Uncovering non-obvious variables in surface preparation processes for bonding and coating

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ABSTRACT

Surface preparation for aerospace bonding and coating operations are still largely manual processes which frequently include some combination of solvent wiping and abrasion. These processes can be very effective if implemented with proper process control feedbacks. However, recent experience with bonding and coating operations across a range of industries has revealed that processes that were successfully demonstrated in a materials and process laboratory don't always translate into reliable and repeatable processes in manufacturing. Root cause analysis has shown that this usually stems directly from a lack of knowledge of all of the variables that can affect the success of a surface preparation process. Process variables that are not identified cannot be measured and controlled. This paper presents a compendium of variables that have been uncovered during failure analysis of aerospace bonding operations, and shows how awareness of these variables permits implementation of simple process control steps that significantly increase bond reliability.

1. INTRODUCTION

Bonding processes are usually treated as a straightforward combination of mechanical and physical steps, such as abrasion and wiping followed by adhesive or sealant application, fixturing, and curing. However, bonding and coating are not physical/mechanical processes: they are chemical synthesis processes. The mechanic is controlling these processes. She is synthesizing a high molecular weight polymer from monomeric or oligomeric precursors. Conceptually more importantly, the mechanic is literally synthesizing a nano-scaled material: the interface (or more correctly, the *interphase*) between the adhesive or coating and the substrate. This interphase region is only a limited number of molecules thick. Bond properties are defined by the quality of this nanometer thick region of the bonded structure, and its composition and properties depend strongly on the quality and consistency of the surface preparation step. Seemingly small variations in the surface preparation procedure, such as a change in the solvent source, a re-used wiper or a wiper from a different supplier, can result in drastic changes in the chemical composition of the bond surface along with unintended effects on bond performance.

Manual surface preparation processes are prevalent in aerospace bonding operations, and because they are manual they can be difficult to control in a quantitative manner. This is highly unfortunate because of the importance of the surface preparation step to overall bond performance. The history of "unexplained" bond failure due to the difficulty in understanding and controlling the various parameters affecting surface preparation and bonding is one of the main reasons that certifiers have been loathe to certify primary bonded structure.

An example of a seemingly minor process variations that results in poor adhesive bond performance is the sequence of abrasion and solvent wiping in a manual surface preparation process. Using contact angles as a sensitive metric of surface cleanliness, careful unidirectional solvent wiping of a metal surface prior to abrasion can reduce the contact angle from perhaps 60° to 30-40° from removal of most of the organic contaminants. Abrasion of this properly precleaned substrate to remove the native oxide will reduce this contact angle to around 10-20°, indicative of an extremely clean, active surface. If adhesive is applied to this surface before it has a chance to recontaminate or oxidize significantly, a superior interface is created and interfacial bond failure is avoided. If on the other hand the surface is abraded prior to solvent cleaning, a contact angle of under 40-50° is almost impossible to achieve. Abrasion creates a near-surface zone of the metal that is highly plastically deformed. Peaks and valleys are created during abrasion; these fold over to encapsulate the contaminants present on the surface. These lacunae of contaminants act as reservoirs; contaminants within them are almost impossible to remove but diffuse out over time to contaminate the bond surface. Thorough precleaning prior to abrasion creates a much cleaner, higher energy surface than cleaning after abrasion, and is perhaps the single most important step in surface preparation.

Another example of the effect of seemingly minor process variations is in the control of surface preparation supplies: wipers and solvents. These problems stem from the common perception that wiping a surface with a visually clean wiper using a visually clean solvent to create a visually clean surface creates a surface that is actually clean. However, successful adhesive bonding depends on controlling composition on the micron or even sub-micron level, well below the threshold of visibility. Confirming this level of cleanliness, and controlling processes to this level, requires measurements that are sensitive to this level of composition. Contact angle measurements are very useful for this, and are being specified as the control metric in an increasing number of applications. A recent trip to an aircraft repair depot where adhesively bonded repairs were being performed was made in response to complaints by the repair personnel that the required low contact angle on the bond surface prior to adhesive application was impossible to obtain. Reviewing the surface preparation process, it was noted that freshly laundered (and visually clean) cloth wipers obtained from a local supplier were being used. It was confirmed that contact angles below about 50° were indeed not achievable. However, replacing the laundered cloth wipers with single-use industrial wipers resulted in contact angles that immediately dropped into the 30° range, well within specification and indicative of a highly bondable surface. Subsequent reflection infrared spectroscopy of clean aluminum surfaces after wiping with the freshly laundered wipers in our laboratory showed that they transferred large amounts of an organic compound consistent with a detergent or fabric softener! Purchasing had been proud to identify a local source of less expensive wipers for the repair process, but the last micron or two of the bond surface was not at all happy with the adhesion-inhibiting residue that was the result.

