A COMPARISON OF ANODIZE PROCESSES ON THE STRENGTH
AND DURABILITY OF ADHESIVELY BONDED ALUMINIUM

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Abstract

The influence of different treatments: FPL-etch, European chromic-acid-etch (CSA), phosphoric-acid-anodizing (PAA) and chromic-acid-anodizing (CAA) of two aluminium alloys in bare and clad state for 2040 T 3 and 7075 T 6 are compared as adhesive bonds. The adhesives were FM 123-5 and FM 73, the primer BR 127. Finally the microstructure of the pretreated aluminium-surfaces are compared.

1. Introduction

Damages in long time stressed metal bonds under hostile environmental conditions, from which humidity is the most important factor, occur in nearly all cases in form of adhesional failure between adhesives or primers and metal surfaces. This is due to the fact, that the adhesional bonds between organic substances and the metal oxides are destroyable by hydrolytic reactions of water, diffusing into the glue line [1].

To improve the water stability of metal bonds especially in aircraft structures beside the application of corrosion-inhibitant-primers in the case of using epoxide adhesives special surface treatments of the aluminium alloys prior to bonding are needed. The different chemical or electrochemical treatment methods customary today in the aircraft industry of the western world are developed empirically without exact knowledge of the adhesional mechanisms due to good stability of the boundary layers.

The European surface treatments as CSA-etching over 30 min. in chromic-sulphuric-acid and chromic-acid-anodizing (CAA) are used in Europe since more than 20 years. In USA a modified FPL-Process and the new developed phosphoric-acid-anodizing (PAA) process are used. These two methods of treatment are more economic than the European CSA-process followed by CAA - but it is not exactly known, in how far the durability of metal-bonds produced with these surface treatments are better than those pretreated with the European methods.

The aim of our study was to test the strength and durability of adhesive bonds made with surface treatments as shown in figure 1.
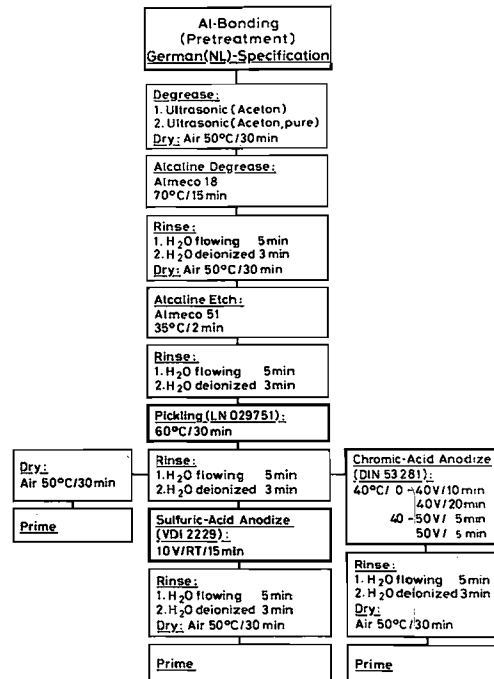

Fig. 1: Pretreatment for Al-Bonding

There are:
The European CSA-process, specified by LN 029751

European CSA-process with chromic-acid-anodizing (CAA), specified by DIN 53 281

FPL-etch (optimized), specified by BAC 5514

and phosphoric-acid-anodizing, specified by BAC 5555.

In addition to these treatments also the sulphuric-acid-anodizing (SAA) was used (CSA etch and 15 min. anodizing in 11,4 % SA under 10 V).

2. Materials and Test Methods for Bond Strength

The aluminium alloys for the comparison used in our investigations were the for aircraft structures important alloys 2024 T 3 (AlCuMg 2) and 7075 T 6 (AlZnMgCu 1,6) which were treated and bonded in bare and clad state.

Adhesives we used were the both one-

component epoxide-nitrile systems FM 123-5 and FM 73 of Bloomingdale in combination with the corrosion-inhibitant primer BR 127 from the same company.

Test specimens for evaluating the bond-strength and the aging behaviour were single overlapped joints with a sheet thickness of 1.6 mm and an overlap-length ov 12.5 mm, specified by ASTM D 1002/72. Aging procedure was storing the specimens in unloaded state over 720 h in an artificial climate of 65 °C and 95 % rel. humidity.

