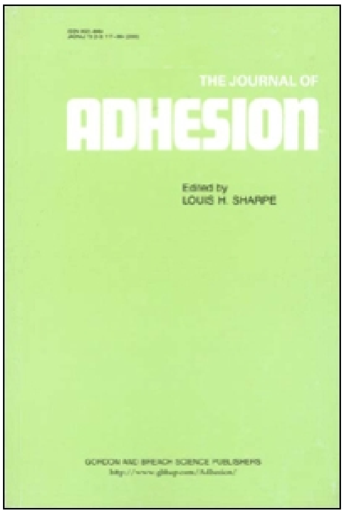
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Durability of Adhesion Between Metals and Polymers

Walter Brockmann[a]
[a] IFAM, Bremen, Lesum, Federal Republic of Germany

To cite this Article Brockmann, Walter(1989) 'Durability of Adhesion Between Metals and Polymers', The Journal of Adhesion, 29: 1, 53 — 61
To link to this Article: DOI: 10.1080/00218468908026477
URL: http://dx.doi.org/10.1080/00218468908026477

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1989, Vol. 29, pp. 53–61
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Durability of Adhesion Between Metals and Polymers†

WALTER BROCKMANN

IFAM, Lesumer Heerstrasse 36, D-2820 Bremen 77 (Lesum), Federal Republic of Germany

(Received November 7, 1988; in final form March 10, 1989)

Adequate adhesion between metals and polymers is primarily the result of chemical bonds in the boundary layer. This region, however, is subject to degradation by moisture. Three modes of deterioration are observed. The first is a largely reversible weakening effect in the polymer layer near the metal oxide surface. The structure of this layer differs from that of the bulk and is influenced by the chemical and physical properties of the surface. The second is a slow transformation of the oxide by hydration and a diffusion of oxide constituents into the polymer. This process is irreversible and is influenced by the state of the surface and chemical properties of the polymer. The third is a fast deterioration of the oxide by primary corrosion usually initiating at an unprotected edge but occasionally arising within the body of a joint.

KEY WORDS Review; durability of adhesive joints; oxide/adhesive interaction; mechanisms of adhesion; boundary layer; oxide stabilization.

1 INTRODUCTION

For almost 200 years, scientists have tried to explain the phenomenon of adhesion between dissimilar materials. For much of this time, available analytical methods permitted only a macroscopic and two-dimensional view of the problem.[1–6]

Until recently, this approach seemed to be scientifically satisfactory. On most technologically important high energy surfaces, cleaning, degreasing and roughening or chemical pretreatment produced bonds with reactive adhesives or varnishes so strong that conventional strength test procedures could not fail them.[7] Furthermore, the first scientific work on adhesion between polymeric adhesives and metals had revealed that, in the boundary layer, chemical bonds of high energy and thus high strength played an important role.[8] It was thus concluded that the joints were not susceptible to failure in the boundary layer. The situation changed in the first half of the seventies when it became obvious that bonded joints exposed to a combination of mechanical and environmental

---

† Presented at the 35th Sagamore Army Materials Research Conference, Manchester, New Hampshire, U.S.A., June 26–30, 1988.