There are many more examples such as these that point to the sensitivity of the bond surface to seemingly minor variations in materials and processes. This paper discusses in greater detail the necessity for carefully qualifying abrasives as to their ability to create chemically clean surfaces that are suitable for high reliability adhesive bonding operations.

Abrasives are generally specified based on backing construction, physical form, grit type and grit size. However, another important characteristic of abrasives is the presence or absence of anti-loading additives. These are designed to reduce adhesion of the sanding debris to the abrasive paper or cloth to increase the life of the abrasive. These compounds are typically stearates (metal soaps of stearic acid). Abrasives are generally not labelled as to whether or not they contain anti-loading additives. A side effect is that these compounds can transfer to the bond surface. This study investigates the detectability of stearates in abrasives by rapid contact angle measurements as well as spectroscopic methods, and evaluates the potential effect of these on adhesive bond performance.

2. EXPERIMENTATION

Two abrasives were evaluated: 3M 202DZ and Mirka P240. The 3M abrasive has been qualified by NAVAIR as a non-contaminating abrasive and is used for the preparation of Al surfaces prior to sol-gel treatment for bonding. The Mirka abrasive was obtained from an aircraft repair depot where it was noted that this abrasive (although being used for surface preparation for bonding) was unable to achieve the low contact angles indicative of a clean and well-prepared surface. Al coupons were solvent wiped twice with Dysol DS108 prior to abrasion with a pneumatic random orbital sander. Reflection FTIR (Nicolet Magna 750 equipped with a Harrick grazing angle reflection accessory) and contact angle measurements (BTG Labs Surface Analyst™ SA3001) used to evaluate surfaces for the presence of contaminants. One contact angle was measured on each bond surface at each step of the preparation process. Single lap joints (ASTM D1002) were made according to ASTM D1002 with RT cure paste epoxy to evaluate the abrasive effect on strength and failure mode.

3. RESULTS

Figure 1 shows the abraded coupon surfaces. Figure 2 shows the contact angles obtained from the surfaces abraded with the 3M 202DZ abrasive at each step of the preparation process.

