Adherence Evaluation of Paint Coatings Using a Three-Point Flexure Test and Acoustic Emission

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ABSTRACT: The adherence of paint coatings on aluminum substrates was tested using a three-point flexure test (TPFT) combined with acoustic emission (AE) evaluation. The mechanical test was defined according to the French Standard. During bending of the paint-coated specimen, acoustic emission signals were recorded and analyzed. Substrate pretreatments were chosen to show a set of visual interfacial ruptures and a set of visual cohesive ruptures in the paint. The formulation of the paint was fixed by industrial regulations. The varying nature of systems showed different AE patterns, particularly for two types of specimens: those that corresponded to solvent degreasings and the others to aqueous chemical pretreatments. The behavior of the paint coating differed, with significant AE, damage, and crack propagation in the first case and instantaneous phenomena in the other case. It is then possible to establish a relationship between the analysis of the recorded AE signal and the type of joint rupture. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1848–1857, 2001

Key words: acoustic emission; adherence; paint coating; aluminum substrate; three-point flexure test

INTRODUCTION

The industry uses primer paints to protect aluminium alloy components against corrosion. The loss of protection correlates strongly with the failure of adhesion, or interphase cohesion, of primer paints. The complexity of metal/paint bonding studies can be reduced by using model substrates, model molecules, or model paints.[1,2] The parameters that affect the paint adherence and that have to be considered are as follows:

1. the paint formulation [nature of compounds, volumic pigment concentration (VPC), molecular weight, etc.], which is fixed by technical regulations;
2. the physicochemical characteristics of substrate surfaces—in particular, two key parameters of adhesion mechanisms that are the mechanical anchorage of the paint and the acid–base properties of substrates;
3. the testing conditions (the load mode, the environmental conditions, the specimen geometry);
4. the mechanical properties of materials (residual stresses, mechanical properties of weak boundary layers).

Numerous techniques exist for adherence measurement,[3] but only a few of them are suitable for paint coatings. Mechanical rupture tests are mainly used such as the pull-off test during the

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Table I Chemical Composition of 1050 A (as per AFNOR A50-411 and A50-451)

%	Si	Fe	Cu	Mn	Mg	Zn	Ti	Other, Each	Al
Max.	0.25	0.40	0.05	0.05	0.05	0.07	0.05	0.03	Balance

1980s and the rapid cross cut test[4] still commonly used, even if it is less sensitive. However, paint coating adherence may be more reliably measured using the three-point flexure test (TPFT).[5–7]

Acoustic Emission (AE) is a nondestructive technique for damage mechanism characterizations[8] where the creation of transitory waves follows an internal microdisplacement of the material. AE was first used for studies on damage of composite materials, especially for fiber rupture and delamination.[9] Elastic waves can be caused, for example, by crack initiation and growth. AE was applied in metallic material studies on the movement of dislocations at grain boundaries, on the formation of twins, on stress corrosion cracking and fracture of brittle inclusions.[10] Even though it may seem an obvious application, this technique for the study of the adherence of polymers on metals was not frequent.[11] Elsewhere, AE was also used to assess the adherence of inorganic coatings applied by plasma spraying[12,13] and for the study of metal/polymer joint aging.[14]

The purpose of this paper is to clarify the damage mechanisms of primer paint coatings on a metallic substrate during mechanical stress. These damage mechanisms correspond to the interfacial paint delamination, to paint decohesion, and to all types of energy dissipation found during stress, and characterized by the emission of elastic waves in materials. We examined the degradation of paint coatings and the potential of AE investigations for the different types of rupture encountered, i.e., paint cohesive or metal/paint interfacial rupture. Thus, using an aluminum substrate subjected to different surface treatments, after painting and drying with a primer, adherence was measured using the TPFT and an analysis of recorded AE signals was carried out.

Table II List of STs of the Metallic Substrate

Number	ST	Chemical Composition of Solutions	Sample Reference	ST Sequences[a]
1	MEK degreasing (25°C, 10 min US[b])	Methyl ethyl ketone	T1	1
2	GAROSOLV (25°C, 10 min US[b])	Mixture of organic solvents	T2	2
3	Thermal oxidation (150°C, 60 min)	—	T3	4 + 3
4	Alkaline degreasing pH 9 (60°C, 10 min)	Sodium tripolyphosphate ($Na_5P_3O_{10}$; 40 g/L) Surfactant (10 ml/L)	T4	1 + 4 + R + D
5	Alkaline degreasing pH 11 (25°C, 10 min)	Anhydrous sodium carbonate (Na_2CO_3; 40 g/L) Anhydrous sodium phosphate (Na_3PO_4; 20 g/L) Liquid sodium silicate (Na_2SiO_3; 1 g/L)	T5	1 + 5 + R + D
6	Alkaline cleaning pH 13 (25°C, 2 min)	NaOH; 4 g/L	T6	1 + 6 + R + D
7	T6 + acidic neutralisation	(HNO_3; 400 g/L)	T7	1 + 7 + R + D

[a] R: rinsing in demineralized water; D: drying for 2 min at 60°C.
[b] US: ultrasounds.

