to foster nucleation of electrodeposited metal at the base of the pores. The current density was then increased to form the nanowires, only partially filling the porous surface. The coloured surfaces were then rinsed with deionised water, and dried using compressed air.

3.3 *Sealing*

Initial corrosion testing demonstrated that the coatings after electrodeposition lacked corrosion resistance. The close contact between the electrodeposited nickel and the aluminium alloy substrate allows for galvanic corrosion to occur. To combat this various, UV-initiated, electrolytically polymerised, and nanoparticle polymer sealing options were applied to measure the improvement in corrosion resistance.

3.4 *Performance Testing*

Sealed coatings, together with unsealed control samples, were subjected to neutral salt spray corrosion testing, as per ASTM B117 [4]. The samples were observed every 12 hours, and the corrosion points were counted. The number of corrosion points over time was used as a metric to analyse the corrosion performance.

Duplicate samples were subjected to the mechanical testing methods, including wear testing, and scratch testing, to evaluate the performance of the coatings. The measurements from these mechanical tests were recorded and compiled to evaluate the potential performance of these coatings for commercial application.

3.5 *Colour Measurement and Modelling*

Samples were photographed in a lightbox, and the images processed in Imagej to determine both the colour (in the CIE-Lab and -RGB colour spaces), as well as the colour variance across a sample surface, measured by ΔE.

$$\Delta E = \sqrt{(\sigma_{\mathrm{R}})^2 + (\sigma_{\mathrm{G}})^2 + (\sigma_{\mathrm{B}})^2} \qquad (1)$$

Colour difference between samples and their simulated counterparts were also evaluated using Equation (1) [5]. Samples were imaged using SEM and optical microscopy. The resulting images were used to measure the anodising morphological dimensions including pore diameter, interpore spacing, side pore diameter, and side pore spacing. The overall coating thicknesses and metal fill were also assessed.

The coating system was modeled as a stack of layers with alternating porosity, where the high porosity layers include the side pores and the low porosity layers were the spacing between the side pores . Optical properties of the layers were calculated as an average of the constituent materials and their respective volume fractions (porosity fraction as air or nickel, and the balance being the anodised alumina) [6] [7] [8]. The effective refractive indices for these layers then allowed for evaluation via the Transfer Matrix Method [9] [10] to produce simulated reflectance spectra. These spectra were integrated with CIE colour matching functions to produce an RGB value [5].

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4 RESULTS AND DISCUSSION

4.1 *SEM and Optical Microscopy*

Figure 3a. shows an SEM image of a Paint-free Colour™ coating that has been bent to expose the metal nano rods.

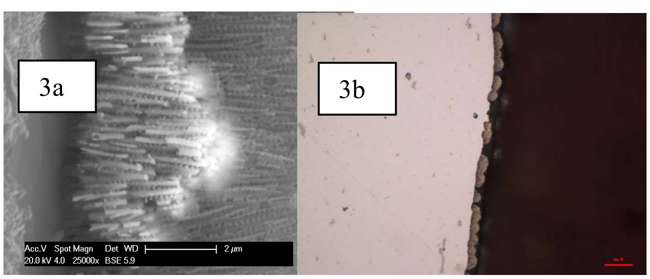

Figure 3: SEM of coating cross section

Here the regular arrangement of vertical pores may be clearly observed. This deposit was created using direct current, and uneven pore filling results from uneven nucleation in the pores, visible also in Figure 3b. Pulse deposition was found to develop more uniform nanowire length and brighter colours. The side pores which periodically connect neighbouring main pores in the oxide layer can be observed in Figure 3a. These side pores are approximately 150nm from centre-to-centre and 70nm in diameter.

4.2 *Initial Modelling of Sample Morphology*

Simulation reflection spectra were produced from the modelling. The detailed results, which will be available in a future publication, show good agreement with measurements of prepared samples. These results demonstrate that the colour generation technology is a unique result of the morphology produced by Cirrus Paint-free Colour™ technology.