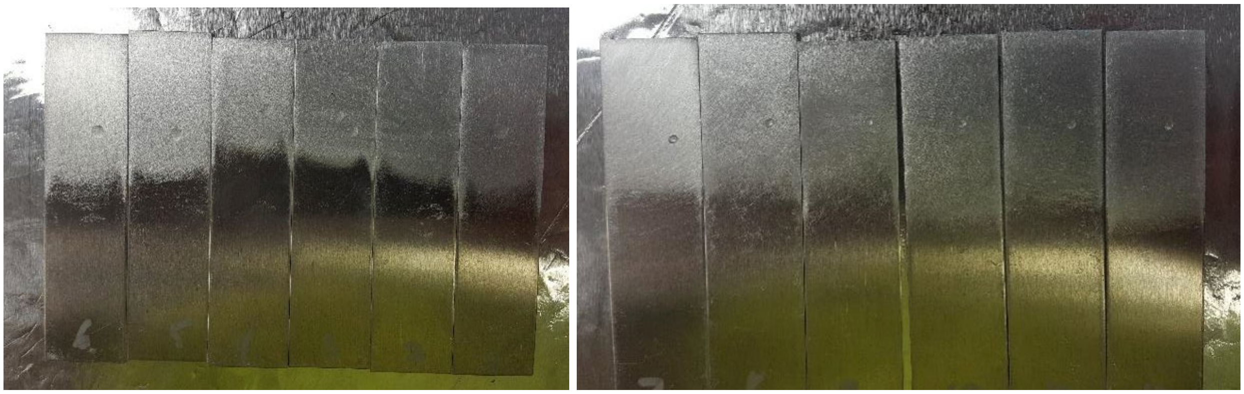

Figure 1. Abraded coupon surfaces prior to bonding. Left: abraded using 3M 202DZ. Right: abraded with Mirka P240. Notice relative size of water drops used for contact angle analysis.

Figure 2 shows a typical response of contact angle measurements to surface preparation with a non-contaminating abrasive. The wide variation in water contact angles obtained after the first solvent wiping show that it is not particularly clean nor uniform at the molecular level. A subsequent solvent wiping significantly improves the uniformity. In particular, the areas that were especially contaminated (indicated by the high contact angles) are now significantly cleaner: the distribution of contact angles is much tighter. Finally, after abrasion with the 3M abrasive, the contact angle distribution is extremely tight with a low mean. This indicates a very clean, high-energy surface with excellent point-to-point uniformity.

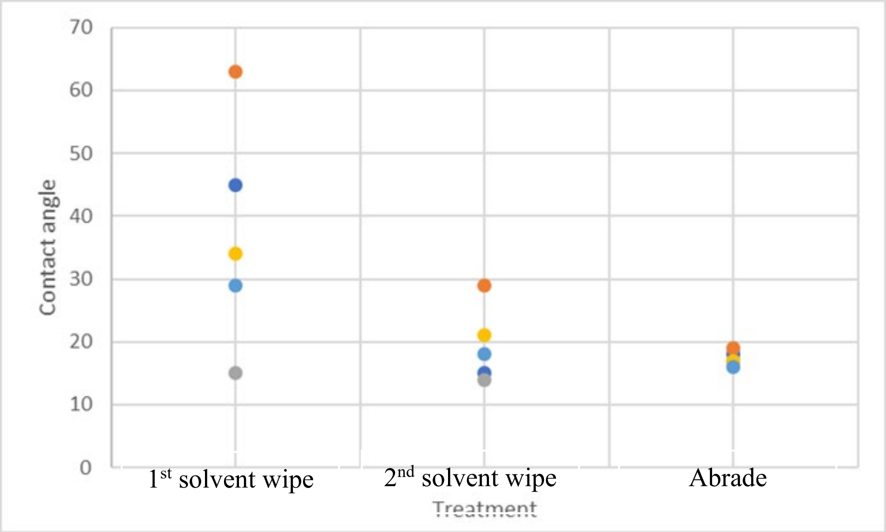

Figure 2. Water contact angles measured on coupons after each step in surface preparation. These samples were abraded using 3M 202DZ.

Figure 3 shows the results obtained using the other abrasive. The behavior after the first and second solvent wipe is very similar. However, this abrasive resulted in an *increase* in contact angle to an average value of about 58°. This surface is fairly uniform but does not show the low contact angles associated with a clean, high-energy metal surface.

