ANALYTICAL SERIES

To Stick or Not To Stick, Part II: Guide to Adhesion Measurement for the Layman

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This two-part article is a condensation of a much larger work[1] that deals with the full range of adhesion measurement, including details of continuum theory, fracture mechanics, measurement of intrinsic stress, and several detailed applications. Part I, published in the August 2015 issue of *CoatingsTech*, gave a brief tutorial on the most relevant aspects of these topics. In Part II, a *Consumer Reports*-style evaluation of several adhesion measurement methods of relevance to the coatings industry is provided.

OVERVIEW OF MOST COMMON ADHESION MEASUREMENT METHODS

Mittal[3] has informally counted some 300 reported adhesion measurement methods as of early 1994. Most of the reported methods, however, are essentially variations on one of the techniques described below.

Peel Test

Within the realm of adhesion tests there are two major classes—those dealing with relatively soft flexible coatings and those dealing with hard brittle coatings. By far the most common test for flexible coatings is the peel test. Anyone who has removed wallpaper from an old house already has considerable practical experience with the rudiments of this test. When dealing with polymer-based paints, for example, the peel test readily suggests itself as the preferred experiment for testing the adhesion of the coating. Such coatings upon curing and drying tend to build up a significant level of internal stress which increases dramatically near the edge of the coating or near any discontinuity, such as a scratch or a particle inclusion. If the level of adhesion between the coating and the substrate is not sufficient, then the coating will delaminate and peel back from the substrate. The now-released film can be grasped with a tweezer and an ersatz peel test performed. Thus, the peel test automatically suggests itself as an adhesion test for flexible paint coatings.

The main task for the experimenter is to standardize and quantify the peel test experiment so that the results can be used to either establish a quantitative ranking among the coatings being tested or to set a numerical specification for adhesion strength which can be subsequently used as a quality control standard. The problem of quantifying the test is readily solved by the use of an appropriate test frame in conjunction with a suitable load cell for determining the peel force. *Figure* 4 exhibits a number of common configurations. *Figure* 4a illustrates the common 90° peel test, which is the favored test for flexible coatings on rigid substrates. This is by far the most prevalent and most thoroughly studied of all the peel tests. *Figure* 4b illustrates the 180° version of *Figure* 4a. This version offers advantages in situations where space is cramped. It is also clear that the peel test can be performed at any angle between 0 and 180°. For most practical purposes, there is little need to consider angles other than 90 or 180° unless there are geometric constraints imposed by the sample or test apparatus. From an analytical point of view,

however, varying the peel angle can provide information on the effect of "mode mixity" on peel strength. When performing a peel test the interfacial region is subjected to both tensile (mode I) and shear (mode II) loads. The ratio of these two loading types is loosely referred to as the loading "mode mixity." The importance of knowing the mode mixity stems from the fact that the apparent adhesion strength of many coatings is sensitive to the mode mixity. For example, glues tend to be much stronger in shear than in tension, which implies that they will exhibit a much higher adhesion strength in a predominantly mode II test as opposed to a mode I test. A very common example of this phenomena is exhibited by the Velcro fasteners discussed in Part I.

Figure 4c illustrates the climbing drum test which is used in testing the adhesion of rubbers in the tire industry. One advantage of this version is that the radius of curvature of the peeling film is fixed by the drum radius which simplifies later numerical analysis of the data. Finally, the T peel test shown in *Figure* 4d can be used to test the adhesion between two flexible films.

Advantages of the Peel Test

The peel test in its various configurations meets many of the criteria of the ideal adhesion test mentioned previously. Sample preparation is typically reasonably simple and straightforward. This single fact more than anything else accounts for the overall popularity of this test. Also, the peel force gives a quantitative measure of the coating adhesion to the substrate which can be readily used for ranking or quality control purposes.

A further advantage of this test is that the rate of delamination and the locus of failure can be controlled fairly precisely. This stems from the fact that a very high stress concentration exists at the point where the coating just lifts off the substrate. This tends to narrowly focus the failure region very close to the geometric interface between coating and substrate, which is the region of most interest in any adhesion test. Since the rate of delamination can be precisely controlled by the test equipment, studies of the rate dependence of adhesion strength can be easily carried out. This can be very important when studying coatings that exhibit strong molecular relaxation behavior (i.e., glass transition and related phenomena) near the test temperature. Finally, the peel test readily lends itself to use under conditions of controlled temperature and environment (for example, temperature and humidity conditions).

Disadvantages of the Peel Test

As noted previously, the peel test works quite well when used as a method of ranking the adhesion of a coating when the substrate has been subjected to a number of different surface treatments. However, when trying to ascertain whether the coating will survive a given set of end-use conditions, several problems arise. The main issue is that the peel test subjects the coating to very high strain levels which most coatings never see under common end-use conditions. The strain in the coating at the peel bend can easily approach 25% or higher, whereas real coatings delaminate under nearly strain-free conditions. Thus, the load state imposed by the peel test does not reasonably approximate the load conditions which cause failure in the field and, therefore, conclusions arrived at on the basis of peel testing can be highly misleading when trying to anticipate the actual service behavior of a particular coating. A particularly illuminating example of how far off you can be was given by Farris and Goldfarb.[4]

These authors tested the adhesion of polyimide films to aluminum and demonstrated apparent peel strength adhesion values in the range of 500–900 J/m^2. However, the very same coatings self-delaminated at an adhesion strength of 23 J/m^2 when the coating thickness was increased to 120 µm. Thus, it is clear that peel test results can lead to highly misleading estimates of the actual delamination behavior of a coating when subjected to realistic end-use conditions.