3. Bond Strength Results

The results of the tests are to be seen in figures 2 - 5. Plotted in fig. 2 is the shear strength of 2040 T 3 clad bonds in unaged state and after aging. For FM 123-5 the European treatments seems to be slightly better whereas in the case of FM 73 PAA, CSA, CAA and SAA lead to good results.
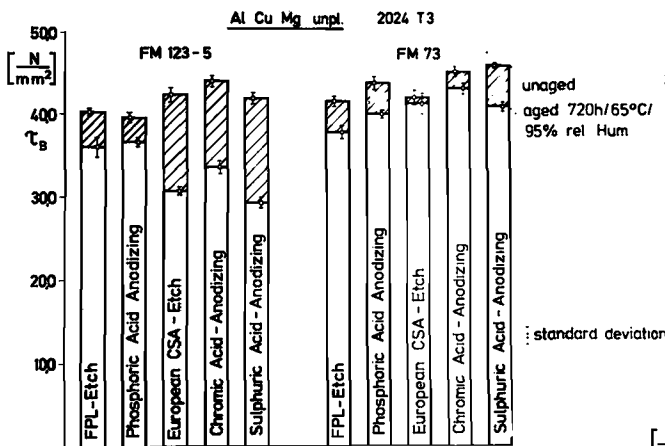
Fig. 2: Shear-strength of overlapped bonds of 2024 T 3 unclad

Figure 3 shows the results obtained with the alloy 2024 bare with FM 123-5 the US-treatments lead to better results because the effect of aging is less than after the European-treatments. In combination with FM 73 the European-treatments are better than the US-processes.

Figure 4 shows the results for 7075 T 6 clad. Here the US-treatments lead to some better results with FM 123-5. For FM 73 with exception of SAA no differences between the treatments are to be seen.

Figure 5 shows the results obtained with this alloy in bare state. Of interest is here that in combination with FM 73 the aging influence in the case of European-treatments is less and the best aging behaviour is reached by sulphuric-acid-anodizing (SAA).
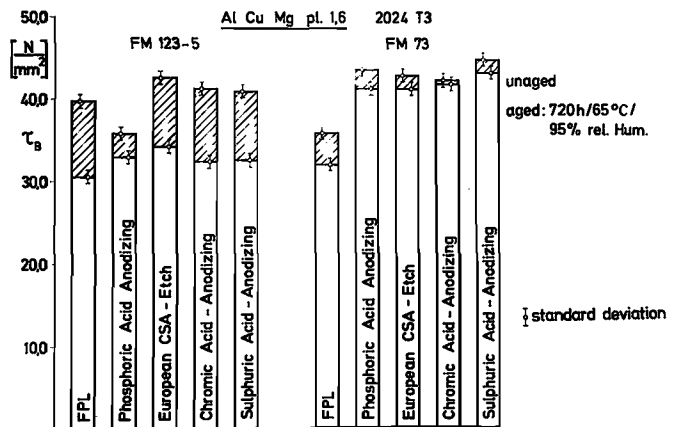
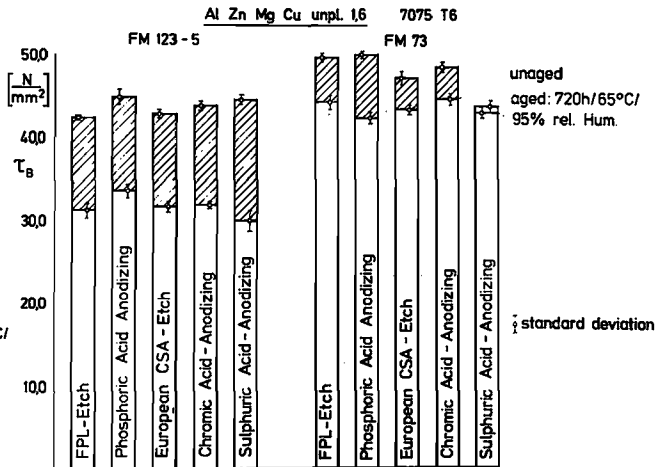Fig. 3: Shear-strength of overlapped bonds of 2024 T 3 clad

