Protection for high flyers

Novel chrome-free system resists corrosive attack on aluminium alloys

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High-strength aluminium alloys used in aerospace applications are particularly susceptible to corrosion damage. A new chrome-free coating technology shows better performance than commercial chrome-free corrosion inhibitors in corrosion tests on these alloys. A stable passivation layer ensures long-term protection of damaged areas.

The quest to replace corrosion inhibitors containing hexavalent chromium has taken many years and still continues. The aerospace industry still relies on the inhibiting power of hexavalent chromium to protect metal parts of aircraft. Over recent years, efforts to develop chrome-free technology have been accelerated by health & safety and environmental concerns and new legislation such as REACH.

This puts pressure on the coatings industry to change and to deliver wholly chromium-free technology solutions, and has yielded several chrome-free pretreatments and coatings systems for the aerospace industry.

Although field experience on aircraft shows that the chrome-free alternatives performed well on exterior surfaces, hexavalent chromium pretreatments were still necessary to comply with the requirements of specific corrosion tests such as the ASTM B-117 neutral salt spray (NSS) and filiform corrosion (EN 3665) test.

Aerospace alloys pose exceptional corrosion problems

High strength aluminium alloys such as 2024-T3 and 7075–T6 [1] are most commonly used in the aerospace industry. Alloys of these series, with Cu and Zn as major alloying elements, are generally less resistant to corrosion than other alloys. Indeed, for this reason 2024-T3 is often supplied in 'clad' form, coated with a very thin layer of pure aluminium. Different tests were carried out on bare and clad sheets, as noted below. Filiform corrosion [2] and especially pitting corrosion [3] are known to be the major damage mechanisms affecting the integrity of these alloys.

Ongoing development work has resulted in many new chrome-free inhibitor technologies intended as alternatives to strontium chromate and other hexavalent chromium compounds.

Although these materials are recommended for use on aluminium substrates, evaluations have shown that they are not suitable for the corrosion protection of the high strength alloys. Generally, the current commercially available chrome-free inhibitors display a lack of passivation when exposed to the ASTM B-117 salt spray test.

Their inability to protect the scribe at an early stage leads to corrosion underneath the paint film (creep from scribe) and pitting corrosion after longer exposures. Also, when tested according to the filiform corrosion test (EN 3665) on the various high strength alloys, these systems show rapid formation of a large number of fast-growing filaments. This makes them unsuitable for the development of totally chrome-free coating systems for aerospace.

With the implementation of legislation such as REACH, the need for more suitable alternatives is increasing and new approaches are needed to provide fully chrome-free coating solutions to the industry.

New approaches in chrome-free coatings technology

AkzoNobel took the decision to investigate some entirely new and innovative chrome-free protection concepts. One of these new approaches has been the development and introduction of magnesium metal as a corrosion inhibitor [4].

Using the principle of cathodic protection, the magnesium-rich technology has been a significant departure from traditional methods and mechanisms of corrosion protection for aerospace. This technology [5] has successfully demonstrated excellent corrosion resistance which actually exceeds the performance of chromate systems.

Another novel patent-pending corrosion inhibiting coating technology for the protection of aluminium alloys has been developed, which is considered to offer corrosion protection that is significantly improved over current "best in class" products. This technology has leaching properties to enhance protection of damaged areas and provides:

» Active inhibition of filiform corrosion;
» Fast and effective passivation of the scribe during NSS exposure;
» Robust performance over several aluminium alloys and chrome-free pretreatments.

As it can be used universally in solvent and waterbased systems, it is possible to develop totally chrome-free coatings to meet aerospace requirements.

Salt spray and filiform corrosion test procedures

To investigate and demonstrate the potential of this new technology, it was incorporated into a solventbased 2-component high solids epoxy amine binder system which performs according to aerospace requirements. The system was then compared to current "best in class" commercially available chrome-free corrosion inhibitors recommended for use on aluminium.

The coatings were applied on the high strength aluminium alloys (ie, 2024-T3 and 7075-T6) using various methods of chrome-free pretreatment (e.g. abrasion fol-

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lowed by solvent cleaning or chrome-free anodising or a chrome-free conversion coating) prior to application.
The full system build-up consists of 25 µm primer and 100 µm of polyurethane topcoat. After 7 days' curing at 23 °C and 55 % RH the systems were tested to ASTM B-117 and EN 3665. Prior to exposure, the panels were scribed using a mechanical milling device or engraver: 2 mm wide and 250 µm deep for ASTM B-117 and 1 mm wide, 100 µm deep for EN 3665 filiform testing.