Further limitations of the peel test stem from the fact that it is applicable only to tough flexible coatings. Attempts have been made to circumvent this limitation by applying a peelable backing coating on top of the coating to be tested and then peeling the composite

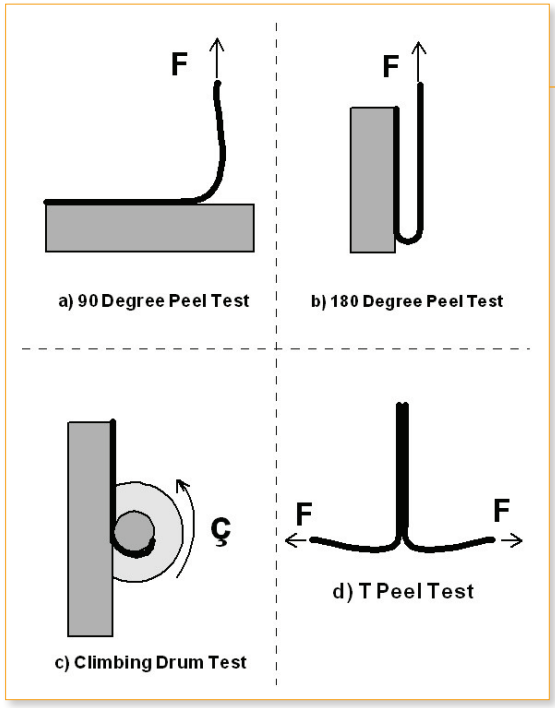


Figure 4—Four versions of peel test used for testing flexible coatings.

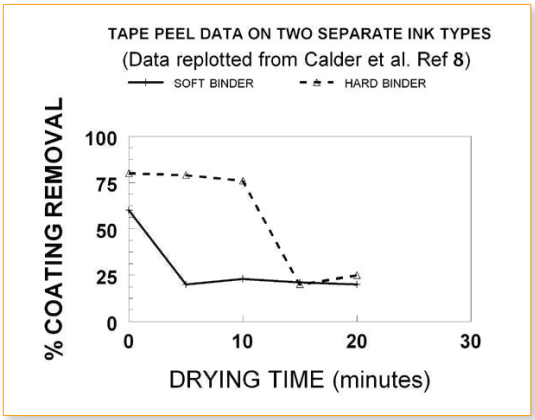


Figure 5—Tape peel data for two printing inks with different binder formulations.

laminate. One major problem with this approach is that the locus of failure at the peel front can become unstable and wander between the backing coating, the test coating, and the substrate, making interpretation of the results unclear.

A number of other drawbacks and limitations apply to the peel test, including difficulty in initiating a peel strip for coatings with strong adhesion and controlling sample-to-sample variability. These problems can typically be dealt with by developing appropriate experimental techniques.

Summary and Recommendations

The peel test will be the method of choice when dealing with tough flexible coatings on rigid substrates as it meets many of the criteria of the ideal adhesion test. First and foremost is the consideration of sample preparation. In this regard, it is typically quite straightforward to fabricate conveniently sized coupons of the substrate material and apply the coating of interest to them. Suitable care should be taken to clean the substrate and apply whatever adhesion promoters are of interest. Further technical details such as providing a release layer so that the peel strip can be easily initiated should not be overlooked. Finally, care should be exercised in interpreting the final data. Peel test data can be a very reliable method for ranking the effectiveness of adhesion promoters or for quality control measurements. As noted above, one should not rely on peel test measurements as a guide to performance of the coating under end-use conditions since the load state imposed by the peel test does not in general reproduce actual load conditions in the field.

Tape Peel Test

The tape peel test is a rough and ready variant of the standard peel test described previously. Its main advantage is the ease of sample preparation. The predominant disadvantage is the fact that the results of the test will tend to be only qualitative, although attempts have been made at systematizing the test to give semi-quantitative results. In a typical application, a strip of specially fabricated tape is applied to the coating to be tested in a predefined manner. The main concern is to be as consistent as possible in order to achieve reproducible results. The tape is subsequently peeled off in a predefined manner and the removal surface is then inspected for whatever resulting damage may have occurred. At the purely qualitative level, the experiment gives a "go/no go" type of result, indicating that the adhesion of the coating is either acceptable or not. A number of techniques have been invented to give a semi-quantitative result by quantifying the level of partial damage that may have happened to the coating. An example of this for the case of ink coatings will be discussed shortly.

The main problem with obtaining truly quantitative results with the tape peel test is that one now has four different materials to deal with: the substrate, the coating, the tape adhesive, and the tape backing material. Satas and Egan[5] have reported the effect of the backing layer and the adhesive layer on the peel strength of pressure sensitive tapes. Their data shows that, depending on the tape backing material, the peel force can vary by as much as a factor of 2 for a given layer thickness.

In a separate study, Aubrey, Welding and Wong[6] investigated the effect of adhesive molecular weight, adhesive layer thickness, backing film thickness, peel rate, and peel angle on the peel strength of polyester backing/polyacrylate adhesive pressure sensitive tapes. They demonstrate that all of these factors have a significant effect on the measured peel force. In particular, the peel force shows a dramatic dependence on peel rate with three fundamentally different modes of peeling. At low rates, the peel force is controlled by flow of the tape adhesive and is strongly rate dependent. At high rates, little viscous deformation occurs and the peel force is largely rate independent. At intermediate peel rates, the peel force exhibits cyclic instability driven by alternate storage and dissipation of elastic energy. The net result is a type of "stick-slip" peeling. Thus, without even considering the coating and substrate properties, we already have a considerable degree of complexity introduced just by the properties of the tape alone. If we now introduce further complexities arising from the mechanical response of the coating and substrate, we see that the problem of deriving a truly quantitative analysis of the tape peel test is prohibitive.

Advantages of the Tape Peel Test

Despite the difficulties mentioned in obtaining quantitative results with the tape peel test, it can still be a useful and effective measurement method in certain applications. This is best illustrated by the study of ink coatings by Calder, Hansen, and Parra.[7] These authors have succinctly summarized the case for using the tape peel test in a cogent manner which bears repeating[8]:

> *"There is a body of experience in the industry that confirms that the tape test is a reasonable predictor of how the ink will remain in place, intact on the substrate under many actual use conditions."*
>
> *"The test is fast and can be performed at press side. It is obviously important to know rather quickly whether an ink has adequate adhesion when the film is being printed at 600 ft/min."*

In their experiments on ink coatings, the authors apply the subject ink coating to the relevant paper or foil substrate. Tapes are applied to the ink coating after a specified drying time and removed rapidly by a 90° peel test. The degree of adhesion of the ink coating is then rapidly evaluated using a light spectrophotometer and is reported as percent coating removal as compared to a standard untested sample. Appropriate calibration methods are used to ensure repeatability. *Figure* 5 illustrates some representative data from this type of experiment. The solid line shows the apparent adhesion vs time for an ink with a relatively "soft" binder matrix and the dashed line illustrates the same behavior for an ink with a "hard" binder matrix. The data clearly reveal that the soft binder gives an ink with stronger adhesion at short times (lower percentage removed) and that both ink types level off to substantially the same adhesion level at longer times. This is the type of information that can be of practical use in the printing industry where different printing techniques have different requirements for ink adhesion.