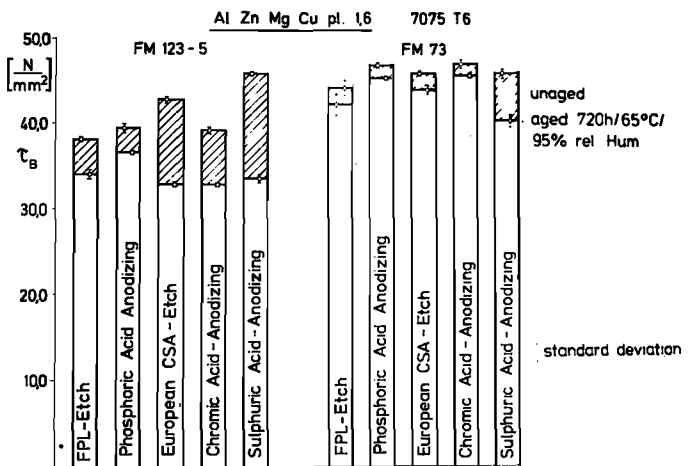Fig. 4: Shear-strength of overlapped bonds of 7075 T 6 unclad

Fig. 5: Shear-strength of overlapped bonds of 7075 T 6 clad

More distinct differences are to be seen on hand of the peel-values of bonds 7075 T 6 clad and FM 123-5, figure 6.
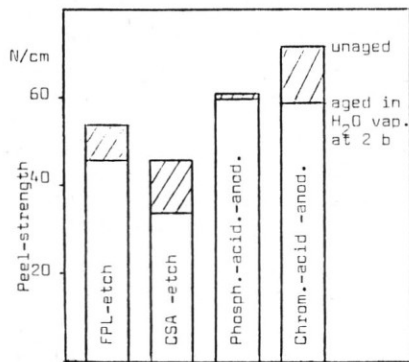

Fig.6: Peel-strength (180° peel-specimens) of metal bonds.
Material: 7075 T 6 clad
Adhesive: FM 123-5

Compared with FPL- and European-CSA-etching both anodizing processes produce higher initial strength combined with an increased stability against invading water. Especially in the case of phosphoric-acid-anodizing there is no difference between initial strength and that after storing in water vapour.

The conclusion on hand of these results is that today exist not only one surface treatment with outstanding properties for producing bonded aluminium structures [2]. But generally it seems to be true, that the anodizing processes lead to better results than the etching-systems.

4. Microstructure of Aluminium Surfaces

In addition to measurements of strength, specimens were prepared to examine the treated surfaces by scanning-electron-microscopy (SEM).

Figure 7 shows the particular steps of the pretreatment after the change of the surface morphology. The as received state is not structured but contaminated. After degreasing a still not really clean surface with some loose particles is to be seen. The alcaline degreased surface shows an irregular structure with pits, but without any micromorphology. These changes in surface morphology up to this step are characteristic for all chemical processes of aluminium alloys. The other two pictures in fig.7 show an etched (CSA) and an anodized (CAA) surface with developed oxide structures in more detail. Clearly visible is here the changing in morphology after etching and anodizing by a magnification of 20.000X.
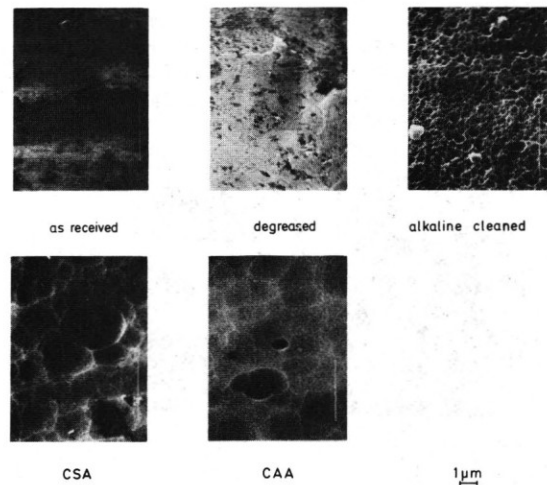

Fig. 7: Steps of pretreatment for 2024 clad

In figure 8 an optimized FPL-treated surface of an 2024 clad specimen is to be seen and compared with equally treated 2024 T 3 bare specimens below. Concave hilly formed overstructure and a hint of a micromorphology with oxide-pits are to be seen. The pictures on the right side show treated surfaces by PAA. The clad state shows a high structured oxid-morphology while the bare state is much less structured.

