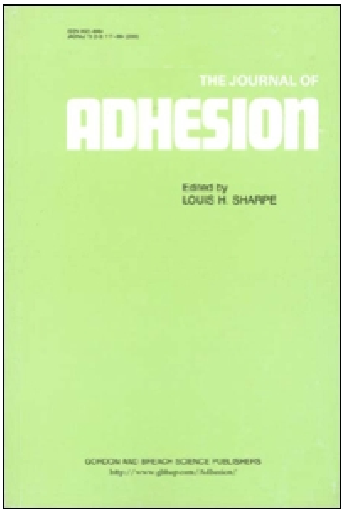

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Adhesion Primer Properties: Microstructural Changes Induced by Ageing

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The use of primers in adhesively bonded joints becomes more and more important in industrial process for improving the environmental strength of bonded structures. In this study we consider bonded joints comprising an aluminium alloy substrate clad with pure aluminium, an alumina layer obtained by surface treatment, a corrosion-inhibiting primer and a structural adhesive film. Observations and analyses (TEM or SEM imaging, electron diffraction, x-ray micro-analysis . . .) show that important microstructural changes of the metal/oxide/primer interphase are induced by ageing. The main modifications observed are: (a) appearance of crystalline areas in the primer layer near the oxide/primer interface, (b) complete disorganization of the columnar oxide morphology, (c) dissociation of the corrosion inhibitor. These phenomena are directly correlated to the strength losses of the bonded joints that are evaluated by mechanical experiments.

KEY WORDS Structural film adhesive; primer; aluminium oxide; interphase; durability; morphology; microstructure.

INTRODUCTION

Bonded joints with aluminium alloys substrates are known to possess high initial strengths when appropriate surface treatments are used. However, in humid and hot environments the bond strength decreases dramatically and some failures can be observed during the life of the structure. The purpose of this work is to improve the understanding of such joint degradation phenomena. In what follows, our interest focusses on the physico-chemical characterization of each joint component and particularly on the corrosion-inhibiting primer layer.

BONDED JOINT CHARACTERIZATION

A representation of the bonded structure studied is given in Figure 1. The overall assembly was carried out at Aerospatiale of Suresnes.

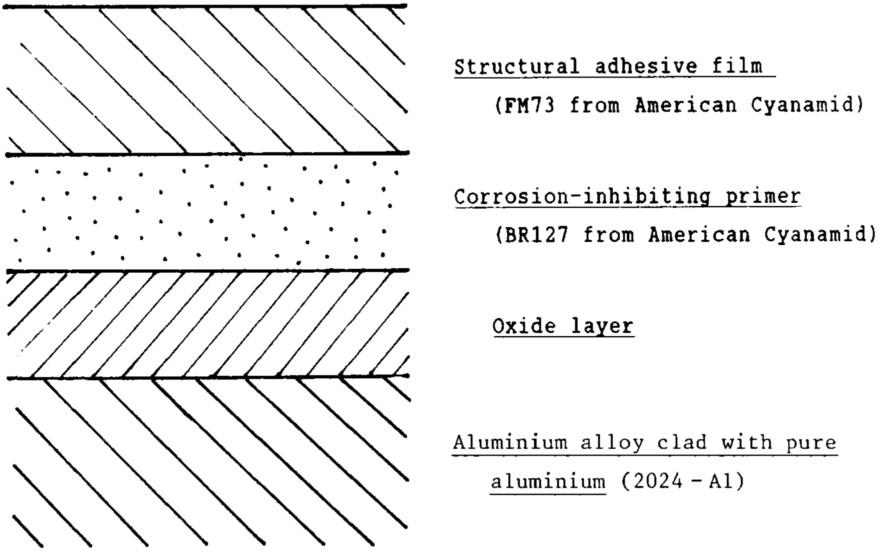

FIGURE 1 Schematic representation of the bonded structure.

A more detailed description of each component of the metal/adhesive interphase is given below:

The microcharacterization is carried out using a Transmission Electron Microscope (TEM) (Philips EM 420) equipped with a scanning unit (STEM), a secondary electron detector (SEM), an energy dispersive x-ray spectrometer (EDS) and an electron energy loss spectrometer (EELS).

