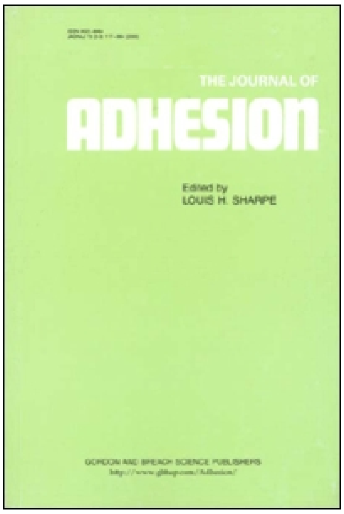

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Venables, John D.(1992) 'The Science of Adhesive Bonding and its Transfer to Technology', The Journal of Adhesion, 39: 2, 79 — 89
To link to this Article: DOI: 10.1080/00218469208026541
URL: http://dx.doi.org/10.1080/00218469208026541

J. Adhesion, 1992, Vol. 39, pp. 79–89
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Printed in the United States of America.

The Science of Adhesive Bonding and its Transfer to Technology

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(Received November 30, 1991)

Author's Note

This article is based, in part, on a lecture given by the author on the occasion of his receipt of **The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M** at the Society's 14th Annual Meeting in Clearwater, Florida, U.S.A., February 1991. The author takes this opportunity to thank the Adhesion Society for the award and the 3M Corporation for its sponsorship. It is an honor to receive such a tribute from a society and a corporation that have done so much to advance the science and technology of adhesive bonding.

KEY WORDS award lecture; technology transfer; adherend morphology; aluminum oxide; contamination by silicones; adhesive bond durability; surface preparation; hydration inhibitor.

ADDRESS TO THE SOCIETY

When first asked to review 16 years of research on adhesive bonding at Martin Marietta Laboratories, I hesitated for a time because, after all, hadn't the full story been said in the more than 60 publications (including review articles)[1-6] that had resulted from our work? But then I remembered the many times we had made some interesting observations or obtained some interesting results but were unable to publish because of the press of other events or because of proprietary considerations at the time. Clearly, this was an ideal opportunity to share a few of these otherwise unpublished observations with the adhesive bonding community.

To set the stage for some of the items I would like to discuss, it is worthwhile mentioning how and why we started our work in the science of adhesive bonding. In June of 1975, the Laboratories was approached by one of our manufacturing divisions with a request for help in solving an adhesive bonding problem that had plagued them on and off for several years, usually during the summer months. We were probably not the ideal group to be consulting on such a problem, for the simple reason that we knew virtually nothing about the subject. I was a physicist studying order-disorder phenomena in very high-temperature materials using electron microscopy and my colleague, Dr. Jar-Mo Chen, was a surface scientist who normally dealt with much different surfaces (*i.e.*, semiconductor surfaces) from those that were involved in this problem. Fortunately, for reasons that I will never comprehend, an engineer at our manufacturing division, Russ Hopping, had more faith in us than we did and so with some persuasion, we agreed to study the problem.

The problem was this. Many aerospace parts that we made then consisted of metal honeycomb cores to which were bonded aluminum faceplates. For quality control purposes, a climbing drum peel (CDP) test sample was constructed along with the actual part and then subjected to a test in which the peel strength of the faceplate was measured. If the peel strengths were below specifications, the part which it accompanied was scrapped and in our case, at that time, the scrap rate was intolerably high. Accordingly, our first step was to examine the surface chemistry of the failed CDP's to look for contaminants. What we found was seemingly a perfectly normal surface of aluminum oxide with some adventitious carbon (to be expected) and a small quantity of fluorine (~10% surface coverage). We discovered that the fluorine probably came from exposure of the (Forest Products Laboratory etch[7] (FPL))-treated panels to fumes from a titanium etch tank that was nearby, but could not understand what its presence meant in terms of bond strength. Indeed, some laboratory tests indicated that the incorporation of small quantities of fluorine onto the metal oxide surface before bonding had little effect upon bond strength.

At the same time, P. F. A. Bijlmer of Fokker Aircraft, The Netherlands, visited us and mentioned his studies of oxides on FPL-treated aluminum surfaces.[8] By stripping the oxide from the metal with a $HgCl_2$ solution, he was able to examine the films by transmission electron microscopy and found they had an unusual structure when viewed at 50,000 × magnification. The effect of the structure on bond strength was unclear, but we decided to do a similar study comparing "good" and "bad" surfaces.