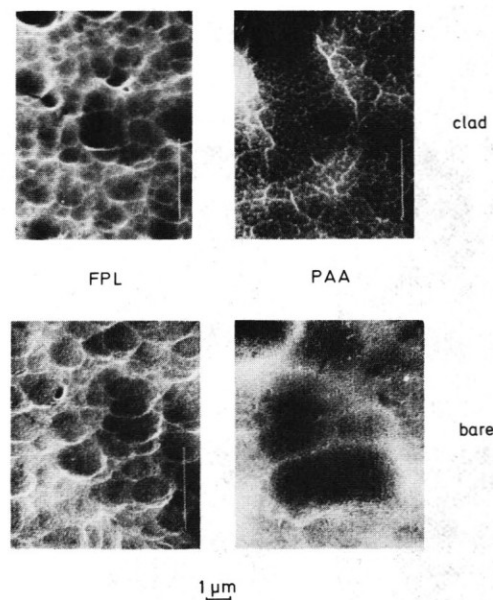In both cases of PAA a very filigree morphology like an "oxid-wood" remains.

Fig. 8: Surface morphology of treated 2024 clad and bare

Figure 9 shows surfaces of the alloy 7075 T 6 clad and bare after the same treatments with similar structures like 2024 T 3, on the one side a hilly overstructure and on the other side a rather filigree wooded type.
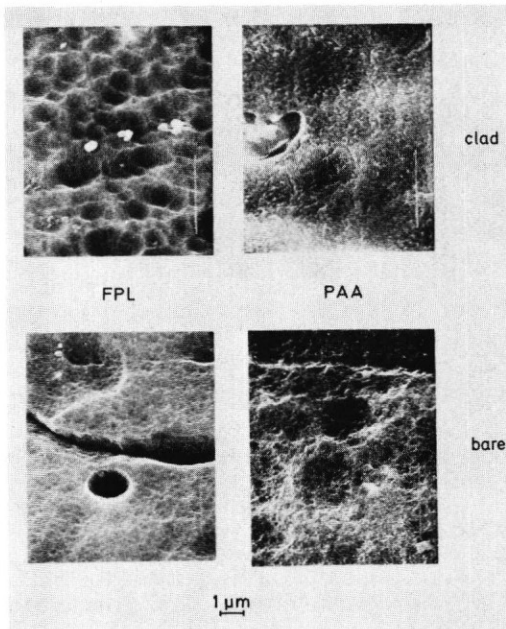

Fig. 9: Surface morphology of treated 7075 clad and bare

Figure 10 contains micrographs of the same aluminium alloys in clad and bare state, but pretreated by European methods, the so-called CSA-etching or Pickling-process and the European chromic-acid-anodizing (CAA) with stepwise increasing of voltage. The CSA-etching may be compared with the optimized FPL. On the left in fig. 10 are to be seen the
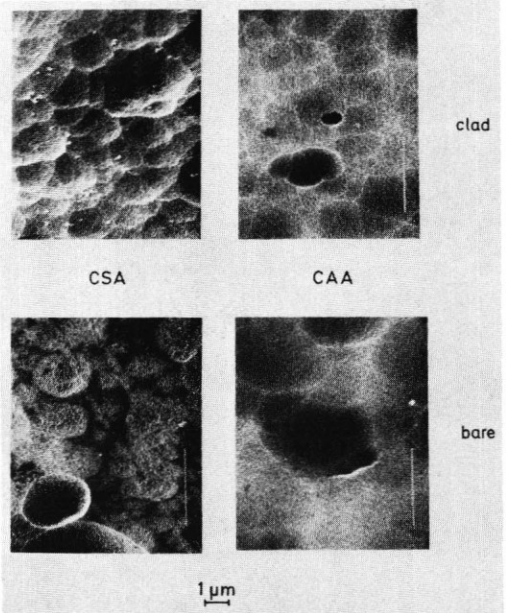

Fig. 10: Surface morphology of treated 2024 clad and bare

CSA-etched surfaces with nearly the same oxide morphology obtained in the optimized FPL-process. On the right are the micrographs of the anodized surfaces with a clearly visible overstructure too and a form like a fine honey comb structure.

Figure 11 shows in the same manner treated 7075 surfaces. The macroscopic structure is quite different but the microstructure is comparable to those of 2024 alloys. Without doubt the size and structure of the oxide layer must be very important for strength and durability of adhesive bonds. But that is only true, if the adhesive is able by wetting the surface to invade the oxide morphology.
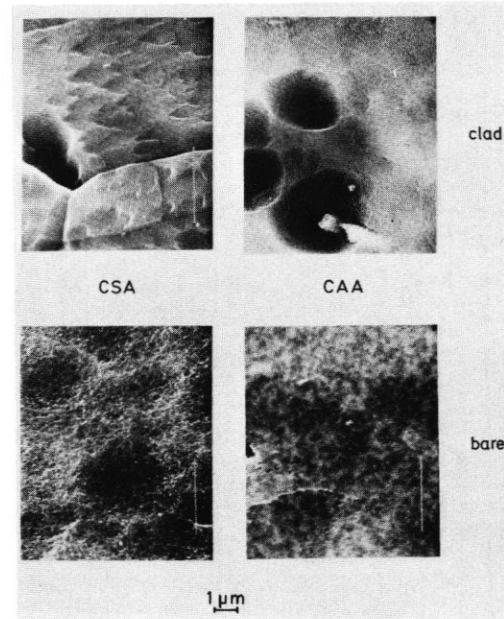