Electron diffraction and microscopy give information about the crystallographic microstructure; x-ray detector with retractable beryllium window allows the chemical analysis of elements up to $Z = 5$ and EELS provides both microstructural information and chemical analysis with high sensitivity to light elements. In addition, the scanning unit gives analytical advantages such as high spatial resolution (~2 nm), x-ray mapping and filtered energy imaging.

Oxide layer

The oxide layers are obtained by one of the following surface treatments: (a) chromic acid anodising (CAA), (b) phosphoric acid anodising (PAA), (c) sulfochromic etching (SCA). In this last case, the surface treatment bath possesses the following composition: H_2SO_4 (250 g/l), CrO_3 (50 g/l), $Al_2(SO_4)_3$ (7 g/l), $CuSO_4$ (0, 2 g/l).[1,2]

The oxide layers were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 2 shows the topography of an oxide layer obtained by CAA. The presence of both macro- ($\approx 1\ \mu m$) and micro-roughness ($\approx 0.01\ \mu m$) is clearly revealed. The same topography is observed for oxide layers obtained by PAA and SCA treatments.

Figures 3 and 4 show high resolution SEM images obtained with the Philips

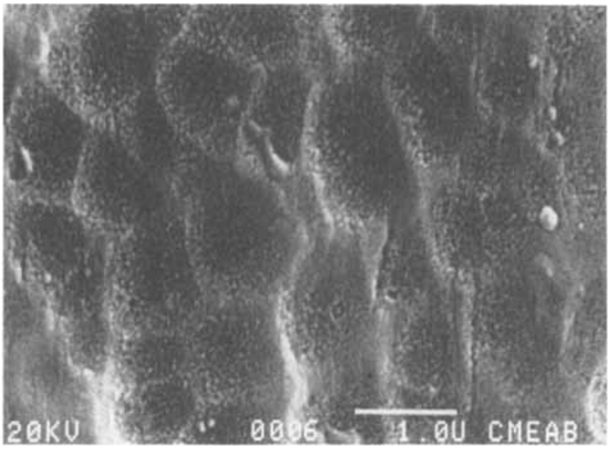

FIGURE 2 SEM image of an oxide layer (CAA treatment).

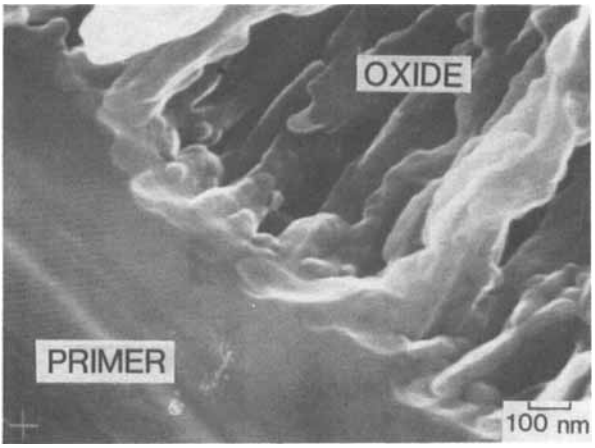

FIGURE 3 SEM image of an oxide (CAA treatment)/primer interphase cross-section.

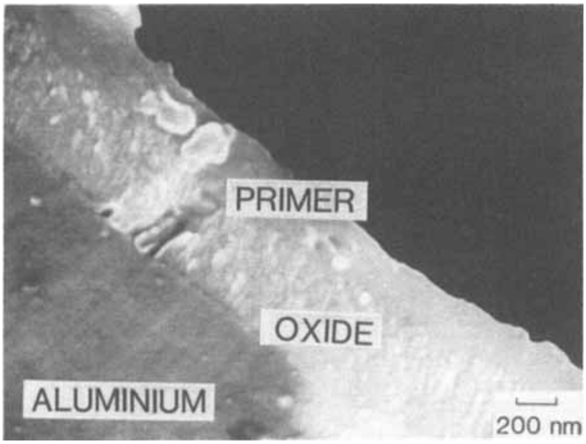

FIGURE 4 SEM image of an oxide (PAA treatment)/primer interphase cross-section.