A different type of application of the tape peel test in the photographic film industry was given by Grace et al.[9] These investigators used the tape peel test in conjunction with a "time resolved salt bath" technique for investigating the adhesion of silver coatings to poly(ethylene terephthalate) (PET) films. In the salt bath test, silver-coated PET films were immersed in a salt bath and the time required for the silver to lift off was noted. These results were then correlated with standard tape peel testing in a manner similar to that mentioned earlier. The essential result of this investigation was the demonstration that the salt bath test was able to better discriminate different levels of adhesion of the silver coatings than the tape peel test alone. The tape test basically gave a good/not good type of result, whereas coatings tested in the salt bath would survive for different lengths of time, thus giving a more continuous scale of adhesion performance. In particular, coatings which the tape peel test indicated to be good were shown to delaminate at intermediate times in the salt bath test. However, films shown to be poor by the tape peel test were also poor by the salt bath test. Thus, the tape peel test supported the salt bath experiments, but did not give the same degree of resolution of adhesion strength.

Disadvantages of the Tape Peel Test

As pointed out above, the tape peel test can give at best a semiquantitative estimate of the adhesion of a coating. The results of the test tend to be confounded by the mechanical response and variable failure modes of the tape backing and the tape adhesive as well as similar behavior of the coating and the substrate material. With so many potential complicating factors, the interpretation of tape peel test data is very difficult if more than a simple qualitative estimate of adhesion strength is required. The use of calibration methods and reference samples is mandatory to ensure a reasonable level of repeatability.

Summary and Recommendations

Though the tape peel test is limited to a qualitative or at best semiquantitative evaluation of adhesion, it has a number of advantages that make it attractive in specific applications. In particular, in situations where a simple rapid test is required, as for testing printing inks or where a straightforward "go/no go" evaluation is sufficient, this test may be perfectly adequate. In some cases, it may be the only reasonable test available. However, great caution is recommended in evaluating tape peel data and the results should not be over-interpreted in terms of trying to understand the fundamental adhesion of a coating since a large number of confounding factors come into play with this test.

Pull Test

Figure 6 illustrates two versions of the pull test whereby a stud is attached to the coating to be tested using a strong adhesive and then pulled off using a tensile test apparatus. The force required to remove the stud cleanly from the sample is taken as a measure of the adhesion of the coating to the substrate.

An excellent evaluation of the pull test as applied to paint coatings was given by Sickfeld.[10]

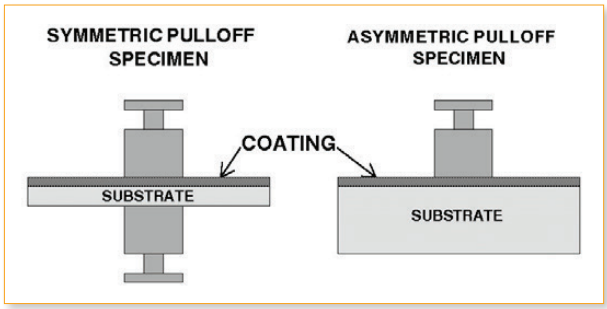


Figure 6—Two configurations of pull test.

This author investigated the two basic pull test configurations illustrated in *Figure* 6. The symmetric configuration is preferable for testing coatings on relatively thin flexible substrates whereas the asymmetric sample is preferred for thick rigid substrates. Similar to the tape peel test, the pull test involves two additional materials besides the coating and substrate being investigated.

The test stud itself is fabricated out of a high modulus metal or ceramic material and, for the case of paint coatings, can be considered almost perfectly rigid. This is not the case for testing stiff brittle coatings such as diamond or ceramics and in these cases, the stud material must be carefully figured into the analysis. In addition, an adhesive is required to attach the test stud to the coating under test. For paint coatings, this is typically an epoxy glue and its properties will always enter the analysis. *Figure* 7 illustrates both a strength and a weakness of the pull test. The basic strength is that it can be applied to such refractory materials as tungsten and diamond.

One would be very hard pressed to get the peel test to work with this material configuration. The basic weakness of the test is readily apparent from the difference in the fracture surfaces of the two samples illustrated in the figure. The top sample shows a clean delamination, whereas the bottom shows mixed behavior with roughly one third cohesive failure in the diamond coating and the remaining clean delamination.

Further complications can be noted as follows:

1. Unless the load is applied very carefully there can be an off-axis component which can impose a bending moment to the sample in addition to the tensile load.
2. Even assuming pure tensile loading, any real sample will not be uniformly bonded and the applied stress field will seek out any defects or bonding weaknesses.
3. Failure will be initiated at the weakest point in the structure and propagate at acoustic velocities to complete separation.
4. Failure can occur either adhesively at any of the three sample interfaces or cohesively in any of the four bulk materials. Mixed mode interfacial and cohesive fracture is the most common failure mode, as shown at the bottom in *Figure* 7.

Given this list of complexities, it should come as no surprise that typical pull-test data shows a wide range of variation. Multiple tests must be run at any given condition and data censoring techniques applied to ferret out unwanted failure modes.

Advantages of the Pull Test

The main advantage of the pull test is its wide ranging applicability to all manner of coatings from relatively soft flexible polymer coatings to hard brittle coatings such as diamond. In addition, as pointed out by Sickfeld,[10] there are two types of information that can be obtained from this test. The first is qualitative, deriving from an analysis of the resulting pull-off fracture surface. Some idea of the integrity of the coating can be obtained by noting whether failure tends to be mainly cohesive in the coating itself or adhesive between the coating and the substrate. In particular, Sickfeld was able to study the effect of moisture and solvent immersion on the failure mode of paint coatings. For the case of immersion of the coating in water, subsequent pull testing showed nearly interfacial failure between the coating and substrate. On the other hand, coatings immersed in gasoline or oil demonstrated a mixed adhesive/cohesive type of failure. This type of data can be very valuable when evaluating a particular coating for use under particular service conditions.