4.3 *Sample Colour Analysis*

The prepared coatings were imaged, and the colour values and variation (ΔE) were evaluated, as described in Section 3.5 [5]. CIE defines a ΔE of 2.3 to be the "Just Noticeable Difference", and many paints are designed to produce coatings with ΔE < 1.0.

Anodising		Colour Analysis				
Volts	°C	R	G	B	RGB	ΔE
60	24.0	130	132	139		1.3
60	25.5	73	75	81		1.0
60	27.0	37	44	52		0.7
70	27.0	48	61	92		0.8
80	27.0	44	72	125		0.7
90	27.0	44	76	144		0.9

Table 1: RGB values and colours, as well as internal colour variation for samples at 60V, 70V, and 90V.

Figure 4: Paint-free Colour ™ on curved geometry

The samples anodised at the same temperature were seen to shift from black to dark blue, to light blue, as the anodising voltage increased as shown in Table 1, which also shows three samples anodised at 60 V, with increasing anodising temperatures. The increased temperature favours electrolyte dissolution of the porous oxide, resulting in higher porosity, and thus darker colours due to the higher volume fraction of light-absorbing nickel in the coating.

The application of Paint-free Colour™ using 70 V anodising at 27.0 °C produced a "French Navy" colouring, which is highly uniform across the curvature despite the dispersion/reflection of the LED lighting visible in Figure 4.

There was good agreement between the simulation results and the real-world colours, thus we may conclude that the optical filtering properties of the air-alumina layers and absorbing/reflective nickel gives rise to the coating colours.

4.4 Corrosion Performance of Coating

Samples were tested for Corrosion Resistance by following the ASTM B117 procedure. Unsealed coatings typically survived no longer than 48 hours, before corrosion points occurred, which indicated the requirement for a sealing layer to protect the underlying coloured surface. The potential for galvanic corrosion between the nickel and aluminium substrate requires sealing material to create a moisture-resistant barrier between the nickel deposits and corrosive media.

Sample	Hours until first corrosion point	Seal colour change ΔE
Unsealed Control	48	n/a
Electropolymer Seal	336	10.7
Polymer NPs	336	1.4
UV Polymer Seal	336	5.1

Table 2: Corrosion resistance and colour change of unsealed and sealed samples

Table 2 shows the effect of three polymer seals on the corrosion resistance, where all of the polymer seals provided approximately an 8-fold corrosion resistance improvement. The electropolymerised seal layer, whilst only ~0.2 μm thick, provided a uniform barrier layer between the corrosive media and the underlying metal nanorod-substrate structure. This seal, as deposited, was not optically clear, so the colour of the coating was masked by its dark brown/black aspect.
Polymer nanoparticles were electrophoretically deposited into the pore openings. This method produced a seal of the coating which changed the colour the least; however, this seal layer was the also the least durable, being easily penetrated by organic solvents.

The UV polymer also provided an effective barrier layer, with corrosion points only observed at the edges of the samples where the monomer had not been applied. Whilst the transparent UV polymer maintained the coating colour better, there was still a change in colour caused by penetration of the monomer into the pores. Modelling polymer in the pores demonstrated that the seal-induced colour changes were principally due to the change in refractive index in the pores. Thus, the pore air-gap is required to preserve the colour. Modifying the model to include an air-gap of variable dimension together with low refractive index polymers sealing suggested that 2 microns of air-alumina are sufficient to retain the coating colour.

The current focus on a dip process to seal the surface combining polymer nanoparticles to plug the pores, with an application of suitable clearcoat polymer system.

5 CONCLUSION

The development of this novel colour coating has allowed for the integration of electrodeposition and proprietary anodising to produce coatings in black, shades of grey, and various shades of blue on aluminium alloys. Further increases in anodising voltage will expand the colour range to incorporate the full visible spectrum. The coloured surface, which is naturally resistant to scratching and UV fade, with an appropriate seal will offer a long-life coloured surface. Making use of this robust, alternative coating technology, in combination with an appropriate sealing system, may offer a low energy and low VOC replacement for paint. The ability to tune the anodised layer morphology allows for fine control over the resultant colour.

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