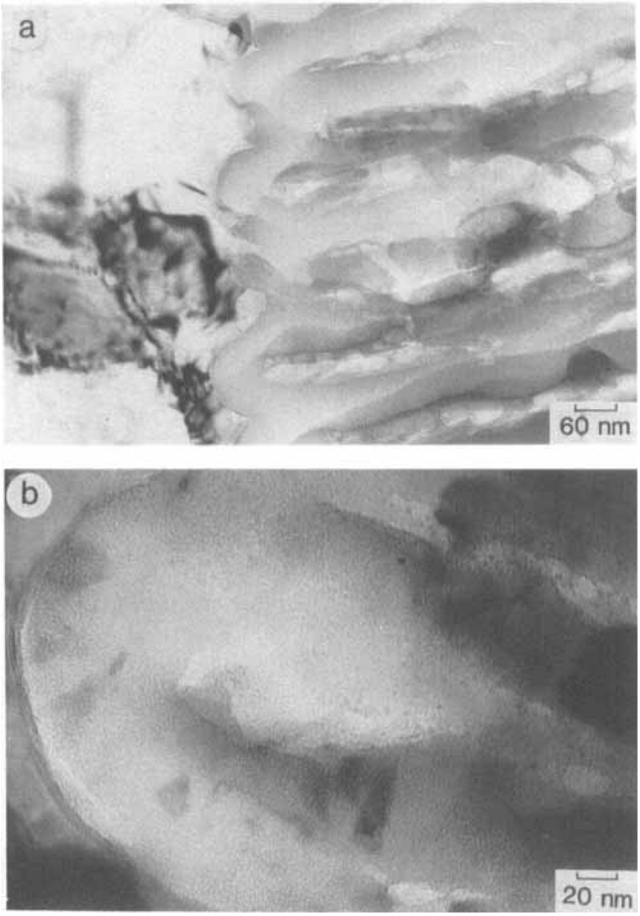

FIGURE 5 TEM images of an oxide (CAA treatment)/metal interface. (a) image showing the continuity between the oxide columns and the barrier layer, (b) high resolution image of the amorphous barrier layer.

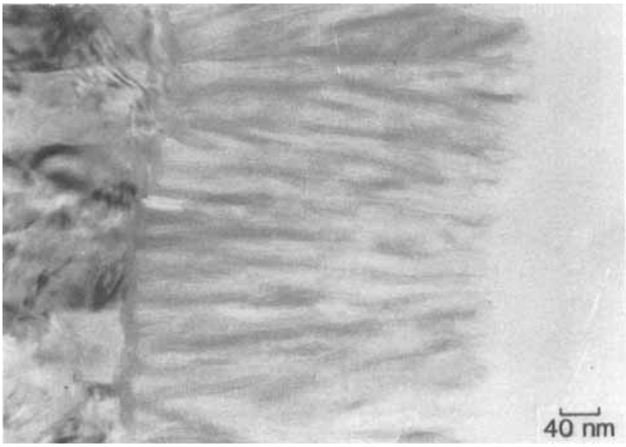

FIGURE 6 TEM image of the oxide layer (PAA treatment).

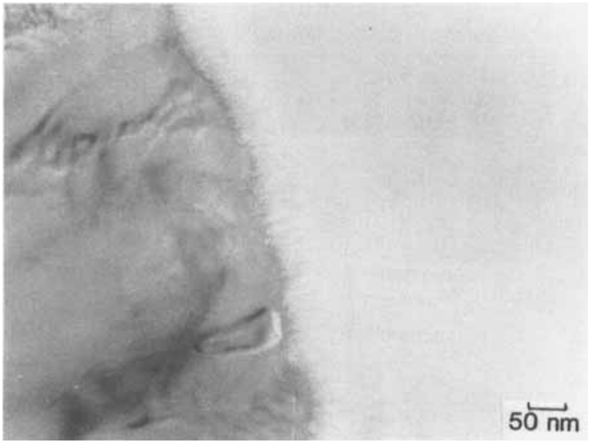

FIGURE 7 TEM image of the oxide layer (SCA treatment).