This work proved to be extremely tedious. It was difficult and time consuming to prepare the samples and, under the influence of the electron beam, they tended to charge up which caused severe image distortion. Fortunately, just at that time, we became aware of an exciting development in electron microscopy; a new type of secondary electron detector developed by JEOL for their scanning transmission electron microscope (STEM) made possible a higher resolving power in the SEM mode than had ever before been possible. Indeed, a visit to the JEOL laboratories with our samples demonstrated that the surface of FPL-treated coupons could be examined directly in the SEM at the required 50,000× magnification. In addition, we were able to obtain stereo pairs very easily which allowed viewing the oxide structure in three dimensions.

Our first glimpse of stereo micrographs taken at these high magnifications had an immediate impact on us; the oxide on failed samples seemed quite devoid of any significant surface roughness but, on the other hand, the oxide from properly prepared specimens exhibited an unusual network configuration along with a fibrous or whiskerlike morphology (Figure 1).[9] It took little imagination to recognize the implication of the observation. Evidently, this rough, porous structure was needed to interlock with the primer or adhesive coating and form strong bonds; in the absence of this unusual morphology, the bonds were not acceptable. We felt that we were well on our way to understanding a very important aspect of adhesive bonding in aerospace structures.

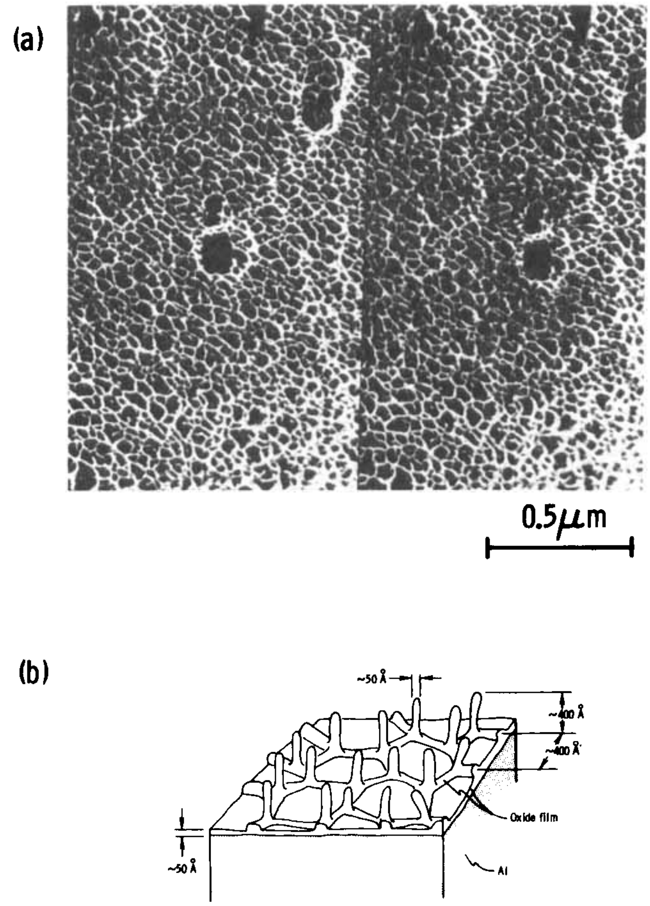

FIGURE 1 (a) Stereo micrograph and (b) isometric drawing of the oxide morphology on FPL-treated aluminum (from Ref. 9, 1).

All the pieces of the puzzle then fell into place. The failed samples, we reasoned, had picked up fluorine vapors from adjacent titanium etch tanks and, while waiting for further processing, had picked up moisture from the humid summer environment in Baltimore. The combination, *i.e.*, hydrofluoric acid, had etched away the porous FPL morphology and this in turn led to the low peel strengths.[10] Based on this analysis, extensive changes were made in the plant and, as a consequence, we saw very significant improvements in the acceptance rate of bonded components.