A second advantage is the quantitative information derived from the pull test. It has been hypothesized that in most cases the failure mode in a given pull test experiment is determined by a pre-existing distribution of flaws in the sample. Thus, as discussed above, the applied stress field seeks out the largest, most vulnerable flaw in the sample. Failure initiates at this point and the initial flaw rapidly propagates at acoustic velocities to ultimate separation of the pull stud and the sample surface. In effect, it is assumed that all samples will have some kind of inherent flaw distribution no matter how carefully they were prepared and the stress field deriving from the pull test will inevitably find the most vulnerable flaw and failure will initiate and propagate from that point. It has further been found that Weibull statistics are very effective in analyzing this type of data.

Pawel and McHargue[11] have used the pull test to analyze the adhesion of iron films to sapphire

substrates. These investigators ion-implanted both nickel and chromium impurities at the interface between an iron film and sapphire substrate. Subsequent pull testing and Weibull analysis unequivocally demonstrated that the chromium interphase substantially improved the adhesion of the iron film over the untreated and nickel-treated cases.

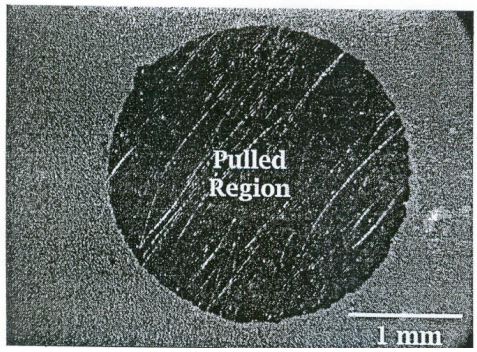
Finally, there are situations that are perfectly disposed toward the pull test, such as evaluating the durability of pins on a microelectronic packaging substrate. For large mainframe machines, such substrates can carry over 100 silicon chips and require over 1000 pins in order to distribute power and signal data to a supporting carrier board. The reliability of these pins is critical to the proper function and performance of the total chip/substrate assembly and each pin must meet very stringent reliability and performance criteria. The pull test is the natural performance evaluation procedure for this application. Coupled with the appropriate Weibull analysis, the pull test provides a crucial engineering and quality control tool for the design and fabrication of such structures.

Disadvantages of the Pull Test

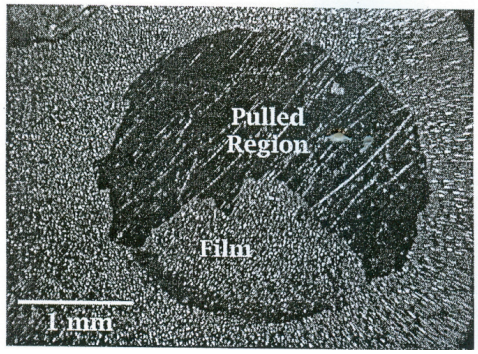
One of the main disadvantages of the pull test is the wide variability of typical test data. This problem has been documented most cogently by Alam, Peebles, and Ohlhausen.[12] These investigators attempted to evaluate the adhesion of CVD diamond coatings to tungsten substrates as shown in *Figure* 7. Due to a variety of conditions affecting their sample preparation, including nonuniformity of film thickness, diamond quality, film cohesion and surface preparation, they observed considerable variability in their pull-test data. In the author's own words:

> *"The measured adhesion values showed larger variations from point to point across the sample surface and from identically prepared samples than variations as a function of the film processing parameters."*

Thus, the data derived from pull testing in this case was mainly qualitative. Every form of sample failure was observed, including clean interfacial delamination, partial delamination with partial film cohesive failure, cohesive failure in the epoxy adhesive coupled with delamination of the epoxy from the coating, and pure cohesive failure of the diamond coating. With such a wide range of failure modes, it was no wonder that the data showed a high degree of variability. With the use of statistical analysis, however, the authors were able to show that substrate preparation, gas flow, and gas pressure were the most important processing parameters.



Photograph of a sample showing a good, clean pull.



Photograph of a sample showing partial film failure.

Figure 7—Typical test results for pulling a diamond coating off a tungsten substrate.

Summary and Recommendations

In conclusion, it is clear that the pull test can be an effective tool for evaluating both the qualitative and semiquantitative durability of a wide variety of coatings. The main advantage of this technique is its versatility and applicability to a wide range of coating/substrate systems. It can be applied to soft flexible coatings as well as hard brittle ones. Pull test equipment is commercially available and can also be set up in any laboratory with a tensile testing apparatus. The use of advanced statistical methods such as Weibull analysis can be very helpful in providing semiquantitative information concerning the durability of various coatings.

The wide variation in typical pull-test data remains one of the main weaknesses of this technique. Multiple tests must be done on a given sample coupled with statistical analysis in order to obtain reliable quantitative data. However, there are a number of specific instances such as pin testing on microelectronic substrates where the advantages of pull testing make it the most natural choice for reliability testing.

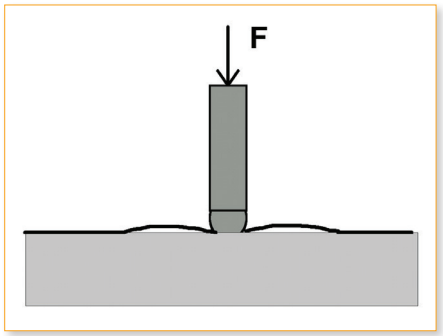


Figure 8—Schematic of indentation debonding test.