EM420 transmission electron microscope equipped with a secondary electron detector. The direct observation of the metal/oxide/primer interphase is made possible due to the ultrathin cross-section ($<0.1\ \mu m$) microtomy process (in these cases the specimens studied do not comprise the adhesive film). Comparison of Figures 3 and 4 brings out the very different morphologies of the oxide layers obtained by CAA and PAA. It must be noted that in both cases the structure of the layers is very different from the geometrical columnar shape currently described in the literature. Under similar operating conditions, the oxide layer obtained by SCA could not be observed owing to its very small thickness.

TEM investigations were carried out on ultrathin cross-sections of the bonded structure (comprising metal, oxide, primer and adhesive successively). The images (Figures 5 [a] and [b]) show the "column" ends near the metal forming the barrier layer with a particular morphology. Microdiffraction experiments carried out on this layer show the diffusion halos typical of an amorphous structure. However, crystalline nuclei induced by the electron beam impact can also be observed.

In addition, characteristic TEM images of the oxide layers obtained either by PAA or by SCA are presented in Figures 6 and 7.

The main features of the oxide layers are summarized in Table I.

Primer layer

According to the technical description of the manufacturer,[3] the primer studied is a mixture of epoxy resins with low molecular weight, phenolic resins, reticulation agents, high molecular weight polymers (to improve the coating hardness), and a suspension of rare earth salts. The analyses carried out during this work do not show the presence of phenolic resins. The following composition (weight %) is

TABLE I
Summary of the oxide layer characteristics

Treatments	CAA	PAA	SCA
Oxide layer thickness (nm)	2000 to 6000	600	50
Porosity	high	low	high
Barrier layer thickness (nm)	60	10	5
Morphology	irregular "columns"	regular "columns"	filamentous appearance
Chemical composition	aluminium oxide	aluminium oxide	aluminiun oxide
Impurities		phosphorus	iron, copper

found:[4]

– solvents:		89.8%
– fillers ($SrCrO_4$):		1.8%
– resins	. epoxy Novolac . hardener CA150 bis(1,1-dimethyluree)-2,4-toluene . high molecular weight polymer	8.4%

The primer is applied using a pneumatic gun after vigourous mixing according to the manufacturer's instructions (under atmospheric conditions as described by the latter). It is applied within four hours of surface treatment drying.

Drying and polymerization conditions are as follows:

- 45 min (±15 min) at room temperature
- 60 min (±5 min) at 125°C (±5°C)

The primer thickness should be within 3 and 5 μm after drying and is obtained by applying two successive layers with an interval of 10 min.

Pieces (stored under normalized climatic conditions) must be bonded within 30 days of primer application.

The topography of the primer layer surface observed by SEM is independent of the nature of the underlying oxide. In addition, this topography does not change with ageing (until 8 weeks). A characteristic image of the primer layer surface (Figure 8) brings out the presence of two phases; one is constituted of agglomerated $SrCrO_4$ crystalline needles and the other of resins. The aggregates of $SrCrO_4$ are merged in the polymer matrix. However, most of the time, the cross-section process used for TEM observations extracts these needles from the polymeric phase and the presence of holes is noticed (an example is presented in Figure 9). This phenomenon reveals the poor adherence between the two phases.

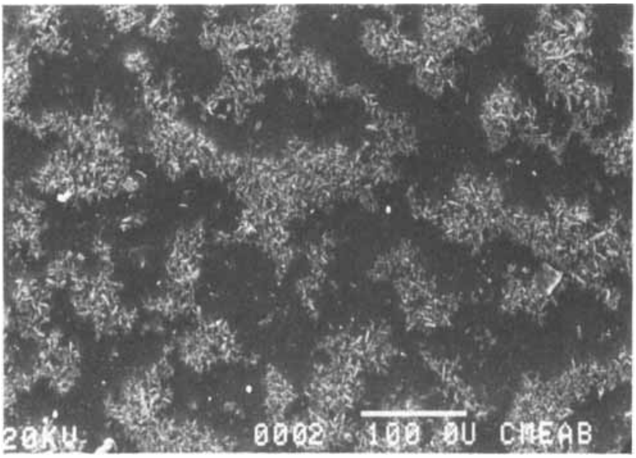

FIGURE 8 Characteristic SEM image of the primer layer topography.