Table III List of TPFT Parameters and Conditions for the Three-Point Flexure Test

Setting Description	Values
Displacement speed of cross bar	0.025 mm/min
Nature of stiffener	EPOXYDE Ref. 20-8130-128 (from Bulher)
Curing condition of assembly with stiffener	2 h at 40°C and 32 h at room temperature
Nb of samples for each set of pretreatment	5
Substrate dimensions (length × width × thickness)	$(50 \times 10 \times 1.5)\ mm^3$
Stiffener dimensions (length × width × thickness)	$(25 \times 5 \times 4)\ mm^3$
Lower bearing diameter	6 mm
Upper bearing diameter	12 mm
Distance between lower bearings	33 mm

SAMPLE PREPARATION AND DESCRIPTION OF THE TEST

Sample Preparation

The substrates used in this study were made of 2024 T3 aluminium alloy (from Pechiney) plated with 1050 A by roll-bonded cladding. The composition of the latter is given in Table I. The substrates were cut from the same 1.5 mm thick sheet.

Surface treatments (ST) were applied to the metallic specimens. They are listed in Table II. These ST were chosen in order to obtain different types of rupture: interfacial ruptures would be expected with organic solvant degreasings (ST 1 and 2) and paint cohesive ruptures with the other treatments.

After each surface treatment, substrate surfaces were coated with the P23 primer paint (from MAPAERO Comp., France). Its composition was

- polyurethane system;
- organic solvents;
- pigments and fillers: $SrCrO_4$, TiO_2, SiO_2 and talcum powders.

P23 was applied at room temperature with a spray gun ($P = 0.5$ bar) to obtain a paint thickness of 30–35 μm. Samples were dried for 7 days at room temperature.

Description of the Test

The Three-Point Flexure Test

As per the works of A. A. Roche,[5–7] the TPFT was performed with a mechanical testing machine (INSTRON 4467) according to the French Standard.[15] Table III shows the different testing parameters and conditions.

Different parameters can be chosen to measure the adherence by the TPFT, as shown in Figure 1(a) (F_{max}, d_{max}, F/d, W_n):

- F_{max}, the maximal load before rupture;
- d_{max}, the maximal deformation before rupture;
- F/d, the slope within the linear zone characterising the system rigidity;
- W_n is the rupture energy of the paint coating (provided that the rupture is paint cohesive or at the substrate–paint interface). It corresponds to the area limited by the load/displacement curve of the painted substrate with stiffener and the load/displacement

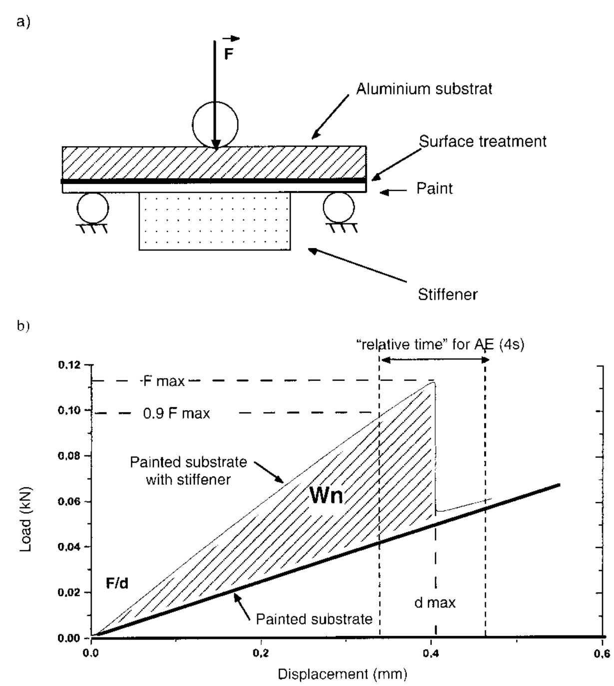

Figure 1 The three-point flexure test: (a) principle of the test; (b) experimental load-displacement curve.

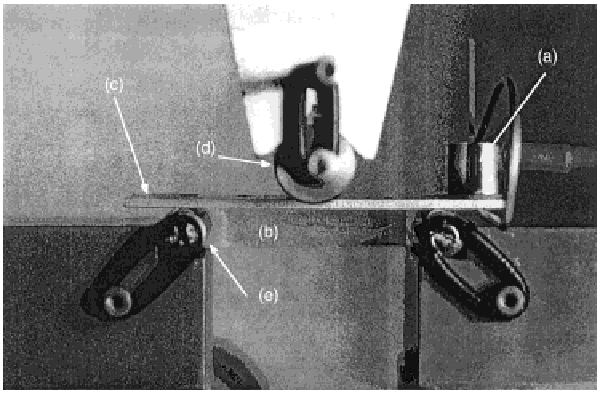

Figure 2 The testing equipment. (a) Transducer. (b) Stiffener. (c) Painted substrate (paint-side down). (d) Upper bearing. (e) Lower bearing.

curve of the painted substrate alone. Studies[16] showed that, in the case of different pretreatments, W_n is appropriate to describe the paint adherence. W is the mean value of a set of 5 samples;

- The definition of "relative time" is given in the next section.