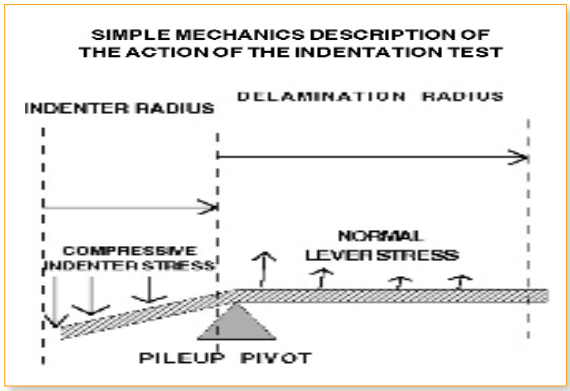


Figure 9—Illustration of the mechanics of the indentation debonding test. A simple lever mechanism is envisioned where material directly under the probe is extruded to the periphery where it acts as a fulcrum for a lever mechanism which induces a normal stress.

Indentation Debonding Test

Figure 8 shows a schematic representation of the indentation test. In this test, an indenter with a sharp point, i.e., having a tip radius which is on the order of the thickness of the coating being tested, is thrust into the coating under carefully controlled conditions. The dominant effect of this maneuver is to greatly compress the coating material directly under the indenter tip.

Surprisingly enough, however, a concomitant delamination of the coating can also occur starting at the edge of the indenter and extending out for a distance which can be several times the indenter tip radius. An early example of the use of this technique for testing the adhesion of epoxy to copper in circuit boards was given by Engel and Pedroza.[13] These investigators worked with epoxy coatings in the range of 25 to 300 μm on a copper metal substrate. Using an indenter tip of approximately .2 mm in radius, they observed peripheral delamination around the central indentation out to a radius of up to 2 mm.

One simple way of understanding the mechanics of what is happening is given in *Figure* 9. As the indenter penetrates the epoxy, coating material is extruded to the periphery of the indenter, causing a pileup at the edge. In this case, the underlying copper material is also pushed to the indenter edge since copper is a highly plastic material; this also contributes to the pileup of material. The excess mound of both epoxy and copper at the edge of the depression can be thought of as forming a sort of pivot for the epoxy coating to act as an ersatz simple lever, as shown in *Figure* 9. The epoxy film will have significant rigidity on the length scale of 1 mm, so the normal stress generated by this levering effect can be quite significant and lead to delamination of the coating if adhesion is not sufficient. A further contributing mechanism is the shear stress generated by the extrusion of the epoxy material from under the indenter. Thus, a combination of flow shear stress coupled with a lever normal stress can operate to delaminate the coating starting at the indenter edge. Engel and Pedroza[14] also use a simple plate model of the coating to estimate the radial strain in the coating and refer to this as the peel strain. Such a strain can be an energy source for driving the indentation delamination.

A far more rigorous analysis of the stresses driving the delamination process in the indentation test was given by Jayachandran, Boyce, and Argon.[15] These authors treated the case of a polymer coating on a rigid substrate. Having access to extensive data characterizing the constitutive behavior of Poly(methymethacralate) PMMA they were able to carry out highly detailed numerical studies of the indentation process using the finite element method including full details of large deformation and visco-plastic strain phenomena. Since these authors assumed a perfectly rigid substrate, their results cannot be compared directly to those of Engel and Pedroza mentioned above. What was found is that there is indeed a massive shear flow and pileup of material created by the indenter all the way out to the edge and beyond. However, due to the assumption of a rigid substrate, only a small tensile normal stress is predicted beyond the indenter edge. Thus, the normal stress in the epoxy copper system is due mostly to the pileup of the copper at the indenter edge which forms a pivot for the epoxy coating to act on, as depicted in *Figure* 9.

The indentation debonding method has also been applied to hard refractory coatings as demonstrated by the work of Weppelmann, Hu and Swain.[16] These authors investigated the TiN/silicon system both theoretically and experimentally. Experimentally, they used a diamond indenter in conjunction with a digital interference microscope

to follow the sample deformation very precisely. Theoretically, they were able to develop a simple formula for the strain energy release rate for delamination due to the radial strain induced by the indentation process. Using their experimental results, they were able to estimate an adhesion strength of approximately 1.2 J/m^2 for the TiN/silicon system.

Advantages of Indentation Debonding Test

The indentation test has a number of clear advantages which can be summarized as follows:

1. Applicable to a wide variety of coating/substrate systems
2. Ease of sample preparation
3. Gives both qualitative and quantitative results
4. Commercial equipment is readily available

The indentation test is readily implemented both in the laboratory and on the production line for a wide variety of coatings. As mentioned, it has been applied to both soft flexible coatings on metals as well as hard brittle coatings on silicon. Engel and Pedroza[17] have commented on the use of this test for quality control in testing the adhesion of epoxy on copper in circuit boards. Other than preparing the coating, no special preparation of the test sample is necessary. The test is clearly applicable to a wide variety of surfaces and has been applied to testing scratch-resistant coatings on curved plastic lenses. As mentioned above, the indentation test can be analyzed to give quantitative results in addition to a simple qualitative estimate of the coating durability. Finally, commercial off-the-shelf equipment is readily available in the form of indentation test equipment and powerful microscopes with digital interferometers for evaluating both substrate damage and deformation.

Disadvantages of Indentation Debonding Test

The main disadvantages of the indentation test can be summarized as follows:

1. Complex mode of loading involving large compressive stress and high shear strains
2. Difficult quantitative analysis and the precise mechanism of delamination is not well understood

The very high compressive load induced by the indentation test coupled with the high shear flow associated with soft coatings may make the relevance of the indentation test questionable for some coating systems. In particular, coatings subjected to large temperature swings may delaminate at edges or other discontinuities under loading conditions which are far different from those induced by the indentation test. A further drawback for hard coatings is the fact that in addition to a large compressive stress, a very significant hoop stress is also generated by this test which can lead to radial cracking in the sample substrate as well as the coating. Thus, multiple failure modes can greatly complicate the interpretation of the data when one is primarily interested in the coating adhesion.

Summary and Recommendations

The indentation debonding test clearly passes many of the criteria required for an ideal adhesion test. Primary among these is the ease of sample preparation and applicability to a wide variety of coating/substrate systems. Ready availability of commercial equipment makes this test a favorite in many industries which have to deal with quality control issues involving coatings. The main problem to be aware of is whether the loading conditions created by this test are reasonably close to those which the coating under test must endure in practice. In general, this is a very relevant test for coatings which must endure abrasive conditions and contact with potentially penetrating surfaces. Great care should be taken, however, if the coating in question will be subjected to large thermal strains which can be induced by large temperature gradients or thermal expansion mismatch between the coating and substrate.