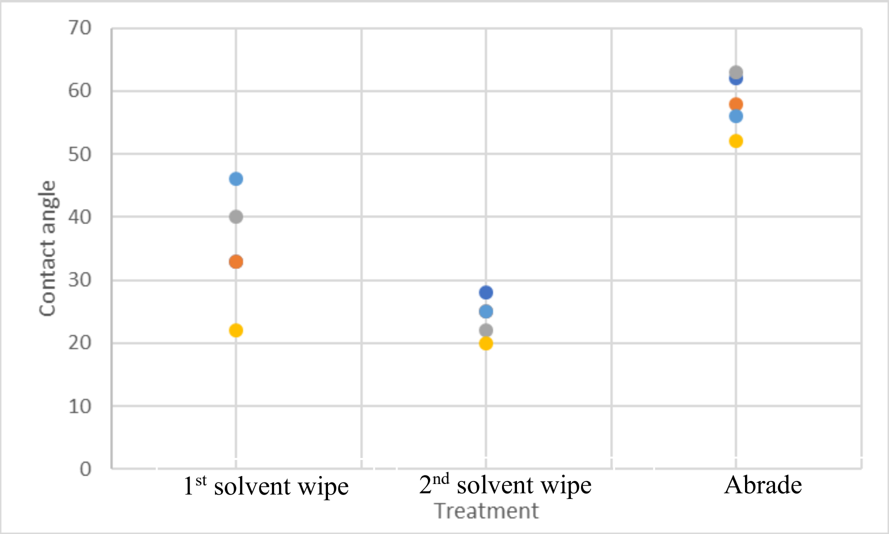

Figure 3. Water contact angles measured on coupons after each step in surface preparation. These samples were abraded using Mirka P240 abrasive.

Reflection FTIR spectra in Figure 4 were obtained from abraded surfaces corresponding to Figures 2 and 3. The non-contaminating abrasive (which produced a surface in this case with an 11° water contact angle) is featureless, while the other abrasive (which produced a surface that returned a 65° contact angle) resulted in a spectrum with significant absorbance from organic functional groups.

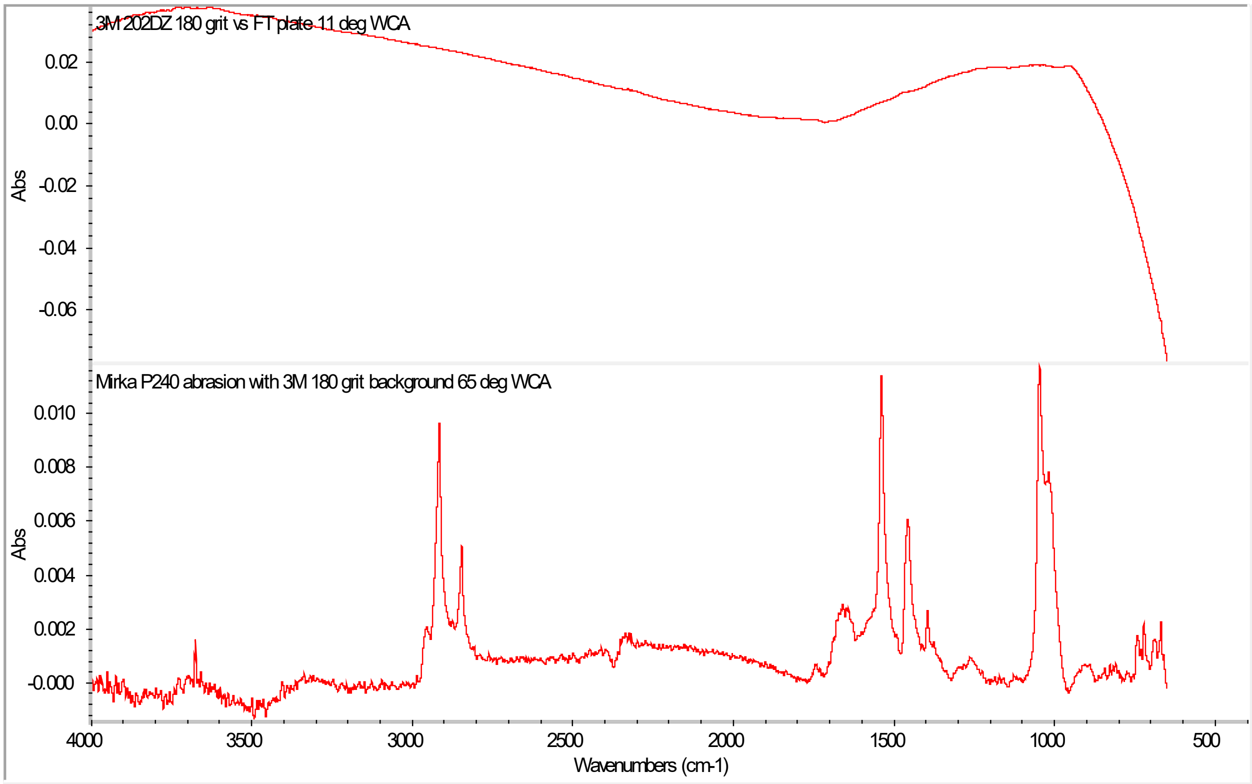

Figure 4. RAIR-FTIR spectra obtained from samples abraded with 3M 202DZ (top) and Mirka P240 (bottom). Corresponding water contact angles were 11° (top) and 65° (bottom).