Acoustic Emission Equipment

The acoustic emission signals were captured by an acoustic emission transducer (nano30/Euro Physical Acoustic), which was mounted on a grease silicone coupling agent between the metallic surface of the sample and the transducer, as is shown in Figure 2. This coupling agent improved the signal transfer between the specimen and the transducer, which contained a piezoelectric ceramic. An additional clamp was used to ensure a constant pressure between the transducer and the specimen.

The very weak signals captured by the transducer were amplified with a gain of 40 dB. The AE signals were monitored, analyzed, and stored in hard-disk datafiles. The AE system (Mistras 2001, Euro Physical Acoustic) was used with a 30 dB threshold and a gain of 40 dB on the frequential window of 20–1200 kHz. The threshold operated as a filter to avoid recording background noise. The acoustic wave can be defined by hits or events due to the material damage and by counts. During an event, a count is identified each time the acoustic wave amplitude curve crosses the 30 dB threshold.

Our AE signal treatment generated data files containing what follows:

1. The number of hits vs time: this number corresponds to the acoustic activity variation overtime during the mechanical test.
2. The number of counts vs time: this number is connected to the frequency of acoustic activity.
3. The energy: this is a complementary parameter of the acoustic wave amplitude. The integration of the quadratic waveform in time corresponds to the signal energy.
4. The waveforms.

We focused our attention on AE signals close to rupture. For this purpose, we defined a constant interval of time [named "relative time" for AE; see Fig. 1(b)] inside which the rupture occurs. This interval started when the load was $0.9F_{max}$ and ended 4 s later. The applied force was also recorded by the AE equipment.

RESULTS AND DISCUSSION

Acoustic Emission

We studied the damage of paint coatings in order to separate the types of rupture in AE terms. The study concerned AE signals close to the rupture that corresponded to the relative time. In order to separate the damage mechanisms, the first part of each study is devoted to two types of pretreatments. Therefore, we arbitrarily chose T1 and T6

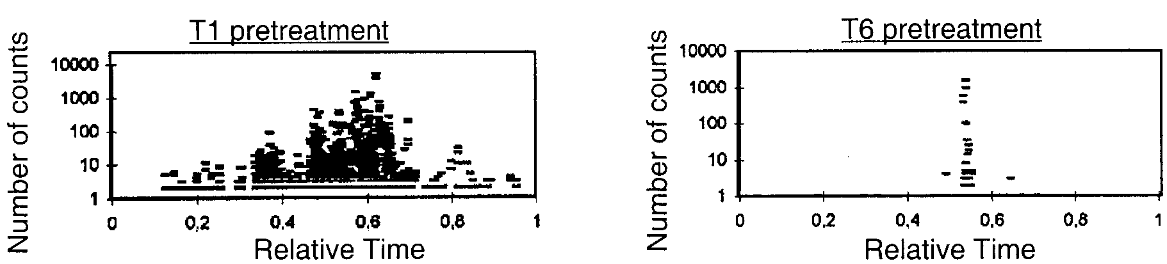

Figure 3 The number of counts of AE signals for T1 and T6 during the relative time.