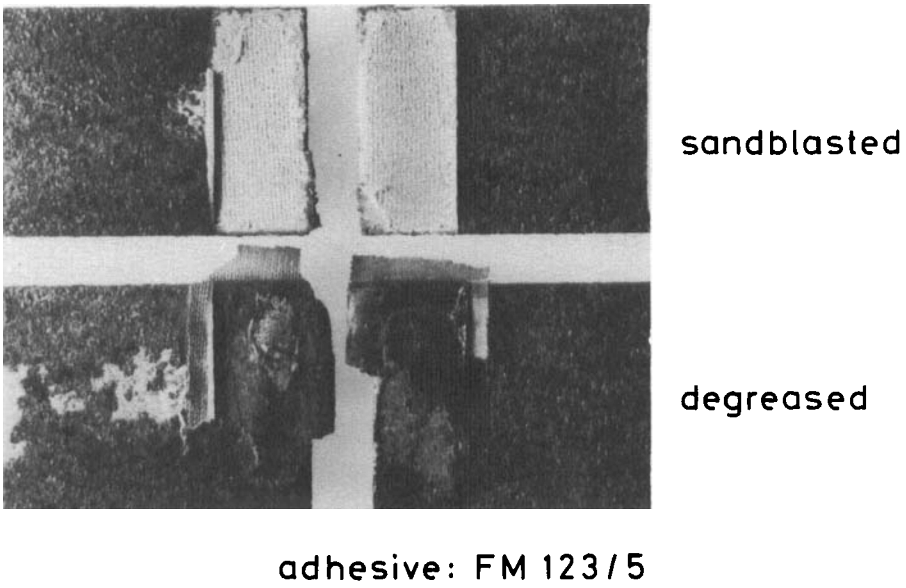


FIGURE 1 Fracture surfaces of bonded steel after one year of aging. Adhesive: FM 123/5.

stresses were losing strength due to diffusional processes in the adhesive layer as well as "adhesive rupture" at the interface between adhesive and metal. This kind of rupture may lead to total destruction of the joint. An example is given in Figure 1 which shows the fracture surfaces of epoxide resin bonded to steel tested after one year of aging in a warm, moist climate. The surfaces shown in the upper part of the figure had been sandblasted before bonding; there is clear cohesive failure. The surface shown below had only been degreased. There is increasing adhesive failure with primary corrosion at the edges, an important factor in residual strength after aging. Delaminations were also observed in highly stressed aircraft structural bonds. This latter gave rise to intensive efforts to develop appropriate test methods.[9,10] At the same time, the phenomenon of adhesion between polymers and metals became the subject of several research programs.[11-13]

2 DEVELOPMENT OF MACROSCOPIC EXPERIMENTAL TECHNIQUES

It was realized that the none of the theories of adhesion were sufficient to explain interfacial failure between polymer and metal. The obvious sensitivity to moisture, for example, had not been predicted. Even the above referenced work on chemical interactions between phenolic resins and various metals provided no clues. These studies had shown the irreversible nature of the adsorption of phenolic oligomers from solution on variously-pretreated surfaces. This strongly suggested the formation of chemical bonds in the boundary layer but the nature of these bonds was not indicated by the quantitative adsorption measurements employed.

Continued problems with moisture resistance led to studies in which radioactively-labeled adhesives were employed. For the first time, desorption tests with water were conducted. It was noted that water, in contrast to less polar organic solvents, contributed significantly to the detatchment of chemisorbed polymer layers. These findings obtained with technologically-important surfaces were confirmed in chromatographic studies on active aluminium oxide. These results were attributed to the hydrolytic instability of the chemical bonds and suggested that replacement of phenolate-like bonding with moisture resistant chelate complexation might be useful. Initial results were successful, although autoradiographic failure analysis of both moisture-weakened and unaged specimens showed the locus of failure to be away from the interface where the enhancement was intended to operate.

These experiments failed to provide insight into the reasons for the beneficial nature of certain surface treatments on bond durability. For example, with aluminium, anodization leads to better aging durability than does chromosulphuric acid etching. Although anodized surfaces adsorbed considerably more phenolic resin than etched surfaces, they desorbed the same percentage when exposed to water. It was concluded that the discrepancy between sorptive and joint performance behavior must be due to the failure to consider mechanisms of adhesion other than chemical bonding. A search of the literature revealed relevant work by Hartman[15] who was probably the first to use electron microscopy to study the phenomenon of adhesion. As early as 1961, he conducted experiments with phenolic resin bonded aluminium using both etched and anodized surfaces. When the aluminium was detached from the cured phenolic, he found a typical button structure on the resin surface suggesting that the resin had mechanically anchored itself in the pores of the anodized surface. Wider use of scanning electron microscopy for the study of variously-pretreated aluminium surfaces confirmed Hartman's results. In fact, scanning electron micrographs of anodized aluminium surfaces obtained in our laboratory were almost precise replicas of those of Hartman.[16] Thus, it seemed that mechanical interlocking was the dominant mechanism of adhesion because it continues to operate even when chemical bonding fails, *e.g.* due to hydrolysis.