W. Brockman[5] has already mentioned the absence of bond between fillers and resin in a similar primer system.

In addition, the techniques employed reveal many anomalies. Some of these are listed here:

– x-ray microanalyses of corrosion-inhibiting agent show the presence of Cr and O in all cases and of Pb or Sr depending on the set of samples analyzed (Figure 10). It must be noted that the presence of Pb is restricted to the mineral fillers and no Pb pollution of the sample has been observed. Moreover, Pb is currently

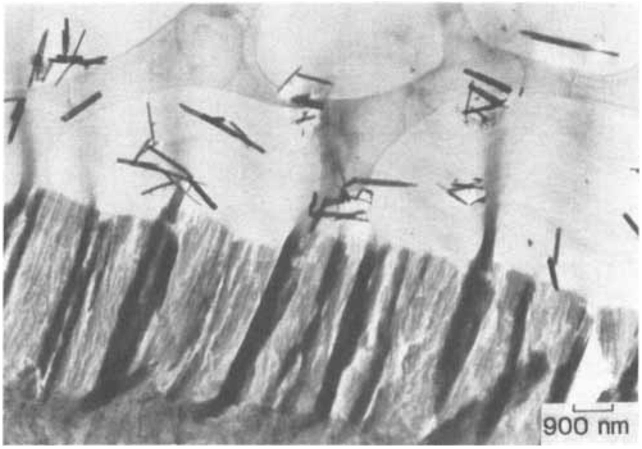

FIGURE 9 TEM image of a primer layer where very little $SrCrO_4$ needles stay adherent to the polymer phase.

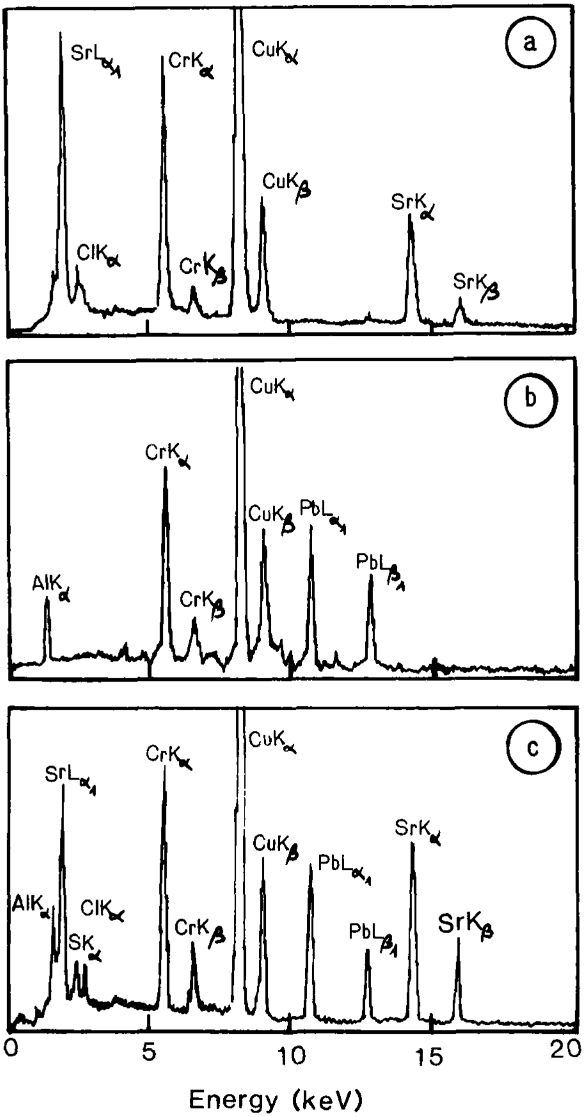

FIGURE 10 EDS spectra of three different sample sets showing the presence of the following elements: (a) Sr, Cr, O, (b) Pb, Cr, O, (c) Sr, Pb, Cr, O.

used as a corrosion inhibiting agent. We can, therefore, conclude that the chemical composition of the primer depends on the batch supplied by the manufacturer.

– in some cases the presence of two superimposed primer layers (coming from the deposition process) can be distinguished and several defects (failures) can be observed at their interface (Figure 11). The total thickness of this layer is generally between 4000 and 6000 nm but in some cases it can decrease to 100 nm.