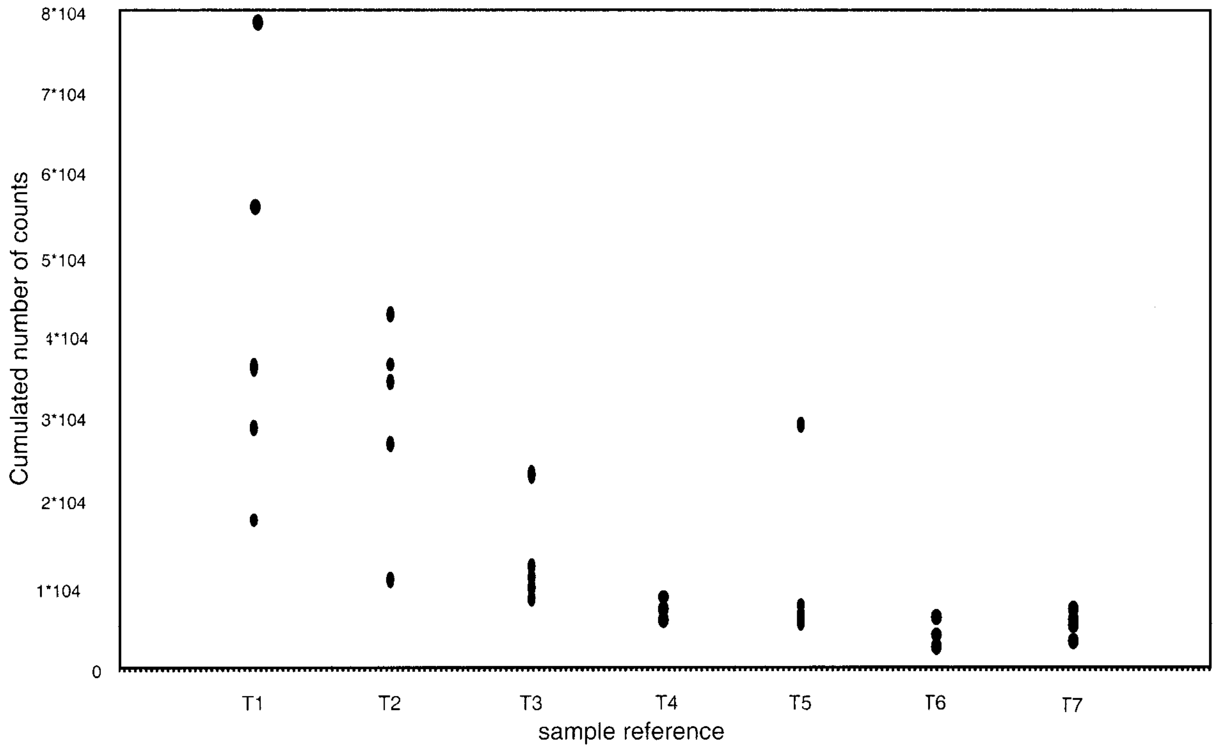

Figure 4 The cumulated number of counts of AE signals, for each surface treatment of substrates (5 samples per treatment).

for interfacial ruptures and cohesive ruptures in the paint, respectively.

Analogical Treatment of AE Signals

The Cumulative Number of Counts Criterion. Figure 3 shows the differences between T1 and T6. The number of counts is localized in time for T6. They are more numerous and more distributed in time for T1.

Figure 4 shows the cumulated number of counts for each surface treatment of the substrate, using a set of 5 samples. These correspond to the sum of the number of counts during the relative time and for each sample. T1 and T2 showed more cumulated counts than the others.

The Cumulative Number of Hits Criterion. Figure 5 shows again large differences between T1 and T6, with a number of hits concentrated in time for T6 and more distributed over time for T1.

Figure 6 shows the cumulative number of hits for each surface pretreatment, still using a set of 5 samples. Using the same methodology, we recorded similar results as per Figure 4, with more cumulated hits for T1 and T2.

The Cumulative Energy Criterion. The levels of energy captured during the relative time show differences between T1 and T6 as seen in Figure 7.

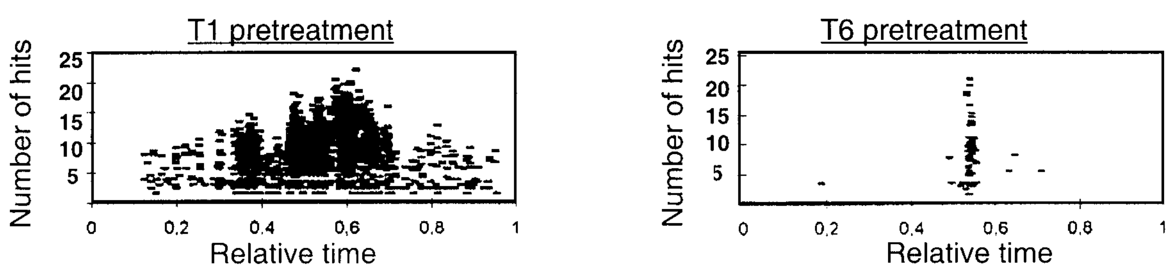

Figure 5 The number of hits of AE signals for T1 and T6 during the relative time.