However, as is known today, it is impossible to separate a polymer from an oxide layer with which it is in contact without perturbing the structure of either or both. It has thus been impossible to assess fully the dominance of interlocking as a mechanism of adhesion.

Continuing investigations have shown that the chemical properties of a polymer situated near the boundary layer are materially influenced by those of the surface on which it was cured. Based on such observations, a first model of selective adsorption was developed.[17] It was based on the first use of transmission electron microscopy to study the dependence of aluminium oxide morphology on surface treatment.

3 MICROSCOPIC AND SUBMICROSCOPIC INVESTIGATIONS

The first microscopic investigations of adhesion and failure characteristics were less than satisfying in demonstrating selective sorption.[18] Refinements in sample preparation, however, permitted transmission electron microscopic examination of an adhesive joint at the desired 20 Å resolution.[19]

Fortunately, some of the best developed oxide morphologies occur on aluminium surfaces treated for adhesive bonding by the aircraft industry so that the importance of this work was readily evident. Figure 2 shows the transmission electron micrograph of the cross section of the interface between aluminium and a polymer. At the top left is shown the characteristically fine aluminium oxide structure obtained from the usual chromosulphuric acid (CSA) etch. It has a thickness of approximately 300 Å. A similar etching process using shorter etching times, as is commonly used in America (FPL Etch), does not produce the same structure (top right). When the aluminium surface is anodized in chromic acid (CAA, bottom left) or phosphoric acid (PAA, bottom right), thick porous oxide layers of 6000 to 30,000 Å develop depending on the composition of the alloy. Today it is known that prepolymers of phenolic and epoxy adhesives may completely penetrate even these fine oxide structures up to a depth of 20,000 Å.[20] There is a preference for molecules of higher reactivity. This may lead to the formation of a polymer zone of lower crosslink density outside the oxide layer where delamination may occur in the event of moisture intrusion. As an example Figure 3 shows the transmission electron micrographs of ultrathin cross sections

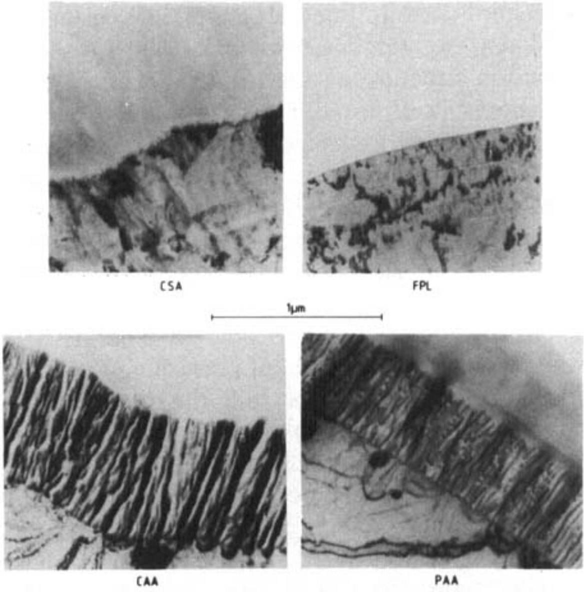


FIGURE 2 Transmission electron micrographs of the interface between metal and polymer in bonded aluminium.

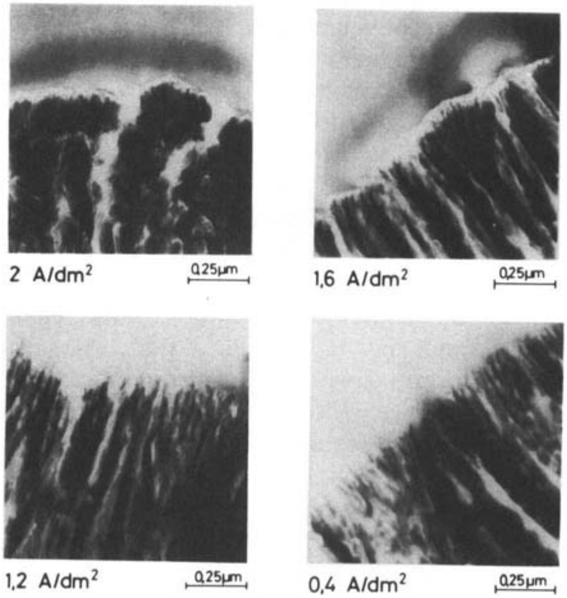


FIGURE 3 Transmission electron micrographs of the interface between oxide and metal after anodization with different amperages.