Our plant engineers were so impressed with this result that they bought their own electron microscope for quality control and we prepared for them a series of micrographs which we called a "Morphology Catalog". Here, my colleague Dave McNamara tried to imagine all the things that might go wrong in a bond shop that could influence the oxide morphology and prepared samples using these "out of spec" procedures. An assortment of micrographs obtained in this manner allowed the quality department to make a quick comparison between them and micrographs taken of sub-standard parts. Several examples of these morphologies are shown in Figures 2 and 3, which demonstrate the consequences of "forgetting" to do the FPL etch after the alkaline cleaning treatment, or having the etching solution contaminated with fluoride or chloride ions.

Much of our subsequent work on oxide morphologies has been described in many publications.[1–6,9,10,14] Basically, what we did was to look at the oxide resulting from a variety of treatments on materials used in the aerospace industry. For example, we showed that the advantage of the phosphoric acid anodize[11] (PAA) treatment over FPL arose in part because of the deeper, more porous structure of the PAA

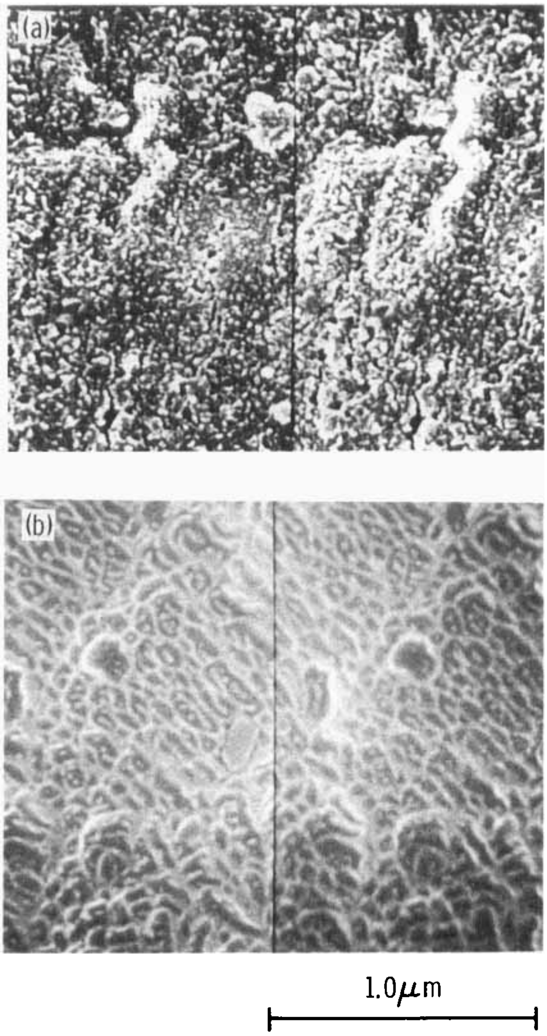

FIGURE 2 Part of a "Morphology Catalog" illustrating the unacceptable morphologies resulting from incorrect surface treatment; (a) TURCO alkaline clean, no FPL etch and (b) AMCHEM deoxidizer, no FPL etch.