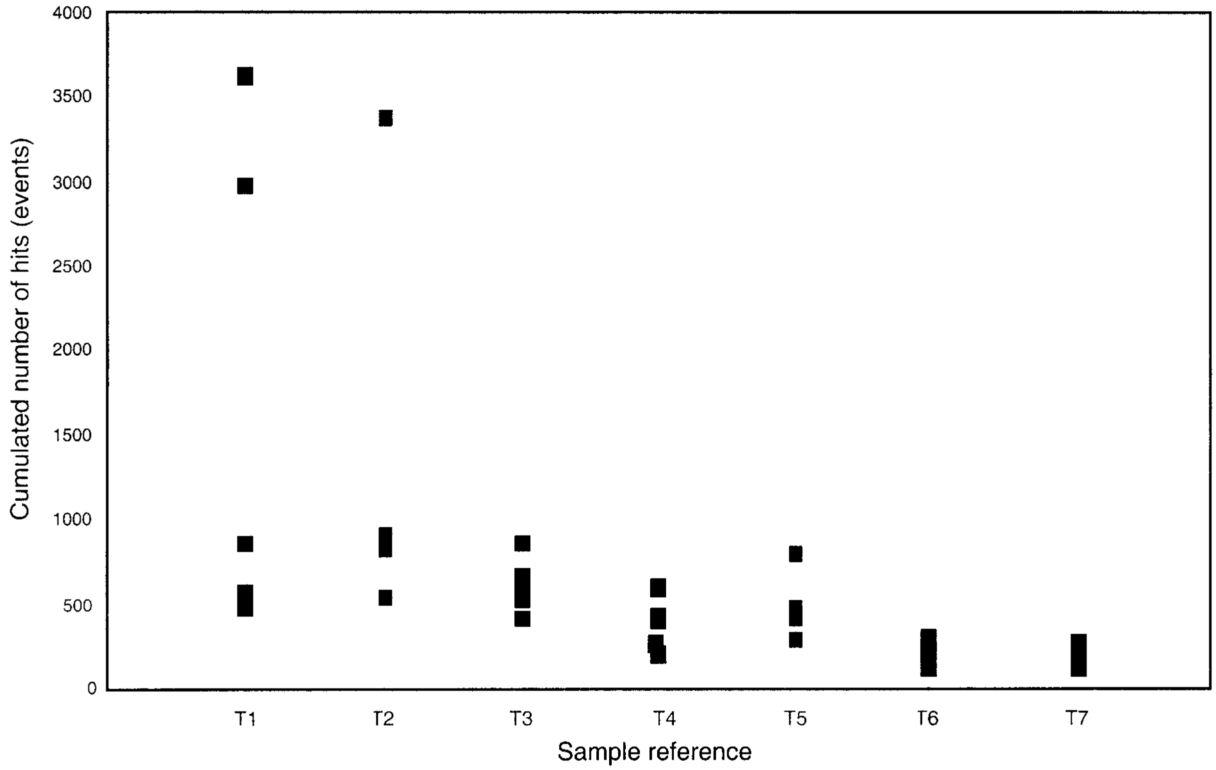

Figure 6 The cumulative number of hits of AE signals for each surface treatment of substrates (5 samples per treatment).

The cumulated energy for each pretreatment (5 samples) is shown in Figure 8.

Discussion. It was noted that there were some variations between AE signals obtained in different experiments using the same experimental conditions. These variations may be related to differences in paint-spraying conditions. It was shown that the adhesion of polymers on metal substrates depends on the metal pretreatment[16] and also on the paint application conditions.[17] These are important parameters, but they are difficult to control in hand spraying.

The analogic analysis of AE signals shows differences between the two categories of pretreatment. The *cumulated number of counts* concerns the acoustic activity. T1 and T2 correspond to high acoustic activity. T4–T7 correspond to low acoustic activity, with T3 between these two behaviors (Figure 4). The *cumulated number of hits* concerns the signal frequency of acoustic activity. The same differences as for the cumulated number of counts can be observed. The signal frequency of the acoustic activity is high for T1 and T2 when it is compared to that corresponding to T4–T7. T3 is again found between these two behaviors (Fig. 6). The *cumulated energy* concerns amplitude, frequency, and duration of AE signals, and the same differences as for the other criteria can be observed (Fig. 8). The relative time curves

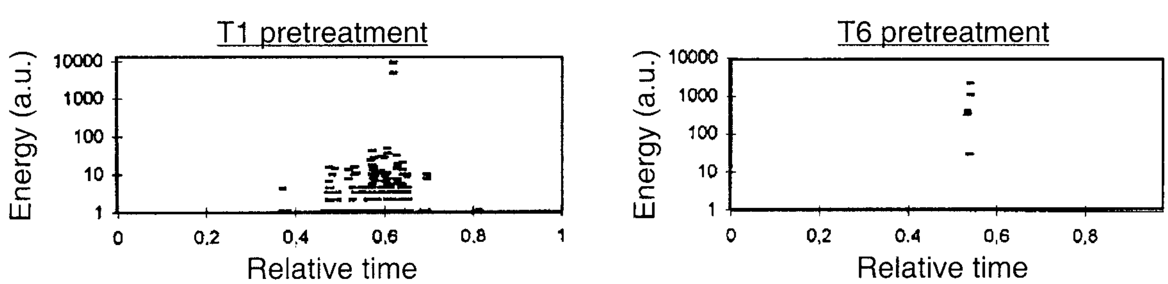

Figure 7 The energy of AE signals for T1 and T6 during the the relative time.