Specific challenges of filiform corrosion

For many years, hexavalent chromium pretreatments and coatings have demonstrated outstanding filiform corrosion resistance. This is not the case for chrome-free technologies. Due to the acidic nature of this corrosion mechanism an inhibitor is required which is active in this environment, provides active inhibition and has the ability to reduce the corrosion rate or stop the filiform corrosion.
The rate of filiform corrosion can be related to the slope of the curve when recording the propagation of the longest filaments during the corrosion test. In addition to the assessment of the longest filaments, the amount of filaments and the total corroded area are important factors to consider in test evaluations.
Figure 1 shows the performance of the new technology compared to chromates and the currently available chrome-free inhibitors on chrome-free anodised 2024-T3 bare substrate after 2.000 hours' exposure to the EN 3665 filiform corrosion test. When following the corrosion rate on this substrate (*Figure 2*), the 'new inhibitor technology' clearly demonstrates improved performance compared to the commercially available alternatives.
The corrosion rate is much lower and the filaments are much shorter and fewer, resulting in a smaller area affected by corrosion. In this case the new technology is even better than the chromate sample. These results are considered typical behaviour for this new technology, regardless of the pretreatment used.

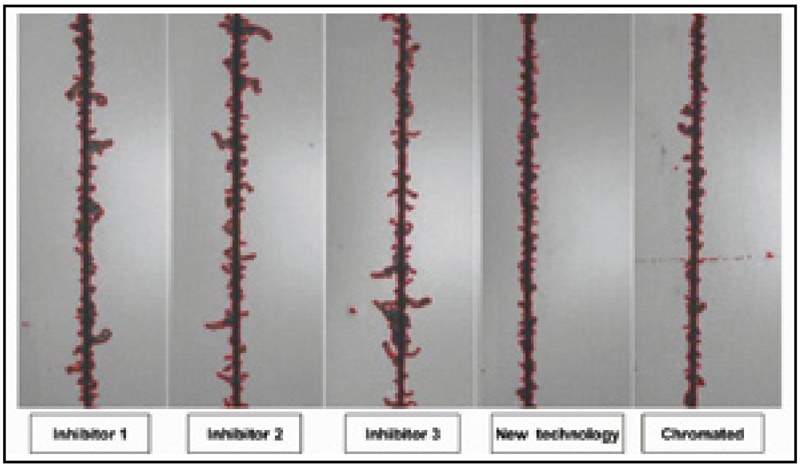

Figure 1: After 2000 hours filiform corrosion (EN 3665) test on 2024 T3 bare chrome-free anodised aluminium alloy, the new technology shows very short filaments and even better performance than the chromate sample

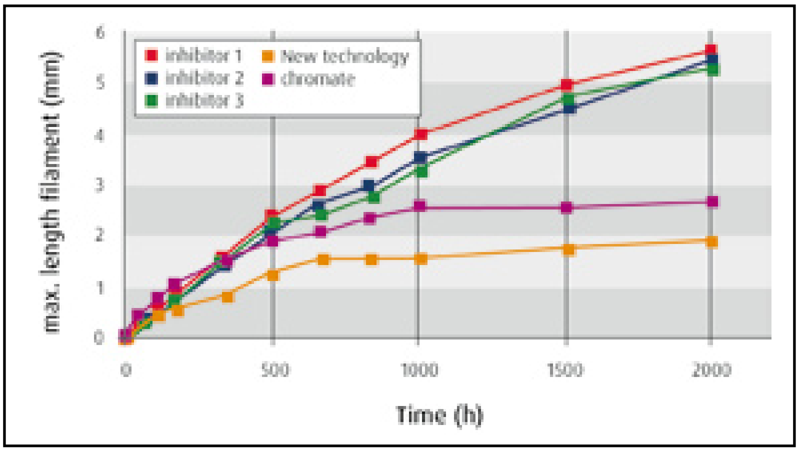

Figure 2: The new technology demonstrates a lower corrosion rate when following the propagation of the longest filaments during 2.000 hours' filiform corrosion testing (on 2024 T3 bare chrome-free anodised aluminium alloy, as Figure 1)

Results at a glance

››› A new chrome-free coating technology has been developed providing significantly improved corrosion protection on high strength aluminium alloys, compared to current commercially available chrome-free corrosion inhibitors.