Scratch Test

Figure 10 gives a highly schematic representation of the scratch test which can be thought of as an extension of the indentation test with the added feature that the indenter is translated along the sample surface as well into the coating. An informative overview of the early history of this technique has been given by Ahn, Mittal and MacQueen.[18] Apparently Heavens[19] and Heavens and Collins[20] were the first to employ this technique to study the durability of metallic films evaporated on glass.

Benjamin and Weaver[21] performed an elementary mechanics analysis of this method and derived the following simple formula for the shear force to be overcome by the scratch stylus:

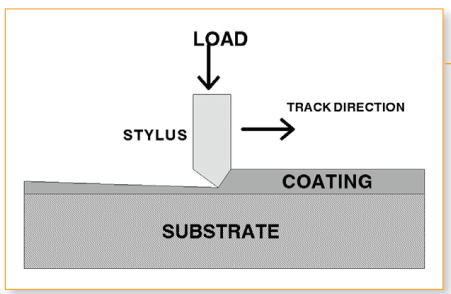


Figure 10—Idealized representation of scratch test.

$$F = \frac{AH}{\sqrt{R^2 - A^2}}$$
$$A = \sqrt{\frac{W}{\pi H}} \qquad (6)$$

where:
A = Radius of stylus contact circle
R = Radius of stylus tip
W = Applied load normal to coating surface
H = Indentation hardness of substrate
F = Shearing force resisting lateral motion of stylus

The hope was that the load W required to remove the coating could be taken as a measure of the coating adhesion by relating it to the generated shear force given in equation (6). However, a number of complications were noted by later workers[22] who discovered a number of difficulties including the following:

1. Delamination of the coating can be observed even before the stylus removes all traces down to the substrate. In addition, the film can be thinned to the point of becoming translucent and not be removed.
2. Complex material properties such as the elasto-plastic behavior of the coating and substrate determine the nature of the scratch track.
3. Multiple modes of failure are observed including mechanical failure in the bulk of the coating or substrate in addition to interfacial delamination.

Given the complications observed in the mechanically simpler indentation test discussed above, none of these remarks should come as any surprise. It should be clear that an experiment such as the scratch test, which involves the penetration and dragging of a stylus through an adhered coating, is going to give rise to a whole range of complex thermo-mechanical response behaviors including visco-plastic flow, bulk fracture, and interfacial failure. The immediate upshot is that, as with all the other adhesion tests discussed up to this point, the scratch test will be at best a semiquantitative technique. However, this does not preclude the usefulness or effectiveness of this method for providing insight into the adhesion and durability of coatings in a variety of applications. In particular, Ahn et al.[23] demonstrated that the scratch test can readily reveal poor adhesion in a coating since in this case lateral delamination of the coating can be observed to occur along the length of the scratch track.

In an attempt to put the scratch test on a firmer footing, Oroshnik and Croll[24] developed the concept of "Threshold Adhesion Failure" or TAF. These researchers noticed that in the thin aluminum films they were investigating, small patches of delamination could be observed in the scratch track well before the scratch stylus penetrated down to the underlying substrate. It occurred to them that the load at which this patchy delamination took place could be used as a measure of the coating adhesion. They in fact proposed the following definition:

> *"Threshold Adhesion Failure occurs if, within the boundaries of a scratch and over its 1-cm path, removal of the film from its substrate can be detected by transmitted light with a microscope (x40 magnification) at even one spot, no matter how small."*

This definition coincides very well with Definition B for adhesion given in Part I and is certainly serviceable for the purposes at hand. Oroshnik and Croll go on to describe the method whereby TAF is obtained for a given coating. The load on the stylus is increased incrementally as it moves over the sample surface up to the point where spots of delamination are just detected. The load is then incrementally decreased until the delamination events just disappear whereupon the load is again increased to the point where the delaminations again appear.

This procedure of successively incrementing and decrementing the stylus load is repeated until the apparent threshold load for producing delaminations is reliably boxed in between an upper and lower load condition.

Figure 11 shows the type of data obtained from this procedure. Note from this figure how the data tend to settle at a fixed level of apparent adhesion strength.

Oroshnik and Croll went on to discover that, even though using a given stylus, the TAF data were highly reproducible and consistent, no two stylus tips were identical, and each gave different TAF results. Using microscopic interferometry, these authors discovered that the stylus tips they were using where neither spherical nor had an unambiguous radius. In fact, data were presented showing measurements taken with different styli on a single film where the Threshold Adhesion Failure load differed by nearly a factor of 2.* Furthermore, it was shown that the Benjamin Weaver result for the shear force given by equation (6) was not verified by the data, which was not surprising given the non-spherical nature of the stylus tips being used. It is, in fact, well established that the most critical factor

*As an aside, round-robin scratch tests on identical samples carried out by several European labs categorically concluded that the quality of the indenter tip was the dominant factor accounting for the variability of the test results among the various labs.

controlling the scratch test is the nature of the stylus tip. Different results will be obtained depending on the stylus material, be it steel, tungsten carbide or diamond, and the precise topography of the tip region which first contacts the coating surface.

Later investigators expanded upon the scratch test to include not only more sophisticated instrumentation for controlling the load program of the stylus and advanced microscopy for observing the scratch track but also coupling of the scratch method with acoustic spectroscopy whereby the sound vibrations generated by the stylus are detected and recorded at the same time that the scratch track is being formed. Typical of the more modern approach is the work of Vaughn, Frushour, and Dale.[25] These investigators performed adhesion measurements on both copper and diamond-like carbon (DLC) films coated onto poly(ethylene terephthalate) substrates. These experiments gave an ideal opportunity to evaluate the performance of the scratch test on two radically different types of coatings on the same substrate material. The highly plastic coatings gave completely unremarkable stylus load vs scratch length plots where the load simply increases monotonically with scratch length, showing no particular discontinuities where the film began to delaminate. Further, these coatings gave no discernable acoustic signal at coating failure events such as delamination. By contrast, the rigid brittle DLC coatings showed a sharp drop in the stylus load vs scratch length curve at points where the DLC coating fractured in the typical "herringbone" style cracks that can appear in the scratch track due to the high tensile stress just behind the advancing stylus tip. *Figure* 12 shows a graphic representation of the type of data obtained from the DLC coatings.