of aluminium bonds. The surfaces had been anodized with different current densities. In the case of high current density, clear, light polymer zones are noted above the oxide layers. They must certainly be attributable to low crosslink density. At 0.4 A/dm, no such light zones are observed. If water penetrates such bonds, there will be spontaneous delamination in the affected polymer zones whereas no such sensitivity to water will occur when there is an unperturbed transition from polymer to oxide.

4 CHEMICAL INTERACTIONS IN THE BOUNDARY ZONE

In and on the oxide layers, the oligomeric precursors of the adhesive encounter oxides of different reactivity or acidity. They are thought to interact with each other by adsorption, chemisorption or catalysis.[21] For example, dicyandiamide, a hardener used with epoxy resins, is at least partially transformed into guanylurea *via* a catalytic reaction after adsorption on anodized aluminium and exposure to the 120°C curing temperature. This may be a problem if moisture penetrates into this region. The adsorption of adhesive precursors is controlled at least partly by acid-base interactions; that is to say the precursors form acid-base complexes with the surfaces oxides. This is especially true of phenolic resin precursors. These selective interactions result in steric effects in subsequent crosslinking reactions in the boundary layer due to the similarity in size of the oxide structures and the prepolymer molecules.

Thus, at least for the case of aluminium, adhesion is not a two-dimensional process but a three-dimensional one with adhesive and adherend each influencing the other. When moisture penetrates into the adhesive layer, unreacted monomer, secondary cure reaction products or products resulting from metal oxide catalysis are given the mobility to move within the boundary layer. This process may change the pH of the oxide zone. For the phenolic resins, this zone remains acid and the oxide is stable. For the epoxy resins however, where guanylurea and its amine degradation products may be present, this region can become basic and the oxide destabilized. Three modes of degradation can be observed. The first has already been suggested—the failure of the adhesive in the region of low crosslink density just above the oxide layer. For thin oxide layers this region of low crosslink density may be located within the pores of the oxide, giving rise to mixed adhesive and oxide failure. With rapid mositure infiltration, such failure is observed in just a few seconds because of the high strains to which the bond is subjected.

The second, also observed with thin oxide layers, is depicted in Figure 4. Here, the aluminium surface was pretreated with chromosulphuric acid and an expoxy adhesive applied. It was aged in a moist, warm environment (40°C, 95% R.H.) without edge condensation, *i.e.* without primary corrosion. After one year of aging, ultramicrotome cross sections were taken approximately 3 mm in from the edge. The figure shows transmission electron micrographs of these sections. The oxide needles originally well developed within the bond (top left) have almost entirely disappeared (bottom right). Since there are no pores in the polymer, this must be the result of a diffusion process. Analysis has shown the presence of