››› The patent-pending technology features active filiform corrosion inhibition resulting in a low corrosion rate with short and fewer filaments. After neutral salt spray exposure, fast and effective passivation of the scribe is obtained. A leaching mechanism forms a stable passivation layer in the damaged area that provides long term protection and prevents pitting corrosion.

››› This coatings solution offers robust performance, comparable to that of systems using hexavalent chromium, to meet aerospace requirements over multiple types of substrates, regardless of the chromate-free pretreatment or binder technology used, and is fully health & safety and environmentally compliant.

Specific challenges of neutral salt spray testing

Neutral salt spray (ASTM B-117) exposure on 2024-T3 and 7075-T6 is one of the most challenging tests for a totally chrome-free technology. Hexavalent chromium corrosion inhibitors such as strontium chromate are well known for their excellent performance under this test. Their leach-

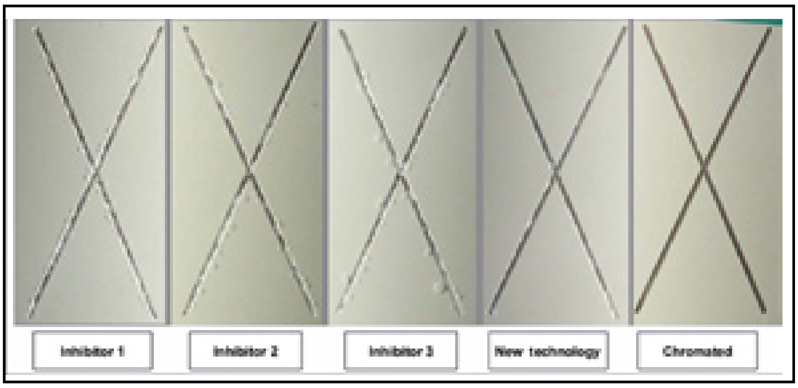

Figure 3: Samples of 2024 T3 clad (with chrome-free pretreatment) after 2.000 hours neutral salt spray (ASTM B-117) show that the new technology outperforms currently available non-chrome inhibitors

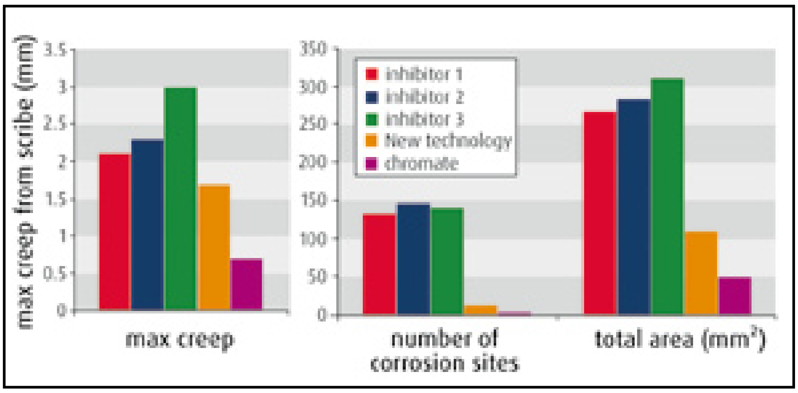

Figure 4: The new technology demonstrates reduced creep from scribe, a low number of corrosion sites and a significantly smaller area affected by corrosion, on 20243 T clad after 2.000 hours NSS (ASTM B-117) test

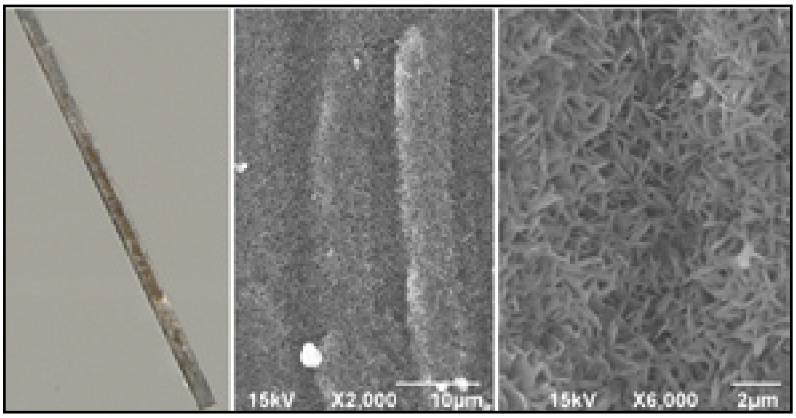

Figure 5: SEM observations of the morphology of the passivation layer formed by the new chrome-free technology during ASTM B-117 salt spray tests: (a) appearance of the scribe, (b) 2.000 times magnification and (c) 6.000 times magnification

ing nature and their ability to provide fast and efficient passivation at the scribe have been the most important factors.