Further attempts at quantifying the scratch test have been reviewed by Bull[26] who examined the scratch test as applied to a number of qualitatively different coating substrate systems. This author basically finds that the following criteria must be met in order to achieve a truly quantitative assessment of adhesion strength using the scratch test:

1. There must be a well-defined delamination mode present under the prevailing test conditions.
2. Knowledge of the sample stress state leading to delamination failure must be available either through direct measurement or calculation.

With these conditions in mind, Bull goes on to examine a variety of coating substrate systems which basically fall into the categories of "hard" and "soft."

Soft systems generally give rise to a high level of visco-plastic deformation and clean failure modes may not be clearly observable. Hard systems, on the other hand, often exhibit brittle fracture in either the substrate, the coating, or both. Combinations of soft and hard materials can give rise to all of the previously mentioned failure modes plus interfacial delamination. *Table* 1 gives a highly qualitative overview of the general trends. This table illustrates the general observation that the scratch test works best when at least one

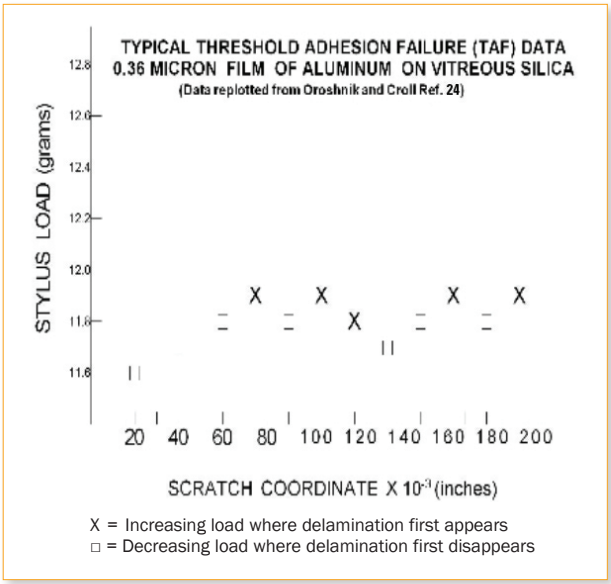


Figure 11—Data illustrating TAF version of scratch test which is intended to make the technique more quantitative.

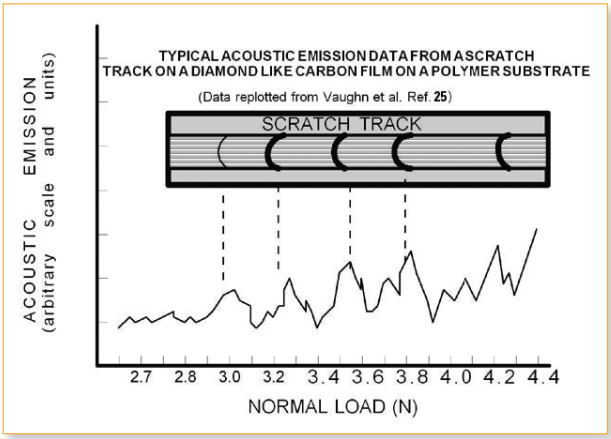


Figure 12—Correlation of scratch track with acoustic emission data for a hard brittle coating on a polymer substrate.

Table 1—Qualitative Summary of Failure Modes in the Scratch Test as a Function of Coating/Substrate Hardness

Substrate Hardness ❐ Coating Hardness ❐	Soft	Medium	Hard
Soft	Plastic deformation extrusion	Coating thinning scrape off	Coating thinning scrape off
Medium	Plastic deformation extrusion	Delamination	Delamination fracture
Hard	Plastic deformation extrusion	Delamination fracture	Delamination fracture

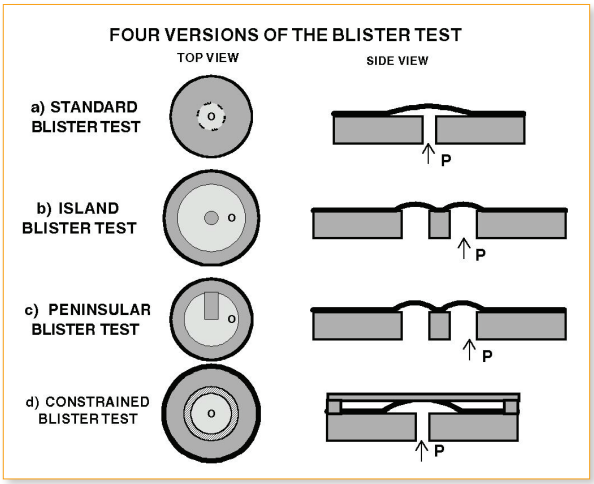


Figure 13—Blister test for measuring the adhesion of coatings at low strain levels, thus more closely emulating conditions affecting coatings under conditions in the field.

component of the coating/substrate system is a relatively hard material which upon reflection is intuitively reasonable. You clearly would not use the scratch test to quantify the adhesion of molasses to chewing gum. However, Bull does illustrate two situations where the scratch test gives promising results for hard coatings on hard substrates.

The first case involves what can basically be called "buckling splallation." For the system TiN on stainless steel, a thin coating of the TiN can be made to spall off the substrate. The scratch stylus creates a compressive stress ahead of itself due to the deformation of the substrate, causing the coating to buckle. High tensile stresses in the coating then cause the buckled coating to crack and then flake off. For thicker coatings, the bending required for buckling does not occur because the coating is too stiff.

However, compressive shear cracks can form ahead of the indenter through the thickness of the coating. These cracks typically have sloping sides which can act as an inclined plane or wedge. The forward motion of the indenter can then drive the edge of the coating up the ramp created by the crack, causing the interface between the coating and substrate to separate, which leads to spalling of the coating. Bull refers to this mode of delamination as "wedge spallation."