Fig. 11: Surface morphology of treated 7075 clad and bare

This possibility is demonstrated on hand of figures 12 and 13. Figure 12 is a micrograph of a sulphuric-acid-anodized 2025 surface with a typical good developed honey-comb-structure. Figure 13 is a SE-micrograph of the surface of a phenolic adhesive cured on a SAA treated aluminium surface after etching the aluminium away. Easy visible are the characteristic pics on the resins surface setting before in the pores of the oxide layer [3]. This example makes it sure that the adhesive can creep into the formed oxide structures, if its molecular weight in uncured state is small enough which is true in the case of phenolic resin.

The remaining question is, how good does it creep into these small honey-combs and how good is the resulting chemical or micromechanical connection. But it is not enough to take only a look on the outer submicroscopical topography of a metal surface to get an reliable answer on the question of bondability.
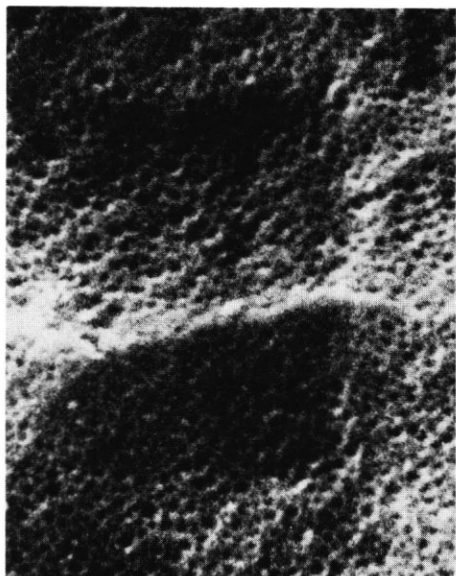
0,5 μm

Fig. 12: Sulphuric-acid-anodized (SAA) 2024 clad

Nach A. Hartman   0,5μm

Fig. 13: Phenolic resin replica of a SAA surface 2024 clad

That demonstrates figure 14. To be seen are pictures made by transmission-electron-microscopy (TEM) with a high magnification of CSA and optimized FPL-etched surfaces and CAA and PAA surfaces. The etched surfaces have always the typical cellular oxide structure with small areas of about 300 Å, fenced by tiny oxide walls with a much smaller thickness of about 50 to 100 Å. The anodized surfaces have a very different structure:

On the one hand a honey-comb-structure with cell areas of about 300 Å in the case of CAA, on the other hand a very filigree down after PAA. There a single pit has a diameter of about 100 to 200 Å, from one to another there will be a

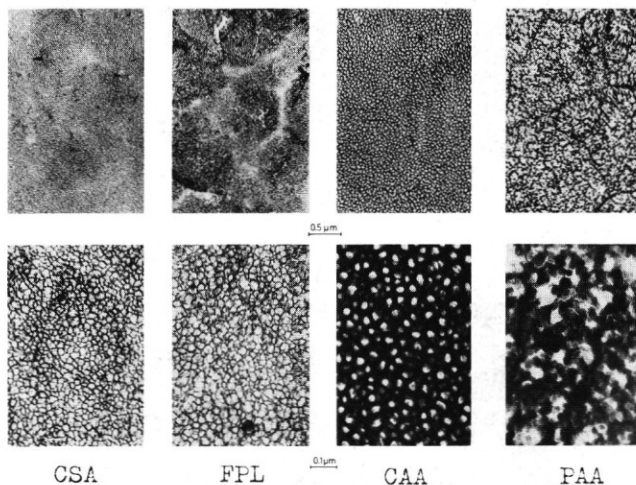CSA   FPL   CAA   PAA

Fig. 14: TEM-micrographs of treated 2024 clad

distance of about 300 to 400 Å. These differences must have an influence on the adhesional properties especially under the aspect of handling the metal parts prior to primer application. One point is the mechanical stability of the oxide structure and it's influence on the bondability under industrial conditions. That the stability of different oxide layers is different, is easy to demonstrate on hand of simple tests as shown in figures 15 and 16.