In contrast, currently available chrome-free inhibitors are often too slow or too fast in terms of leaching but, more importantly, do not provide sufficient passivation in the scribe-damaged area, resulting in:

» Rapid darkening of the scribe;
» Early formation of corrosion-induced blisters along scribes;
» Excessive formation of corrosion products in the scribe;
» Pitting corrosion, especially on bare substrates.

Once corrosion starts in the scribe, it is very difficult to stop or slow this process down. This makes it very challenging to comply with the high standards set by chromate inhibitors. In order to obtain a good performance in NSS tests a coating/inhibitor technology needs the following characteristics:

» Adequate solubility and leaching characteristics;
» Fast and effective formation of a protective layer in the scribe and underneath the coating;
» Irreversible nature of the protective layer;
» Maintaining good coating integrity (barrier function).

Absence of any one of these characteristics will lead to corrosion and early failure in the corrosion test. The new inhibitor technology has these leaching properties, providing fast and effective passivation of the scribe. The scribes are clean and shiny with a low number of corrosion sites and a significantly lower area affected by corrosion after NSS exposure.

The current state of the art chrome-free technologies, on the other hand, show darkened scribes with a lot of corrosion. *Figure 3* shows the positive effect of the new inhibitor technology compared to the state of the art chrome-free corrosion inhibitors. 2024-T3 clad substrates are very sensitive to corrosion, but like chromate, the new technology shows a clean scribe with very little corrosion.

Once corrosion occurs in the scribe, the clad layer underneath the coating will sacrifice itself to protect the scribe, resulting in creep or blistering along the scribe. *Figure 4* shows that the new technology provides a lower creep from scribe, a low number of corrosion sites and significant reduction of the total area affected by corrosion. These evaluations demonstrate that an effective protective mechanism has been protecting the scribe when it was exposed to the neutral salt spray.

Effective passivation confirmed by interferometry

Experiments have shown that commercial chrome-free corrosion inhibitors produced severe corrosion at the scribe within 500 hours of exposure, while with the new technology the scribe remained clean and bright thanks to a passivation layer, which can be observed using an electron microscope.

Figure 5 shows the typical morphology of this passivation layer. The formation of this layer with sufficient thickness and resistance to the corrosive environment is essential to obtain long term corrosion protection. The effect and stability of the layer has been studied using white light

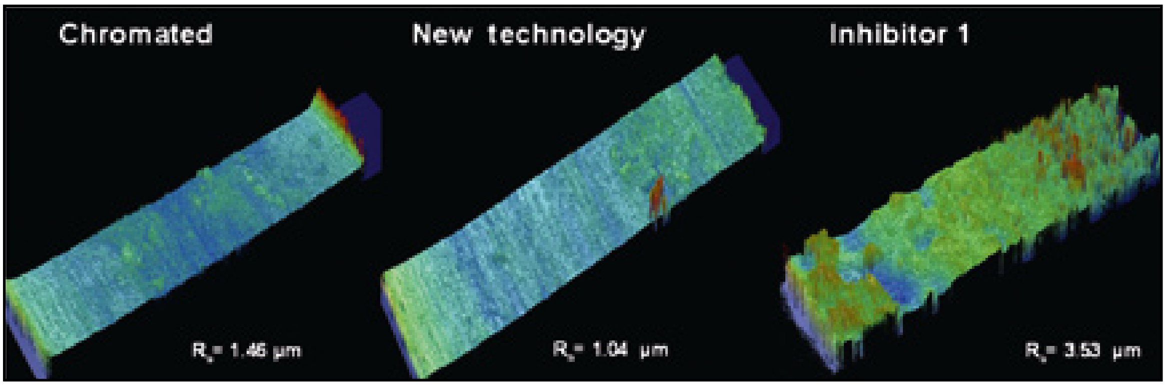

Figure 6: White light interferometry shows the surface roughness of the scribe on 2024 T3 bare metal after 500 hours NSS exposure: the passivation layer protects the substrate well, whereas the substrate under inhibitor 1 shows severe attack by the corrosive environment