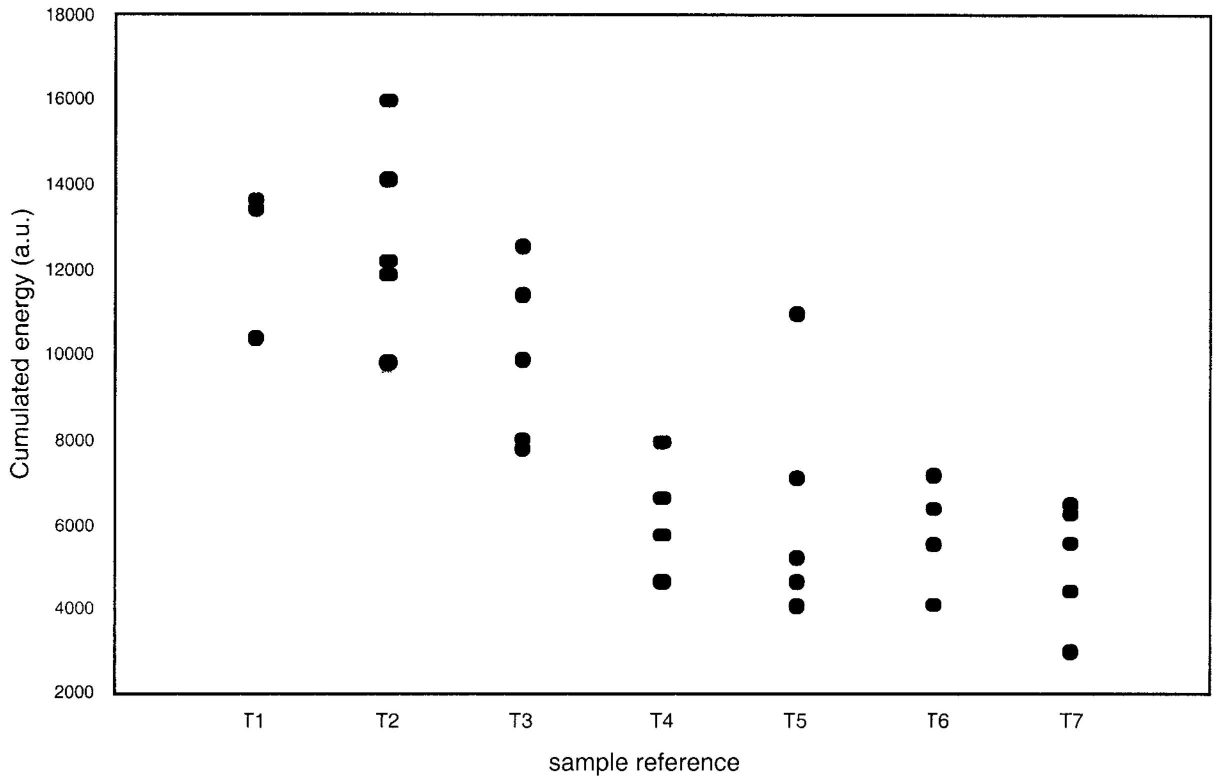

Figure 8 The cumulated energy of AE signals for each surface treatment of substrates (5 samples per treatment).

provide information on the rupture mechanisms of paint coatings (Figures 3, 5, and 7), which appear different for T1 and T6. Thus, the rupture seems instantaneous for T6, whereas damage mechanisms and crack propagation precede the rupture for T1.

Numerical Treatment of AE Signals

In order to compare the most significantly different AE signals—namely, those obtained with the substrate surfaces treated with T1 and T6—we chose the more energetic signal for T1 and T6, during the relative time, and we decided to name it "rupture hits." In what follows, we focuse on the temporal and the spectral treatment of these rupture hits.

Temporal Treatment. Figure 9 shows the amplitude of the electrical signal vs time (wave amplitude in volts) in order to observe the whole wave. We noticed strong differences in the waveform (both amplitude and duration) during the relative time for the two surface pretreatments T1 and T6.

Spectral Treatment. Spectral treatment concerns the frequential response of the AE signal. Figure 10 shows the amplitude of the electrical signal vs frequency. The acoustic wave amplitude is here in dB. Again, they are different frequential responses for T1 and T6.

Discussion. Numerical treatment allows a description of AE signals within simple parameters such as the amplitude and the duration of the acoustic wave. However, the analysis of these results is always difficult because the transfer functions of the acquisition line (transducer response, attenuation, etc.) can disturb the signal.

The temporal analysis shows large differences between T1 and T6, just like in the analogical analysis. Thus, the duration of the acoustic wave is long (1.90 ms) as is the maximal amplitude (close to 0.31 V) for T1 when they are compared to those of T6 (270 μs and 0.025 V, respectively).

Spectral analysis presents the same differences. The rupture hits of T1 had displayed a large spectral response between 0 and 1.4 MHz by comparison to that of T6, and only some frequencies are emitted in the latter scenario. This observation must be correlated to the higher number of counts observed previously in Figure 3 for T1 than for T6.