This spectrum was readily identified as a stearate. Figure 5 presents the spectrum obtained from the aluminum coupon sanded with the Mirka P240 abrasive along with an authentic spectrum of zinc stearate. With the exception of a band due to Al-O near 1000 cm^{-1} in the spectrum of the abraded surface, the spectra are almost identical. Zinc stearate is a soap known to be used as an anti-loading additive in abrasive papers. This indicates that the Mirka P240 abrasive has transferred this compound to the surface.

Finally, single lap joints were constructed from the coupons shown in Figure 1. Average breaking strength obtained with the non-stearated abrasive was 580 psi; with the stearated abrasive, the average strength was 330 psi. In both cases, failure was close to one interface. However, failure in the samples abraded using the non-stearated abrasive occurred at least partially within the epoxy. Figure 6 shows images of the aluminum side of the failure surfaces. The surface prepared with the non-stearated abrasive shows visible epoxy left on the aluminum surface. None is visible on the surface prepared using the stearated abrasive.

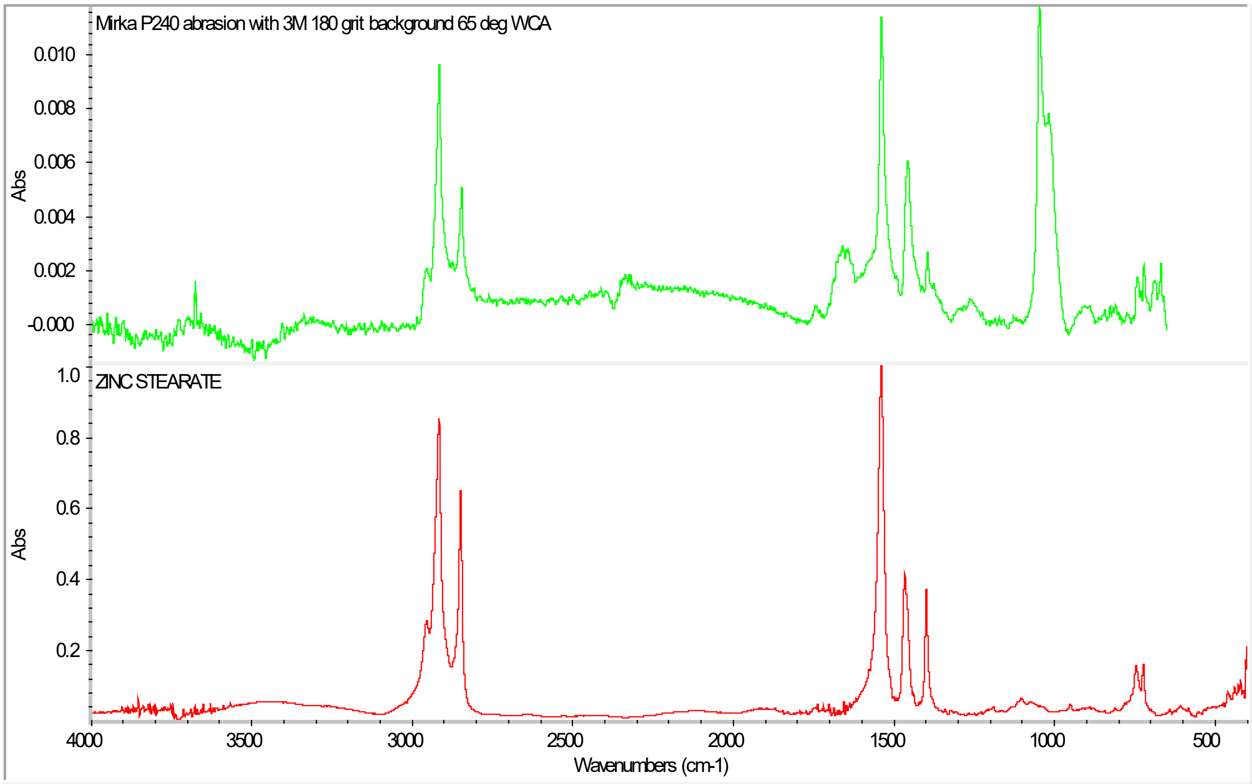

Figure 5. RAIR-FTIR spectra obtained from a sample abraded with Mirka P240 (top) and zinc stearate (bottom). Band at ~1000 cm^{-1} in the spectrum of the abraded aluminum is due to Al-O in the aluminum oxide.

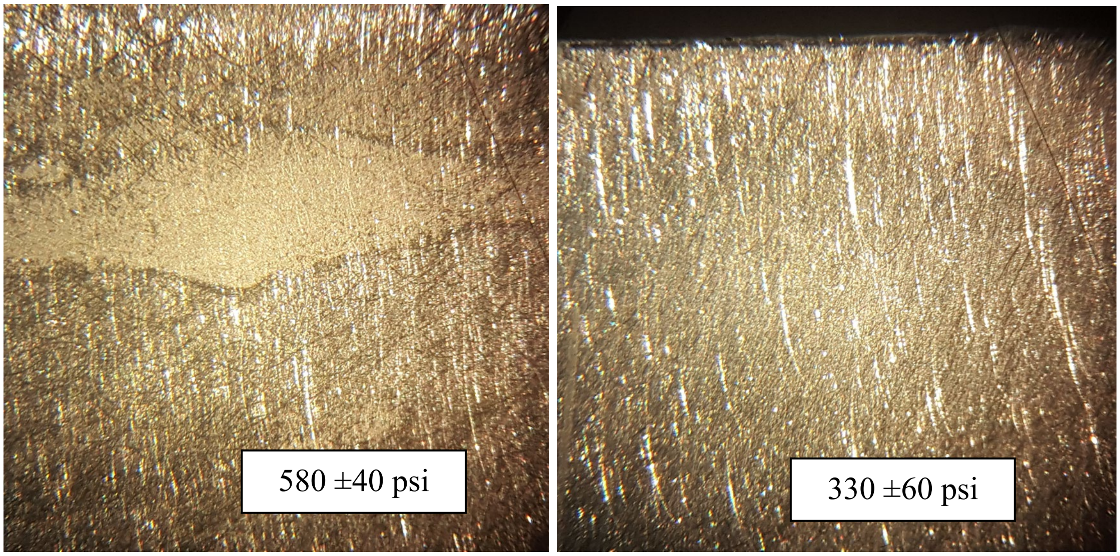

Figure 6. Aluminum side of failure surfaces. Left: Substrate sanded with non-stearate containing abrasive (average lap shear strength of 580 psi); right: Substrate sanded with stearate containing abrasive (average lap shear 330 psi).

The surfaces prepared using the started abrasive may be at least partially remediated by solvent cleaning. Figure 7 compares the spectra of the freshly abraded contaminated surface with one obtained after solvent wiping. The solvent-cleaned surface shows a small amount of organic material on the surface (bands near 2900 and 1710 cm^{-1}), but the strong characteristic band of the stearate near 1500 cm^{-1} is absent. The oxide may have grown and hydrated somewhat during wiping (perhaps simply due to the elapsed time), but the overall intensity of the oxide peak is similar, indicating that the amount of oxide has not increased much if at all.

