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Corrosion protection of Helicopters through Organic Coatings.

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Abstract:

In the helicopterindustry Aluminium has been an important construction material for decades.
This extensive use of Aluminium is caused by its favourable mechanical strength-weight ratio.
The Aluminium qualities used, however are in general very rapidly corroding and therefor have to be protected.
This protection can be done in two ways:

1. By Inorganic Coatings

2. By Organic Coatings

The protection through Inorganic Coatings is based on the reproducible built-up of the protective Alumina layer on the Aluminium-alloy.
Organic coatings provide protection by masking the Aluminium from its corrosive environment.
To ensure protection even in case of damages the organic Coating system is fitted with an unique self-repairsystem.
Apart from their ability to provide corrosion protection, Organic Coatings also give the possibility for Decoration, Invisibility towards IR detection, Conductance, Heat-resistance, Chemical resistance and Texture.
Additionally the Organic Coating system is a system, that can easely be maintained by every user of aircrafts in general and helicopters in particular.

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Introduction:

In the helicopterindustry as in the total aircraft industry, Aluminium has been the most important construction material for decades.
Probably this will not change dramatically in the coming years, although new materials, among which fiberreinforced-plastics, are extensively tested.
One of major reasons for the nearly exclusive use of Aluminium in Aircraft construction is certainly its favourable "mechanical strength-weight" ratio.
If however one reason has to be mentioned, that might encourage the use of new materials, it is the limited corrosion resistance of the alloys that are mainly used.

Although it is less noble than the rapidly corroding iron, pure Aluminium metal is in fact very corrosion resistant. This is caused by the very impermeable oxide or alumina layer, which is rapidly formed upon exposure to oxygen and which prevents the metal from further attack.
Pure Aluminium however is unfitted as construction material, due to its siftness.
For these purposes alloys are needed, among which the 4% copper containing 2024 T3 is the most widely used.
Copper however, very noble as it is, makes Aluminium anodic. In corrosive environments this results in the dissolution of the Aluminium adjacent to copper. (This is visible as pitting).
For this reason many alloys are treated with a thin layer of pure A.uminium.
Such a thin layer has however in case of damage an adverse effect due to the short circuited battery which is formed by the clad-layer and the more noble alloy.
The corrosion phenomena which exhibit on the alloys, as a result of these short-circuited batteries are listed in table 1.

Table 1:

Pitting corrosion	
Intercrystalline corrosion	
Layer	"
Stress	"
Contact	"
Filiform	"

This is why aluminium alloys have to be protected.

Inorganic coatings

In the protection of these alloys: coatings, both organic and inorganic can be of help.
The protection by inorganic coatings is established through the reproducable built-up and reinforcement of the aluminiumoxide layer.
Reïnforcement is possible with the use of anticorrosive chemicals.
Nowadays two main types of inorganic coatings are widely in use.

Table 2:

Chromatizing	- $Cr_2\ (CrO_4)_3$
	- $Cr\ PO_4$
Anodizing	- Cr-acid
	- H_2SO_4
	- H_3PO_4

In both processes the mill scale of the Aluminium is removed by an acidous pickling.
The chemical reactions occuring at the chromatizing process are listed in figure 1.

Fig. 1:

1) $2Al + 6H^+ + 6F^- \longrightarrow 2AlF_3 + 3H_2$

2) $3H^2 + 3/7\ Cr_2O_7^{2-} \longrightarrow 6/7\ Cr^{3+} + 3H_2O$

3) $2AlF_3 + 6H_2O + nH_2O \xrightarrow{cat.} 2Al(OH)_3\,nH_2O + 6H^+ + 6F^-$

In the wet stage the $Al(OH)_3\ nH_2O$ will be a gel. All soluble salts (incl. hexavalent chromium salts) will be encapsulated by the gel.
The coating is formed upon drying of the gel.

The chemical reactions occuring at the Chromium-anodize process are listed in figure 2

Fig. 2

Anode	$2Al + 3H_2O \longrightarrow Al_2O_3 + 6H^+ + 6e$
Cathode	$2HCrO_4^- + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 8H_2O$

The thickness of the oxide layer will vary with the applied voltage but can be as high as 2µm at 22 volts.
These processes have a distinct influence on the corrosion-resistance of the aluminium object.
Tested in a Saltspraykabinet, these pretreatments give the following results

Table 3:

pretreatment	corr. res.
none	2 wks
pickling (chrome acid)	6 wks
chromatizing	9 mnths
anodizing	21 mnths

Apart from the excellent corrosion resistance these processes have also some drawbacks.

Table 4:

1) Difficulty applicable in maintenance

2) Strippability of subsequent layers of organic coatings difficult

Additionally for Anodic coatings.

3) Mechanically vulnerable

4) Decreased fatique strength

5) Recoatability troublesome

6) Costs

In practise an inorganic coating is seldom used as the sole measure to prevent corrosion. Rather we find in aircraft-construction a combination of inorganic and organic coatings.
This brings us to the second way of corrosion protection, by organic coatings, an area in which Sikkens is active and in which it can benefit from many years of experience, as this slide is showing.

Organic Coatings

The organic coating system for exterior protection is built op of several layers in which every layer has its own particular function, as can be seen in the next table.