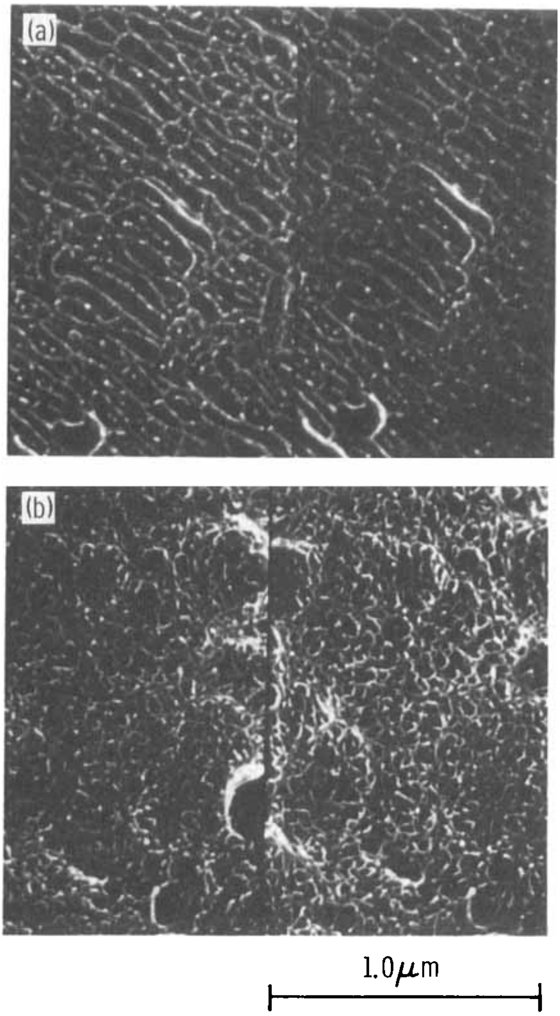

FIGURE 3 Part of a "Morphology Catalog" illustrating the unacceptable morphologies resulting from contaminated etch solutions; (a) FPL with ~600 ppm F^- and (b) FPL with ~400 ppm Cl^-.

oxide (Figure 4). In addition, we evaluated a large number of metal preparation procedures that had been developed for titanium and came to the conclusion that only one of them, the chromic acid anodize[12] (CAA) process exhibited an oxide structure that was similar in dimensions, porosity, and roughness to those on PAA- or FPL-treated aluminum. The fact that this treatment also gave the best performance in wedge tests[13] was, in our view, further confirmation that mechanical interlocking was a very important requirement for achieving good strengths in structural bonds.[14]

Word of our activities spread to other segments of our Corporation and we spent a great deal of time consulting on many highly visible aerospace programs including the Patriot missile and the External Tank (ET) for the Space Shuttle. The work we did on the ET was particularly fascinating because we found ourselves over the

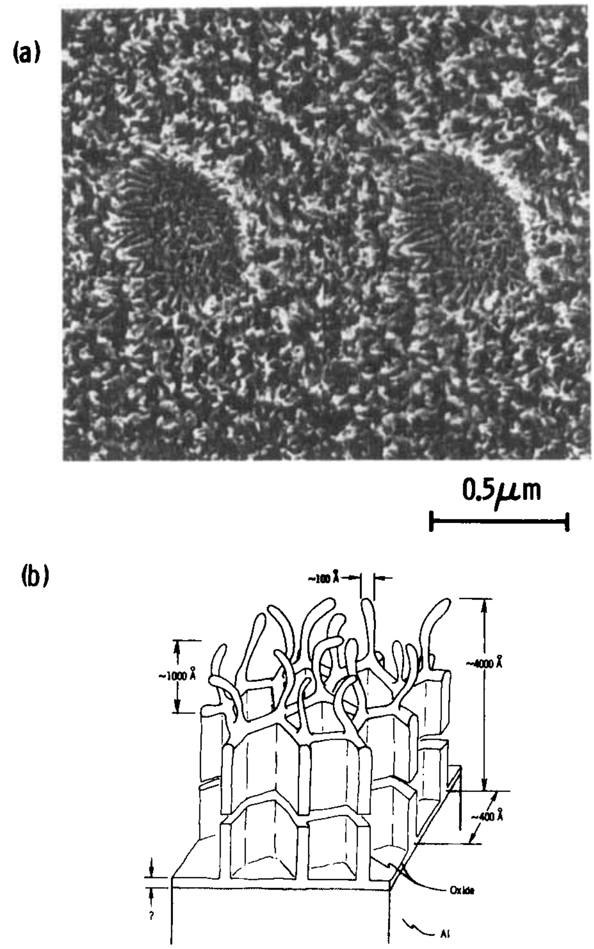

FIGURE 4 (a) Stereo micrograph and (b) isometric drawing of the oxide morphology on PAA-treated aluminum (from Ref. 9, 1).

years playing a very vital role in America's largest space program by contributing to its reliability. We did this by helping our engineers and production staff, who build the tank for NASA, devise tests and failure analysis procedures designed to improve the reliability of the polyurethane thermal protection system (TPS) that is bonded over the entire one-quarter acre of tank surface. Stringent control of this bonding process is necessary to ensure that no insulating foam comes off during launch, because even a small piece could potentially damage the delicate tiles on the orbiter.