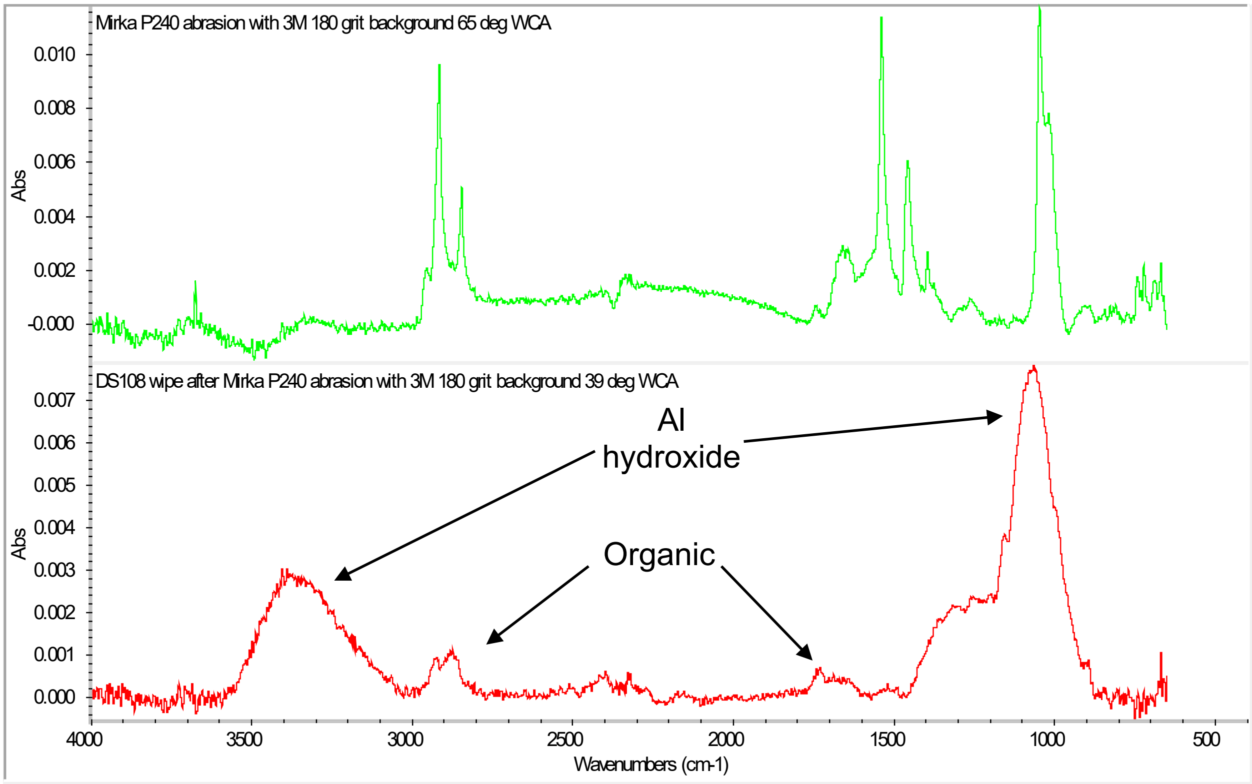

Figure 7. RAIR-FTIR spectra obtained from a sample abraded with Mirka P240 before (top) and after wiping with Dysol DS-108 solvent.

4. CONCLUSIONS

Successful (i.e. controllable, reproducible) adhesive bonding requires control of variables that may be non-obvious to the casual practitioner. It does not lend itself to an ‘artisan’ approach that places trust in a technician who may have (or may be working under someone who has) years of experience. The success of a bonding process depends on control of the composition and properties of a sub-microscopic region of the bond surface that is only a few molecular layers thick. This is thousands of times thinner than a fingerprint. For example, simply changing brands of abrasive paper without evaluating the ability of the abrasive to create a surface with chemically identical properties can result in significant changes to both bond strength and failures mode.

It is important to point out that adhesive bond performance is the result of the interplay of all components in the system. The results discussed here, obtained using aluminum substrates and an RT cure paste adhesive, could be very different if a HT film adhesive and/or a composite laminate substrate were employed. HT curing adhesives are known to be capable of tolerating larger amounts of contaminants than RT curing systems. However, even if no detrimental effect on static properties were detected, use of an abrasive that leaves significant amounts of a non-adhesive residue in the near-interfacial regions of the bondline could affect other properties, such as environmental or fatigue resistance: adhesive + contaminant represents an adhesive that has a different composition than the adhesive that was originally qualified.