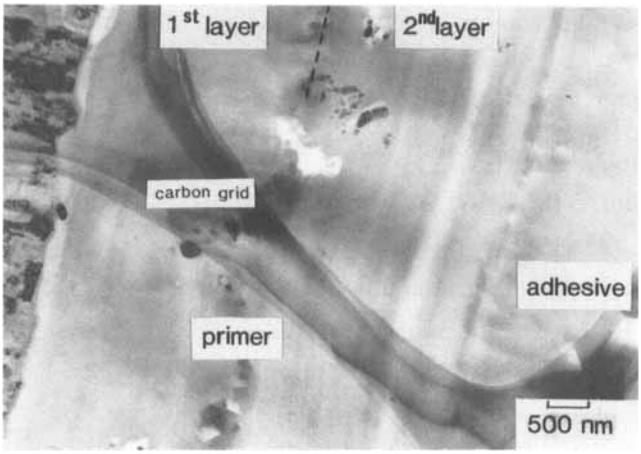

FIGURE 11 TEM image of the two superimposed primer layers (with SCA oxide).

This irregularity in thickness could be due to the means of film deposition employed (pneumatic gun).

– in some particular cases it is observed that the primer reticulation induces the appearance of polymeric nodules in the resin matrix. This phenomenon is probably connected with the reticulation of the hardener.[5] The mean diameter of these nodules is about 100 nm (Figure 12). However, microanalytical techniques do not allow the characterization of these two phases.

Structural adhesive film

FM 73M06 (American Cyanamid) is a modified epoxy adhesive film supplied with a random polyester mat carrier.

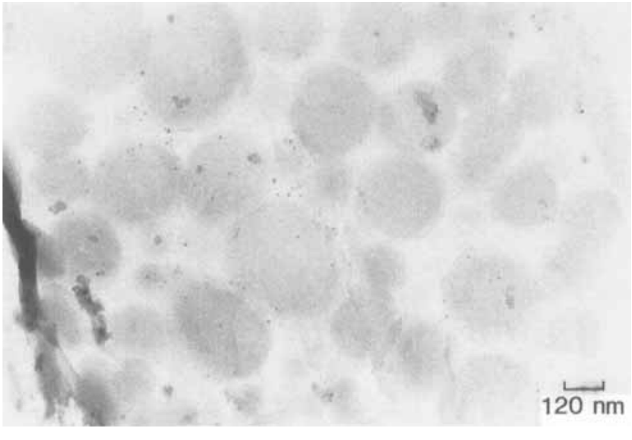

FIGURE 12 Visualisation of nodules induced by the polymer reticulation.

The chemical composition (weight %) of the adhesive system has been found to be the following:

– resins	. epoxy base (DGEBA and DGEBA tetrabrominated)	
	. hardener CA 150 (bis MUT)	
	. toughener (CTBN)	3.9%
– inorganic fillers ($MgSiO_4$)		0.2%
– frame (Mat Dacron)		5.5%

The adhesive is polymerized in a hot platen press. The cure cycle is as follows:

- pressure 3 bars (±0.5 bar)
- temperature gradient of 2 to 4°C/min up to 125°C
- level of 60 min (±5 min) at 125°C (±5°C)
- cooling under pressure down to at least 60°C

TEM observations reveal the presence in the adhesive of two extended polymeric phases forming areas about ten microns across (Figure 13). One phase (1) is uniform and relatively transparent to electrons. The other (2) is much more opaque with randomly distributed fibres (with a mean diameter of approximately 0.5 μm). Many failures can be observed between the fibres and the matrix coming, probably, from the cross-sectioning process. The origin of this phenomenon of phase separation has not been clearly shown yet. However, different hypothesis can be envisaged:

– phase separation between the two epoxy resins, DGEBA and DGEBA brominated

– poor compatibility between the matrix and the hardener (by analogy to the micelles of hardener observed in the primer)

– limited compatibility between the matrix and the toughening rubber (CTBN). A similar phenomenon has already been observed.[6]