In figure 15 the upper pictures show the micrographs of 2024 surfaces as treated state, below is the same surface
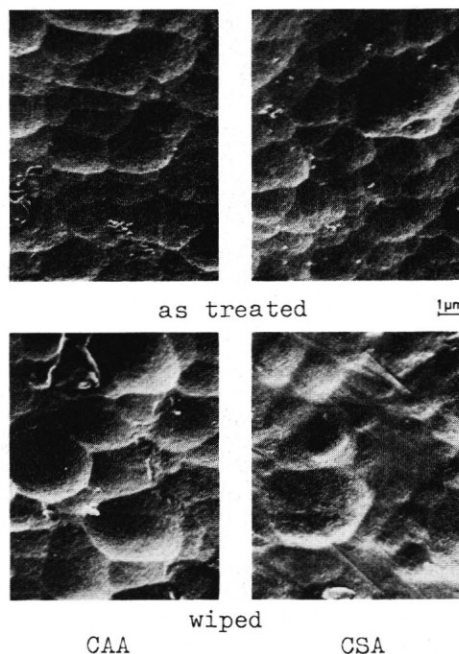

as treated   1μm

wiped

CAA   CSA

Fig. 15: Pretreated 2024 clad

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but wiped with lens cleaning paper. For CAA there is no change, for CSA the top areas of the overstructure are marked by greeves.

Figure 16 shows the same alloy by PAA and FPL. After wiping there is nearly no structure leaving.

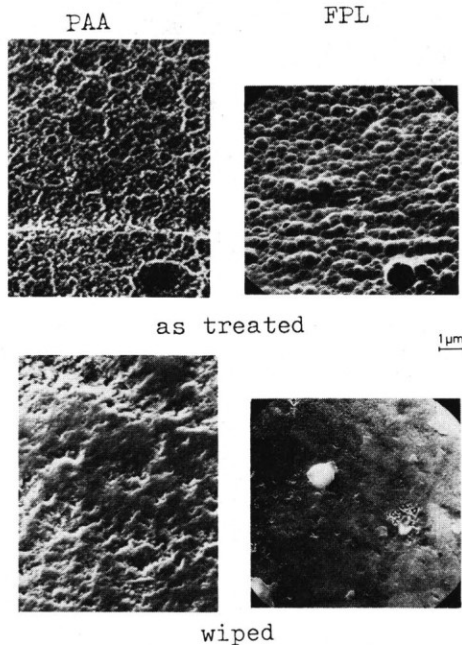PAA   FPL

as treated

1 µm

wiped

Fig. 16: Pretreated 2024 clad

The question arising from those effects is, in how far such different changings of the oxide morphology will influence the adhesional properties especially under hostile environments. To get here more informations, special peel specimens with fresh and wiped surfaces were bonded for testing the initial and residual peel strength after aging in water vapour of 133 °C over 168 h. In these specimens in all cases the adhesional zone between metal and primer or adhesive will be destroyed, so that the peel-strength gives a direct hint to the quality of the adhesion.

In these tests only in the case of FM 123-5 the superiority of phosphoracid-anodizing is loosed by wiping the surfaces. In combination with FM 73 after wiping no reduction of water stability occurs if a primer was used. If we worked without a primer, the mechanical wiping reduces the adhesion stability on FPL- and PAA-surfaces in an extremely manner, whereas on CSA and CAA surfaces practically no reduction of adhesional quality was to observe.

These results lead to the conclusion that the primer in its low molecular state invades into the oxide cells re-

maining undestroyed the equalized upper layers. Only the molecules of the adhesive itself with higher molecular weight remain on the equalized surface and as a result we have bad adhesional properties.

5. References

[1] Brockmann, W.: Interface Reactions and their Influence on the Long Term Properties of Metal Bonds; Adhesives Age 20 (1977) No. 7, p. 30/34

[2] Brockmann, W. and O.-D. Hennemann: Comparison of Surface Treatment of Aluminium and their Influence on Long Term Strength of Metal Bonds; 11th National SAMPE Technical Conference November 13-15, 1979, p. 804-806

[3] Hartmann, A.: An Investigation on the Effect of the Pretreatment of the Metal and the Strength and Adhesion of Adhesive Bonded Joints Making Use of Electron Microscopy; National Luchtvaart Laboratorium, Amsterdam, July 1961.