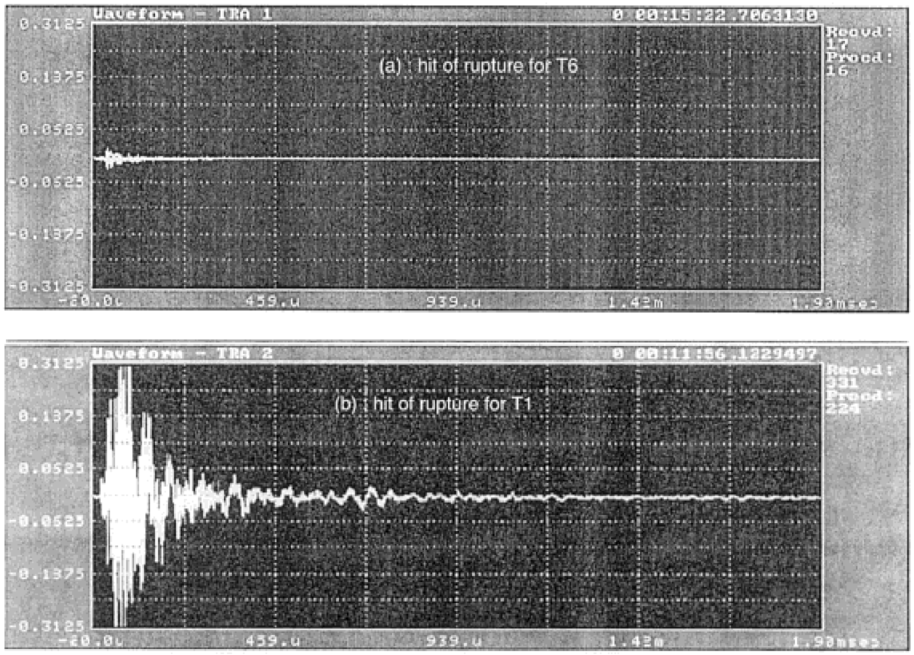

Figure 9 Example of rupture hits for surface pretreatments T1 and T6. Temporal treatment: amplitude (V) vs time (ms).

Three-Point Flexure Test

Since adherence is not only a matter of the mechanical characteristics, the rupture energy values measured by means of the TPFT must be associated with surface analysis. A complementary visual observation of the failure location and

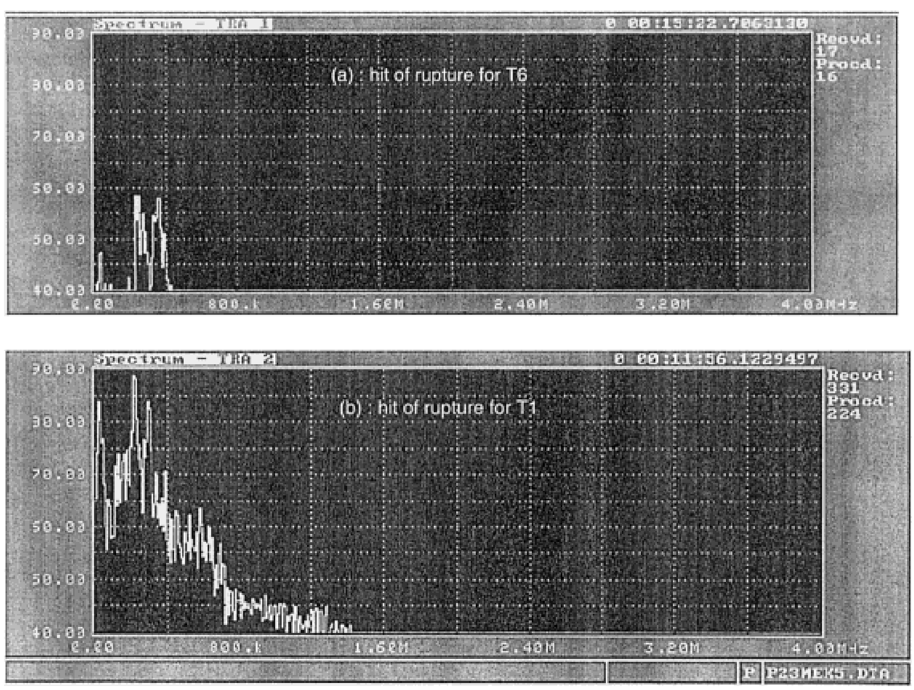

Figure 10 Sample rupture hits for surface pretreatments T1 and T6. Spectral treatment: amplitude (dB) vs frequency (MHz).