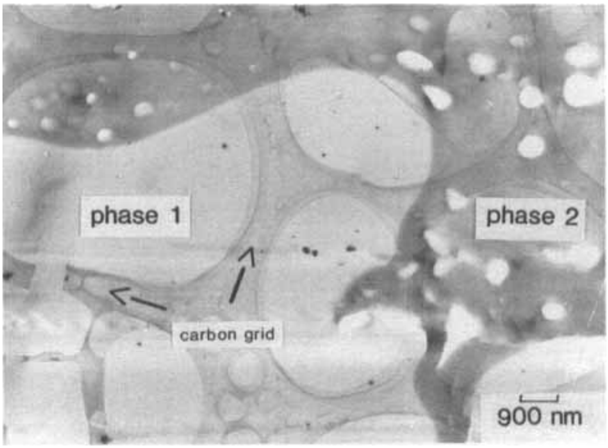

FIGURE 13 Typical TEM image of the adhesive.

AGEING EFFECT ON THE BONDED JOINT

Under the effect of hot and humid environments, bonded assemblies may, in certain cases, show adhesive fractures. The causes of these fractures are as yet not completely understood and is it difficult, therefore, to determine the long term performances of metal/adhesive bonds.

The object of this part is to understand better the degradation mechanisms of bonded joints using relationships between properties of metallic surfaces and interfaces and bond ageing behaviour

Microstructural changes of the different components of the bonded joint

The purpose of this part is to determine the effect of ageing on the microstructural properties of each component of the bonded joints. The latter are still constituted by the substrate, the oxide (obtained by PAA, CAA or SCA etching), the primer and the adhesive. They are aged under hydrothermal conditions (70·C, 95% relative humidity) for 15 days exposure. These ageing conditions are commonly used in the French industry and particularly at the Aerospatiale to obtain visible degradation after short periods.

The microcharacterization of the bonded joints after two weeks ageing reveals various microstructural changes. In particular, the following phenomena have been observed:

– major disorganization of the oxide morphology (Figure 14), *i.e.* disappearance of the barrier layer, spider-webbed morphology of the porous layer, appearance of destroyed areas (with presence of voids). This phenomenon has been observed for the three treatments but its importance is connected to the nature of the oxide. Indeed, when the substrate is treated by SCA etching we observe the more important degradation and an increase of the oxide thickness induced by the penetration of the oxide in the substrate.

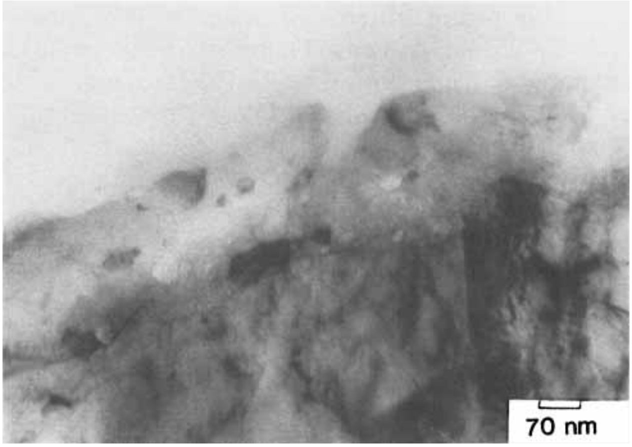

FIGURE 14 TEM image of a metal/PAA oxide/primer interphase after two weeks ageing.

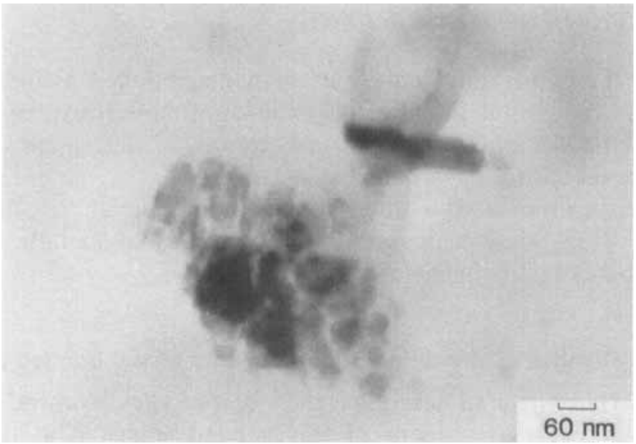

FIGURE 15 Morphology of the corrosion inhibiting agent after ageing.