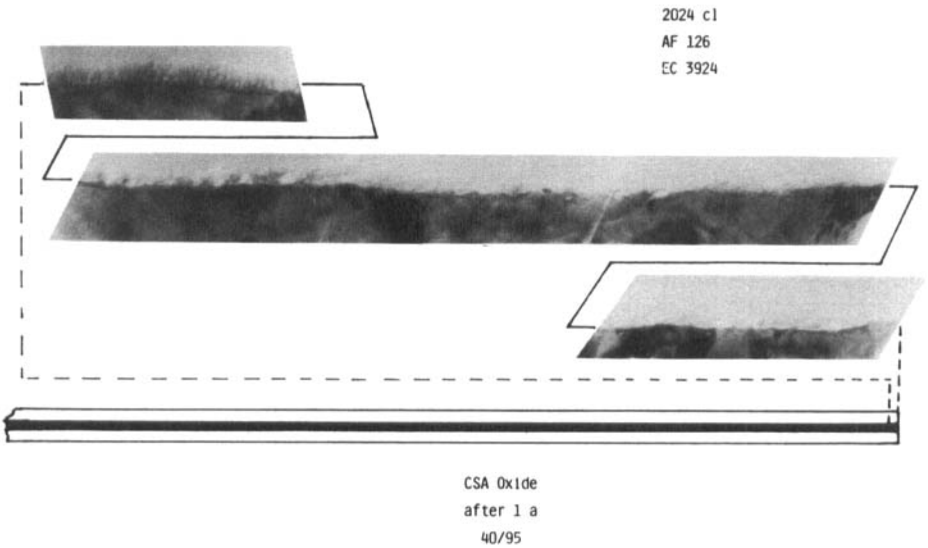


FIGURE 4 Crosscut of the interface between oxide and polymer of bonded aluminium after one year of aging in moist and warm climate. Surface pretreatment: pickling. Adhesive: epoxy resin.

aluminium-containing species in the surrounding polymer. This diffusion is accelerated by the alkaline nature of epoxy based adhesives, particularly those employing a dicyandiamide hardener. When phenolic adhesives are used, this process is slower because the cured resin remains acidic. Bonds whose oxide layer has been reduced in this manner fail almost as soon as a load is applied. With the thick oxide which results from anodization, this is a much more lengthy process. In the case of epoxies, the first detectable changes are noted after three or four years of aging while with phenolics there are no practically important effects even after twenty years of service. It can thus be concluded that phenolics actually have a stabilizing effect on these oxides.

The third failure mechanism to be observed is a rapid and dangerous bond-line corrosion process initiating as primary corrosion of the metal at the edges of the joint. The consequence is rapid bond failure followed by corrosion of the adherend surface. Apparently, a "gelatinization" of the oxide occurs at the crack tip prior to corrosion as is shown in Figure 5 (anodized aluminium). The

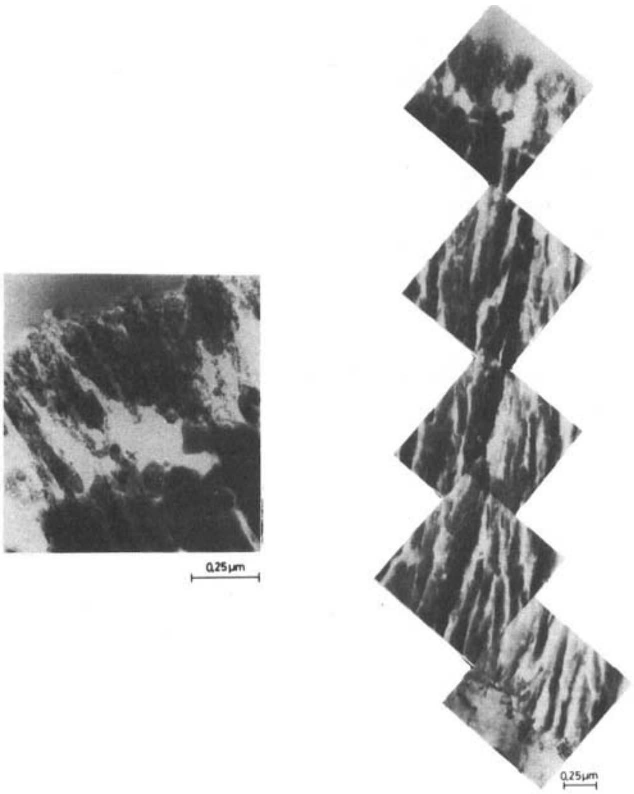


FIGURE 5 Crosscut of the interface between oxide and polymer of bonded aluminium oxide and polymer of bonded aluminium after 2000 h of salt spray testing. Pretreatment: chromic acid anodization. Adhesive: epoxy resin.

transformation of the oxide is accelerated by subsequent primary corrosion. Significantly, adherend surfaces are degraded by this mechanism in as little as one thousand hours. This mechanism, too, is influenced by adhesive type. Again, phenolic resins have a stabilizing effect, whereas epoxies such as those used in the aircraft industry are actually destabilizing. This mode of degradation may be prevented by edge protection (sealing) such that condensation does not initiate primary corrosion. A similar failure mechanism is responsible for the delamination of varnishes from metal surfaces.