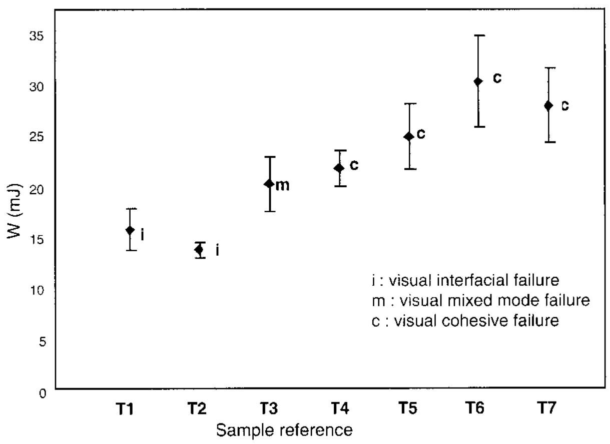

Figure 11 Variation of the average rupture energy (W) and rupture types for different substrate pretreatments, using the TPF test on P23-coated aluminum substrates.

of the crack propagation direction is always necessary. We will differentiate between the following failure types:

1. Interfacial rupture (type i): when the failed substrate surface is observed to be metallic in nature.
2. Cohesive rupture (type c): when the remaining colour of the failed surface is the same as that of the bulk paint.
3. Mixed mode failure (type m): when the failed surface involves both ruptures (metallic and paint).

As a typical example of the effects on the P23 adherence that can be observed with different metal pretreatments, the average subtended area value (W) for a set of 5 samples and for each type of pretreatment is shown in Figure 11. Vertical lines correspond to the standard deviations. Results of visual observations are mentioned.

In these experiments marked differences were noted in that adherence depends on pretreatments. Solvent pretreatments (T1 and T2) showed visual interfacial ruptures with a low value of W. All types of aqueous pretreatments (T4–T7) showed visual cohesive ruptures in the paint coating, with higher values of W than with solvent pretreatments. Thermal oxidation (T3) is especially interesting. Interactions at the interface are responsible for the visual mixed mode interfacial/cohesive ruptures with a medium value of W. These observations demonstrate the importance of the physicochemical characteristics of substrates. Several studies[18–20] on aluminum/lacquer systems showed that adhesion loss can be attributed to varying degrees of hydration.

CORRELATION BETWEEN AE INVESTIGATIONS AND ADHERENCE MEASUREMENTS BY THE TPFT

The analysis of the adherence of paint coatings revealed the same tendancies in behavior for AE investigations and TPFT measurements. Figure 12 shows the variation of the TPFT characteristic values W_n vs an AE characteristic, here the cumulated number of counts.

We can identify three different domains:

- D1: Domain of cohesive ruptures were W_n values are higher than 20 mJ and the number of cumulated counts lower than 100.
- D2: Intermediate domain where all types of rupture can be found.
- D3: Domain of interfacial ruptures where W_n values are higher than 20 mJ and the number of cumulated counts lower than 200.

The experiments showed that the rupture location is important for detecting AE signals. An *interfacial visual rupture* is characterized by the separation of the paint coating at the metal/paint interface. In this case, the ruptures are characterized by high AE characteristics and a relatively low rupture energy (D3 domain). This can be explained by high local unloadings accompanying long cracks on the one hand and by a lower fracture toughness of the metal/paint interface on the other. However, the stress capacity of the latter being high (due to high Young's modulus substrate), more elastic energy will be released as acoustic wave pulses. Therefore, strong AE signals will be recorded because the waves are

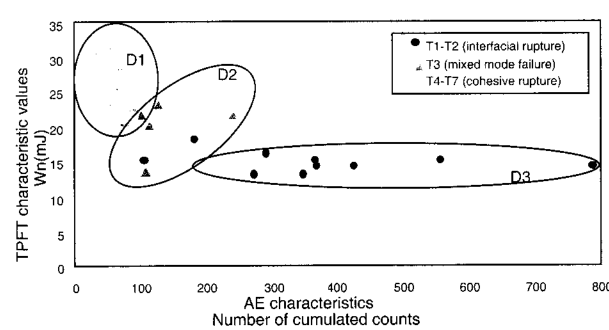

Figure 12 Variation of TPFT characteristic values (W) vs AE characteristics.

weakly attenuated during their propagation in the metallic substrate. A *cohesive visual rupture* is characterized by a localized phenomenon of usually small dimension surrounded by the paint coating. Here, lower AE characteristics accompany higher rupture energy than previously (D1 domain). This higher energy corresponds to a higher fracture toughness of the paint coating than that of the metal/paint interface. However, the rupture energy is probably dissipated by plastic deformation of the paint, and consequently, the corresponding AE signal is weak.

CONCLUSION

A correlation was observed on the measurement of adherence by TPFT and AE investigation. Thus, a visual interfacial rupture will be characterized by

1. a significant acoustic activity;
2. a significant frequency band of acoustic activity;
3. significant energy;
4. damage before rupture and crack propagation;
5. a weak value of the rupture energy.

The opposite applies for a visual cohesive rupture. All these characteristics correspond to a relationship between the analysis of the recorded AE signal and the type of rupture of 1050A plated 2024 A5 aluminum substrates coated with P23, a polyurethane primer paint. Last, the acoustic emission in addition to the three-point flexure test appears to be an efficient tool able to provide additional information on the damage mechanisms for the adherence evaluation of paint coatings.

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