– appearance of microcrystalline areas in a primer layer close to the oxide. This is pointed out by the modification of the diffraction contrast on TEM images and the appearance of spots on the diffraction pattern. The mean thickness of this modified layer depends on the nature of the underlying oxide and varies between 100 nm with CAA oxide to 300 nm with SCA etching oxide.

– disintegration of the mineral fillers present in the primer, probably due to a chemical reaction between water and chromate species (Figure 15).

– appearance of numerous failures between the two extended phases of the adhesive.

Correlation with the mechanical properties of the bonded joint

In this part, the mechanical test used is a three-point flexure test. The sandwich samples (represented in Figure 16) are constituted by two substrates of different sizes (10 × 50 and 10 × 25 mm) to avoid compressive stress in the adhesive film. A strain at constant speed (0.5 mm/min) is applied to the middle of the sample. The instrument used (ADAMEL LOMARGY DY.25) possesses a 1000 N full scale load cell. The span is fixed at 40 mm.

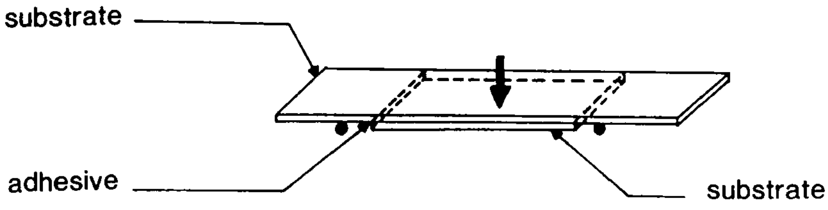

FIGURE 16 Schematic representation of the three point flexure test.

During these tests all the substrates used had been treated by CAA (and the bonded assembly was carried out in industrial conditions by AEROSPATIALE). Six specimens were tested in each case to obtain a sufficient statistical sampling.

As an example, three characteristic results are presented here.[5] They correspond respectively to:

(a) initial state,

(b) two weeks ageing of the primed surfaces (before the bonding treatment),

(c) two weeks ageing of the bonded assembly.

Sample state	(a)	(b)	(c)
Max. strength before failure	880 kg ±4%	675 kg ±9%	686 kg ±5%

Before ageing (case (a)), the fracture is localised in the adhesive and the mechanical strength of the bonded joint is limited by the cohesive strength of the adhesive film.

After ageing, in both cases the strength loss compared with the initial state is approximately the same (~20%) but the fracture is not localised in the same area. After primer ageing before bonding (case (b)), the fracture is located in the primer. This result could be induced by the microstructural change observed in the primer layer. After ageing of the bonded joint (case (c)), the fracture is located in the adhesive film. Thus, the adhesive is the first component to be degraded. This result is connected to TEM observations showing numerous cracks in the adhesive.

DISCUSSION AND FUTURE PROSPECTS

The purpose of the primer coating is to fulfill the following requirements:

(a) to protect the oxide layer against an agressive atmosphere.

(b) to improve the adherence of the multi-layer system,

(c) to retain at the same time the mechanical properties of the assembly (no brittle primer layer).

This study has pointed out some problems in the primer coating properties. The main results are the following:

- the oxide/primer interphase undergoes important microstructural changes during ageing, induced by water penetrating into the interphase.[6]

- the accelerated ageing of the primed surfaces induces a 20% strength loss of the bonded assembly (under the exposure conditions used in this study). This result poses a problem concerning the primer coating effectiveness for pieces stored in an industrial environment.

– the chemical composition of primers and adhesives is modified by the manufacturer without due warning.

This study has pointed out the great advantages of using TEM and microanalytical techniques and the quality of the information obtained by these techniques. From a fundamental viewpoint it would be interesting to investigate:

– understanding of the anti-corrosion mechanism of the primer (role of the corrosion inhibitor: the effect of its presence and of its distribution in the resin matrix); determining the resin/resin and resin/corrosion inhibitor interactions,

– determining the metal oxide/primer interactions and, in particular, the effect of the nature of the metal on the primer characteristics,

– establishing correlations between microstructural and mechanical properties of each component, and the final strength of the bonded joints.

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