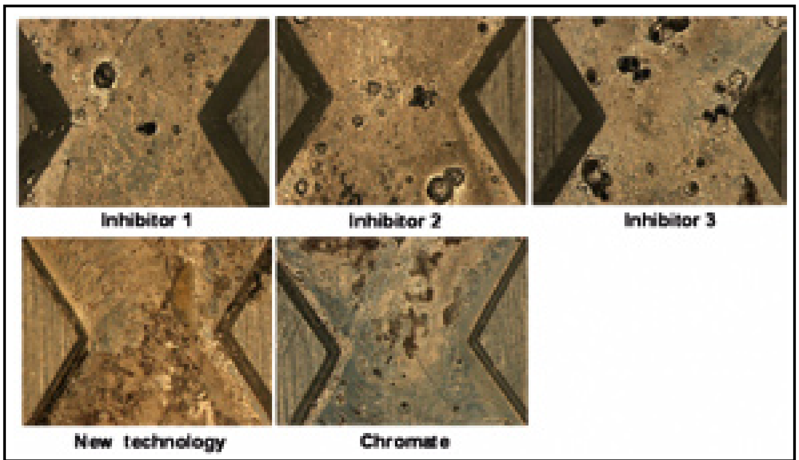

Figure 7: Evaluation of pitting corrosion on 2024 T3 bare after 2.000 hours NSS: the commercial chrome-free corrosion inhibitors show several deep pits, whereas the new technology shows no pitting corrosion, indicating fast and effective passivation

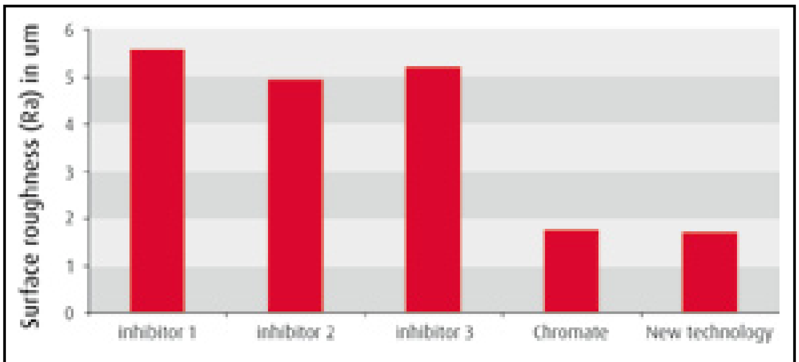

Figure 8: Surface roughness determined using white light interferometry analysis of the scribes of 2024 T3 bare after 2.000 hours NSS exposure; the new technology again shows performance comparable to chromate technology

interferometry, a non-contact measurement of surface topography.
The surface roughness of the scribe during the corrosion test indicates the degree of corrosion that has been occurring. *Figure 6* shows the surface roughness of the scribe after only 500 hours of NSS exposure. The scribe of the new technology shows a smooth surface like the chromate, confirming the fast and effective formation of a stable passivation layer in the scribe whereas the commercial chrome-free inhibitor shows insufficient activity.
The image clearly demonstrates that the commercial inhibitor was not able to protect the scribe in the early stage of the exposure. The aggressive environment has been attacking the substrate, resulting in a significantly higher surface roughness.

Good protection against pitting corrosion

Pitting corrosion is one of the biggest concerns for engineers designing structural parts for aircraft as this type of corrosion affects the strength of the structural parts. The fast and effective formation of a passivation layer, preventing early damage from pitting corrosion, is one of the most important features of the new chrome-free technology.
The technology was tested on 2024-T3 bare aluminium alloy and compared to the commercial chrome-free inhibitors. After 2.000 hours NSS exposure the samples were evaluated for pitting corrosion and surface roughness in the scribe using white light interferometry.
The analysis of the panels clearly revealed numerous sites of pitting corrosion (*Figure 7*) and a high surface roughness (*Figure 8*) of the scribe for the commercial chrome-free inhibitors. The new technology, on the other hand, showed an excellent performance with a smoother surface and excellent resistance to pitting corrosion. These observations demonstrate again that the passivation layer is stable enough to provide long-term protection.

New technology has broad applications in coatings

Compared to the "best in class" commercial chrome-free inhibitors, the new technology demonstrates significantly improved corrosion protection in multiple corrosion tests such as filiform corrosion and neutral salt spray, without compromising application characteristics and coating properties in the dry paint film.
Independently of the pretreatment, a robust and significantly improved corrosion protection is found on these various alloy substrates. The technology can be used universally in solvent and waterbased systems. This makes this new technology an important step forward in the development of sustainable and eco-efficient fully chrome-free coating solutions for the protection of aluminium alloys.

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