Table 5:	Washprimer	adhesion corr. resistance maintenance
	Primer	corr. protection chem. resistance H_2O "
	Topcoat	chem. resistance H_2O " Durability Appearance Smoothness

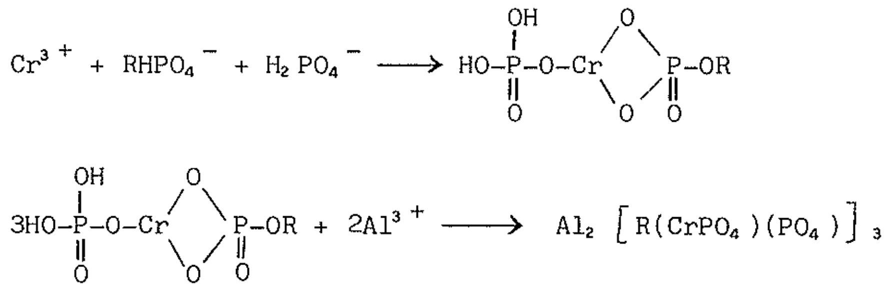
The Washprimer has been designed to ensure adhesion on a in principal poor substrate. This adhesion is established through a chemical reaction between parts of the Washprimer and the aluminium.

Fig..3

$$Al + H_3PO_4 \longrightarrow Al^{3+} + 1\tfrac{1}{2}H_2 + 3H_2PO_4^{-}$$

$$4H_2' + CrO_4^{2-} \longrightarrow Cr^{3+} + 4H_2O$$

$$H_2PO_4^{-} + ROH \longrightarrow RHPO_4^{-} + H_2O$$



R = binder

Because R is part of the binder system, the binder will be incorporated in the protective/adhesive layer.
It has to be said that this is not more than an assumption, because this process is actually not very well understood. For the actual corrosion-protection of the organic coating system the primer/surfacer is designed. For this reason this primer/surfacer is formulated with Chromates with a very distinct solubility.
This solubility ensures the leaching of the anticorrosive pigmentation at places of damage. Due to oxidative action chromates are capable of passivating the exposed aluminium.

Fig. 4

The exact passivating reactions are not fully understood, although it is expected that chromates are capable of repairing the protective Alumina layer.
Because chromates itself supply oxygen upon their reduction, this repair is even possible under the absence of oxygen, f.i. under intact coating systems.
As it is already said, a certain solubility is needed to ensure the leaching and by that the corrosion resistance.
It is however not only the watersolubility of the pigmentation which influences the leaching of the anti-corrosive pigments, also the nature of the chosen binder system in the primer/surfacer has a distinct influence. An example is shown in the next figure.

Fig. 5

The selection of this binder in both primers and topcoats is determined however by other demands too: f.i.

1. Chemical resistance (Lubricating, Hydraulic oils)

2. Water resistance

3. Adhesion

4. Durability (gloss retention, colour retention)

5. Appearance (gloss, smoothness, sagging)

6. Elasticity

In the helicopter industry the resistance against hot hydraulic and lubricating oils is very important.
In regard of all the demands only epoxy- and polyurethane binders exhibit the right properties for High duty/high performance coating systems.
Both binders however have their own specific strengths and weaknesses which clearly limit their application.

Table 6: Polyurethane

Caracteristic reaction:	$R{-}N{=}C{=}O + R_1OH \longrightarrow R{-}\underset{\displaystyle}{\overset{H}{\overset{\vert}{N}}}{-}\overset{O}{\overset{\Vert}{C}}{-}O{-}R_1$
Prop: excellent dur ability possible limited contribution to corrosion resistance excellent chemical resistance excellent adhesion on washprimers	

Table 7: Epoxy

Caracteristic reaction : $\overset{O}{\overbrace{C-C}}-R + R_1NH_2 \longrightarrow R_1\overset{H}{N}-C-\overset{OH}{C}-R$

Prop: poor durability (yellowing/chalking)
distinct contribution to corrosion resistance
good chemical resistance
poor adhesion on washprimer
good adhesion on solvent cleaned Aluminium

Because of the poor adhesion of epoxy primer on washprimers only P.U. primers are used over wahsprimers.
If we take in regard the durability it is understandable that we advice only Polyurethane binders for topcoats.
The same goed for chemical resistance, because P.U. appeared to be the only binder system that does not discolour upon exposure to hot Mil-C-23699 and Mil-C-83286 oils (mixture of 98% diisooctyladipate and 2% tricresylphosphate).

Conclusion

Summarizing we may state that on most aircraft one of the following two protective coating systems can be found.
Table 8

O.E.M.	chem. Pretreatment chromatize/anodize	Epoxy primers	Aerodur finishes P.U.
	Mil-C-5541	Mil-P-23377 DTD 5567 BMS 10-11t2	
Maintenance	Metaflex wash/etch primers	Aerodur P.U. primers	Mil-C-27227 Mil-C-83286
	Mil-C-8514		NT-10118/10077
	NT-10.113	NT 10.112	BMS 10-60 t2
	DEF 1408	DTD 5580	DTD 5580
	BI-CP 4511	VTL-A-003	NAF 62-2
	TL-8010-000	BMS 10-79	TH 5702
	AA-MP-26	TH-5701	DMS 2143

Topcoats can be supplied in different gloss grades and for specific purposes like

Table 9

Reflex	tecture
Walkway	infra red reflectance/absorbance
Friction	plastic parts
Erosion	solar heat reflectance
conduction	
Heat resistance	

Sikkens aircraft finishes exhibit excellent corrosion protection as you can verify on the next slide.

Fig. 6

This all brings us to the conclusion that organic coatings are indispensible to reach the best possible protection of Aircrafts in general and helicopters in particular in both OEM and maintenance.