To help ensure TPS reliability, we devised various state-of-the-art tests including (1) electron microscope morphology studies of aluminum "witness" panels that had been surface treated along with the tank, (2) surface cleanliness studies on witness panels using x-ray photoelectron spectroscopy (XPS) to look for contaminants such as silicones and (3) Fourier transform infra-red (FTIR) analysis to make sure that the foam chemistry was correct. All of this, I believe, serves as a good example of how an industrial research laboratory can be of invaluable assistance to its parent corporation by making its scientists available to its engineering and production staff for consultation. This type of technology transfer can be very rewarding to the production staff because it is an effective way to make them aware of state-of-the-art technology developments, and further, once the scientists are involved, many of them take great pride in having aided a major program or product line.

During the course of our consulting activities, we were frequently asked this question by members of our engineering staffs: What do we do when we are not allowed to use chromates anymore? This is an excellent question because many of the processes do use large amounts of chromates. For example, the FPL etch, which is heavily chromated, is used extensively in the treatment of aluminum either by itself (the FPL process) or as a precursor step in the PAA process. In addition, many of the conversion coatings used for corrosion protection on aluminum are chromate-based as is the CAA process for titanium.

In response to these queries, we studied and evaluated some non-chromate-based metal preparation treatments including the P2 etch developed at Picatinny Arsenal several years ago.[15] The active ingredient in this etch is ferric sulfate in an aqueous solution—thus it satisfies the non-chromate requirement. It also appears to satisfy another requirement that we feel is extremely important, *i.e.*, it leaves a microporous oxide on the surface, Figure 5, which, when viewed in stereo, appears to be intermediate in thickness between an FPL oxide and that produced by the PAA process, but probably closer in appearance to the PAA oxide. Work is continuing at Martin Marietta to evaluate the P2 process fully but, judging by initial results shown in Figure 5, the P2 etch may be a candidate for replacing the FPL etch as it is used in the FPL process, or as a precursor etch in the PAA process. More importantly, the excellent interlocking nature of the P2 oxide suggests that it might also be a candidate to replace the PAA process itself, and thereby remove requirements

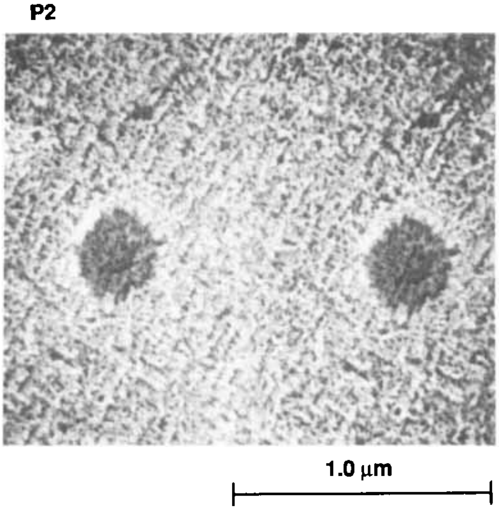

FIGURE 5 Stereo micrograph of oxide morphology on aluminum resulting from the use of the P2 etch. The oxide structure appears intermediate in roughness between FPL- and PAA-treated aluminum.

for electrical anodizing equipment. Many more tests will be needed before such a judgement can be made, however. In any event, we believe that morphology studies of this type will be very helpful in making an initial evaluation of new processes which are needed to replace those that are chromate-based.

Another issue that I would like to touch on, because it occupied so much of our attention while consulting on production problems, is that of silicone contamination. It is no exaggeration to state that well over one-third of our serious bonding problems with epoxy-based systems were eventually shown to be due to silicones. There are many sources for these compounds but the ones that can be found around a bond shop are mold releases, tapes and silicone adhesives. Their presence, if not controlled, can cause havoc with epoxy-based systems in quantities so minute that they may be difficult to detect. For example, we have found that as little as ~½ monolayer coverage of a silicone (2–3% silicon by XPS) on a surface can cause severe reductions in strength.[16]

The method that we have successfully used in our failure analysis effort is high resolution XPS. If XPS is used in a more-or-less routine manner, it will not distinguish between the element silicon which may be in a silicone compound on the one hand or a silicate compound on the other. Since some epoxy systems contain silicates as flow control agents, a routine application of XPS for failure analysis could lead to false positive conclusions by suggesting the presence of silicones when there are none. However, by using XPS in the high resolution mode it is possible to distinguish between those two alternatives by taking advantage of a chemical shift difference, as shown in Figure 6.