5 CONCLUSION

It is concluded that traditional macroscopic theories do not provide a complete understanding of the phenomenon of adhesion. Neither do they provide useful guidance as to the optimization of procedures for specific bonding processes. Investigations at the molecular level, on the other hand, show that by viewing adhesion as a multi-dimensional phenomenon involving a variety of materials interactions, it is possible to identify rational approaches to optimization. The molecular structure of the adhesive precursor and its reactivity must permit it to interact with those of the surface to be bonded. By appropriate chemical modification, the adhesives may also serve to stabilize oxides which are otherwise thermodynamically unstable. In such a case, it is unnecessary to rely on micromechanical interlocking. This approach may be especially useful in the development of pretreatments for metals such as steel which do not form the same well-defined oxide layers as aluminium.

Acknowledgment

The author thanks Dr. Stanley E. Wentworth, Program Director of the 35th Sagamore Conference, for his various help during writing the manuscript in fluent English.

References

1. T. Young, "Cohesion of fluids," *Transactions Royal Soc.* (London) **95,** 65 (1802).
2. A Dupré, *Théorie Mécanique de la Chaleur* (Gauthier-Villars, Paris, 1869).
3. G. A. Dykerhoff and P.-J Sell, *Die angewandte makromolekulare Chemie* **21,** 169–185 (1972).
4. K. L. Wolf *et al.*, *Dechema Monogr. no. 51* (Verlag Chemie, Weinheim, 1964), pp. 31–46.
5. H. Potente and R. Krüger, Adhäsion **1979,** No. 12.
6. M. Michel, "Theorie der Haftung am Beispiel Kunststoff." Paper from Symp. *Haftung von Verbund-werkstoffen und Werkstoffverbunden,* DGM, Konstanz, June 12–13, 1986.
7. R. Houwink and G. Salomon, *Adhesion and Adhesives, Vol. 1* (Elsevier, Amsterdam, London, New York, 1965).
8. W. Brockmann, *Adhäsion* **169,** No. 9, 335–342; No. 11, 448–460; **1970,** No. 2, 52–66; No. 7, 250–252.
9. E. B. Murphy, in *SAMPE Vol. 2, Aerospace Adhesives and Elastomers* (SAMPE, Covina, California, 1970), pp. 603–608.

10. W. Brockmann, *Adhäsion* **1973,** No. 3, 72–83.
11. See *Aspects of Polymeric Coatings,* K. L. Mittal, Ed. (Plenum Press, New York and London, 1983).
12. See *Durability of Structural Adhesives,* A. J. Kinloch, Ed. (Appl. Sci. Publ., London, New York, 1983).
13. *Adhesive Joints etc.*, K. L. Mittal, Ed. (Plenum Publ. New York, 1984).
14. W. Brockmann, Untersuchungen von Adhäsionsvor-gängen zwischen Kunststoffen und Metallen. *Adhäsion* **19,** 4, 34 (1975).
15. A. Hartman, "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).
16. W. Brockmann and H. Kollek, Haftprobleme beim Metallkleben. *Deutsche Farben Zeitscher.* **32,** 166–170 (1978).
17. W. Brockmann, H. Kollek and O.-D. Hennemann, *Farbe u. Lack* **86,** 420–425 (1980).
18. H. Kollek, in *Surface Contamination, etc.*, K. L. Mittal, Ed. (Plenum, New York, 1979), pp. 713–721.
19. O.-D. Hennemann and W. Brockmann, *Beitr. elektronenopt. Direktabb.* **15,** 149–154 (1982).
20. W. Brockmann, "Adhesion mechanisms on aluminium surfaces," in *Xth Internat. Conference on Organic Coatings Science and Technology.* **Proc. 10,** Athens, 1984, pp. 11–20.
21. W. Brockmann, H. Kollek, O.-D. Hennemann and C. Matz, *Adhäsion* **30,** No. 7/8, 31–38; No. 9, 24–35; No. 10, 20–35 (1986).