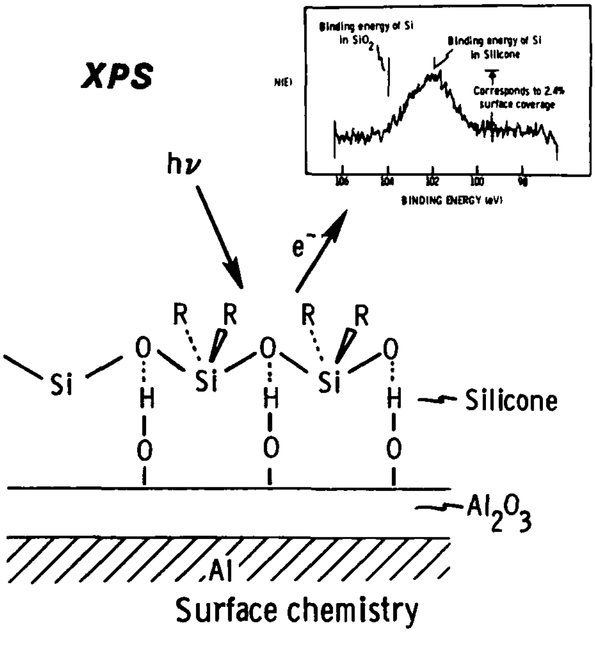

FIGURE 6 XPS spectrum of a failed FPL surface that had been contaminated accidentally with a silicone containing mold release. Binding energy differences make it possible to distinguish between silicon in silicones (which can cause bonding problems) and silicates (which may be used as resin fillers).

The spectrum shown in Figure 6 was obtained from a part that had been accidentally contaminated with a silicone-containing mold release and had failed its mechanical properties tests. As indicated in the figure, the silicone component is readily distinguished from the silicate component due to its different chemical shift, and it can be detected at less than a monolayer coverage. The message indicated here is quite clear. Avoid silicone containing substances in bond shop areas because even very small quantities can severely degrade the performance of epoxy bonded systems.

Our extensive use of XPS in failure analysis, and later in the study of bond durability, led Dr. Guy Davis to develop Surface Behavior Diagrams (SBD's), a technique which was one of the finest contributions that our group made to the science of adhesive bonding. This type of diagram is analogous to a phase diagram for bulk phases, but is intended to represent effects that are specific to surfaces, *e.g.*, reactions between a surface and its environment. A tutorial treatment of the subject has been given in Reference 3 but, briefly, the idea is that changes in surface chemistry (as measured by XPS or other means) can be analyzed much more effectively when the results are presented graphically as an SBD rather than as raw data.

This technique aided immensely in our studies of bond durability by helping us to understand how the oxides on aluminum surfaces hydrate upon exposure to environmental moisture, and how this process eventually leads to long term degradation of properly prepared aluminum adhesive joints.[1-2] More importantly, however, the SBD approach was particularly valuable in the development of hydration inhibitors that would form a protective monolayer on the surface oxide and, thereby, provide significant improvements in bond durability.

For example, in studying the mechanism whereby a particularly effective hydration inhibitor, NTMP,* attached itself to aluminum oxide surfaces, we used XPS to determine the chemistry of an FPL surface as a function of inhibitor concentration and plotted this on an SBD, Figure 7.[17] The diagram indicates that the original surface contained water, undoubtedly in the form of hydroxyl groups, and that the application of the inhibitor served to displace some of it while adsorbing on the surface. This scenario is inferred from the fact that the surface composition follows path (a) rather than path (b) which it would have taken if no water (hydroxyl groups) had been displaced. Another piece of information can be deduced from the curved nature of the adsorption curve as described in Reference 17. Thus, the curvature (rather than linear nature) of the adsorption curve suggests that the NTMP molecule is attached to the oxide surface with only one phosphonate group at low surface coverages, Figure 8, but at higher concentrations all three phosphonate groups are attached. At saturated coverage (one monolayer) we, therefore, have a very stable situation in which all of the original hydroxyl groups are displaced and all three phosphonate groups associated with the NTMP molecule are attached to the oxide surface. It is this type of understanding, obtained mostly through the use of SBD's, that was extremely valuable in guiding our work on inhibitors to achieve improvements in bond durability as discussed in many of our papers.[3,4,17]

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*nitrilotris methylene phosphonic acid

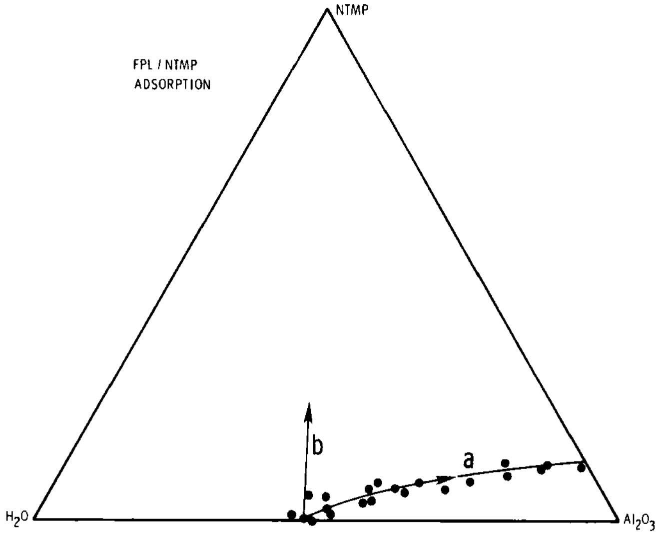

FIGURE 7 Al_2O_3-NTMP-H_2O Surface Behavior Diagram (SBD) showing (a) FPL surface compositions after 30 min immersion in aqueous solutions of NTMP at concentrations ranging from 0.1 to 500 ppm (solution concentrations increase from left to right); and b) the path representing no displacement of water (from Ref. 17).

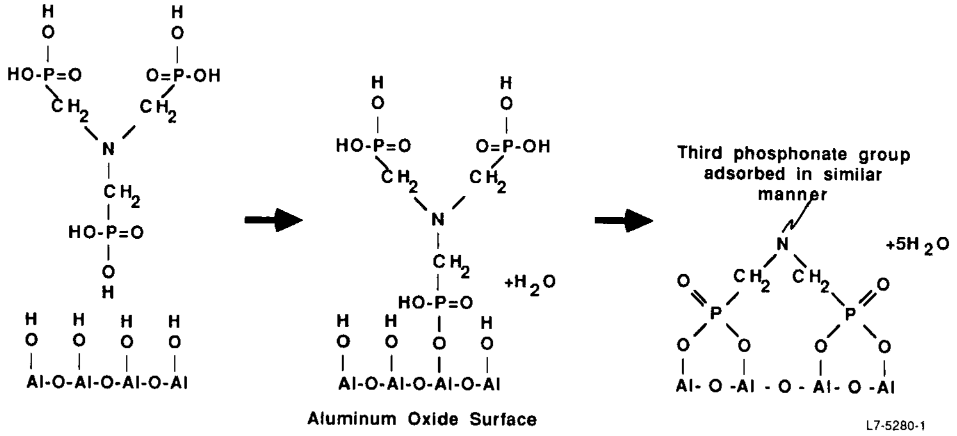

FIGURE 8 Adsorption mechanism of NTMP on aluminum oxide surface as deduced from SBD studies. The NTMP molecule at low solution concentrations displaces hydroxyl groups while attaching with only one phosphonate group. At higher solution concentrations, all three phosphonate groups adsorb in a similar manner.

I hope that I have been able to convey some of the excitement and pleasure that we have had in doing some interesting science and then applying it directly to solving a variety of technical problems on major aerospace programs. To me, this work serves as a good example of what can be an important function of an industrial research laboratory. However, to make the whole thing work, it is critical that a good balance be maintained between the science and the applied aspects. Otherwise, if upper level management does not support the more fundamental work, the technical talent needed to execute the technology transfer properly will disappear and the research and the product line will suffer. I think that maintaining such a balance is something that the sponsor of the award, the 3M Corporation, does in a very elegant manner and for that reason I am particularly grateful to receive this honor from them and the Adhesion Society. Finally, I would like to acknowledge the many colleagues of mine who made this work possible. Their names are too numerous to mention here, but their contributions are documented in the many papers that we published together.

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