Finally, even though the scratch test has proven most effective for hard brittle coatings, work by Bull et al.[27] has shown that this test can also give very valuable information concerning the adhesion and durability of polymer coatings such as epoxies. The application in this case was the evaluation of epoxy coatings for protecting the inner hull of coal-carrying vessels. The epoxy is intended to shield the metal hull from abrasion by the coal and corrosion due to the brackish marine environment. Lumps of coal settling against the inner hull have an abrasive effect and thus, the scratch test was deemed an appropriate method for evaluating the performance of the epoxy coatings. A number of different coating formulations were investigated and all showed varying tendencies to either crack or delaminate under the action of the scratch stylus. One interesting failure mode arose due to the tensile load imposed on the coating behind the moving stylus. This would cause a through crack to form behind the stylus which would then drag the coating along, opening up the crack and further buckling the coating in front in much the same manner as a rug buckles when pushed laterally at one of its edges. In addition, it was found that coatings with extender pigmentation tended to crack more readily than the unfilled coatings. However, the filler also retarded adhesion degradation as determined by aging studies. Thus, scratch testing can be used to determine the optimal tradeoff between coating toughness and adhesion by comparing scratch results on coatings with varying levels of extender pigmentation.

Advantages of the Scratch Test

As with the indentation test, the main advantage of the scratch test lies in the relative ease of sample preparation. One simply prepares coupons of a convenient size out of the relevant coating and substrate materials in the same manner as one would on the manufacturing line or in the build shop. In addition, the newer commercially available equipment can be fitted with a number of auxiliary tools such as microscopes, acoustic spectrometers, and surface profiling attachments. Since the stylus can also act as an indenter, the coating hardness and elastic properties can be determined. Thus, a single instrument can give valuable information on surface topography, mechanical properties, and modes of deformation and delamination.

Semiquantitative information can be obtained by recording the stylus load at failure and thus scratch testing can be used to rank the durability of a series of coating formulations. In some cases a fully quantitative estimate of the surface fracture energy of the coating/substrate interface can be obtained if care is taken to measure carefully all relevant mechanical properties and carry out the appropriate fracture mechanics calculations.

Disadvantages of the Scratch Test

There are two primary disadvantages to using the scratch test as an adhesion measurement tool, with the first being that this test is essentially limited to hard brittle coatings even though some exceptions such as brittle epoxy coatings may be

successfully investigated. The softer metals and most polymer coatings tend to visco-plastically flow and deform around the scratch stylus, causing mounding at the edges of the scratch track and pileup in front of the stylus. In addition, these coatings do not give a distinct acoustic signal at the failure point, thus negating the use of acoustic spectroscopy. Moreover, some coatings can be thinned down to the point of optical transparency without achieving complete coating removal, complicating any attempt to assess adhesion strength.

The second limitation arises from the fact that, as with the indentation test, the scratch test is mechanically very complex. The act of pushing the stylus into the coating gives rise to very high stresses and deformations in both the coating and the substrate, thus bringing into play the full range of highly nonlinear visco-plastic material behavior. Therefore, the usual type of elastic mechanical calculations do not give quantitatively reliable results and can be used only for a more heuristic analysis of scratch test data. Because the basic failure modes of the scratch test are only poorly understood, experience gained on a given coating/substrate system may not be reliably carried over to a different one.

Summary and Recommendations

The scratch test is one of the most popular adhesion tests currently in use both in industry and academia. This stems largely from the great versatility of this technique for evaluation of a wide range of coating substrate systems and the ready availability of commercial equipment which can perform a variety of functions such as surface inspection, surface roughness measurements, and the evaluation of coating mechanical properties. For the case of hard brittle coatings, the scratch test is quite likely the best available technique for most situations. For softer coatings, this method may also be able to give useful results under certain conditions and can be used in a complimentary manner with other techniques such as the pull test.

Blister Test

One constant complaint about all of the adhesion tests mentioned previously is the fact that they involve a mechanically complex process with large deformations and strains giving rise to highly nonlinear visco-plastic response behavior on the part of the coating/substrate system being investigated. An immediate consequence of this is the fact that the analysis of these systems in terms of continuum and fracture mechanics concepts is exceedingly difficult, if not impossible. The blister test is an attempt to circumvent these difficulties by developing a blister in the coating in a well-defined manner which will propagate a delamination front between the coating and substrate in a controlled manner inducing only relatively small deformations and strains.

Dannenberg[28] was apparently the first investigator to apply this technique to measure the adhesion of polymer coatings. Lai and Dillard[29] have given an insightful account of the mechanics of several versions of this test. *Figure* 13 gives a schematic representation of four different versions of this test mentioned by these authors. *Figure* 13a illustrates the standard blister test configuration. The main limitation of this version occurs when the film ruptures before the coating can delaminate. This problem limits the standard blister test either to coatings with a very high fracture toughness or relatively low adhesion to the underlying substrate. To circumvent this problem, Allen and Senturia[30,31] devised the island blister test shown in *Figure* 13b. Due to the much smaller debond front presented by the inner island, the driving force for delamination is much greater here than at the much larger circumference at the outer radius. Thus, delamination can be made to occur at the inner island at a much lower applied pressure than would be required in the standard blister test. One problem with the island blister test is that it tends to be unstable. To overcome this difficulty, Dillard and Bao conceived the peninsular blister test depicted in *Figure* 13c. This version of the blister test maintains the high driving force for delamination as in the island test while maintaining a steadier delamination front.

Figure 13d shows the constrained blister test which cleverly supplies a simple cover for the standard blister test in order to prevent the problem of film rupture. The earliest investigations of this technique were apparently carried out by Napolitano et al.,[32,33] and nearly simultaneously by Dillard and coworkers.[34-36] In reference (33), Napolitano and co-workers managed to derive the following formula for the expanding area of the propagating blister using simple thermodynamic arguments:

$$\frac{A(t)}{A(t_0)} = \exp\left[\frac{\beta p^2 h}{ph-\gamma}(t - t_0\right] \qquad (7)$$

where:

A(t) = Blister area at time t

p = Applied pressure

h = Spacer height

γ = Interfacial fracture energy

β = Dissipative coeffiecient

t_0, t = Initial and current time

Equation (7) was used to analyze constrained blister test data taken on a pressure-sensitive

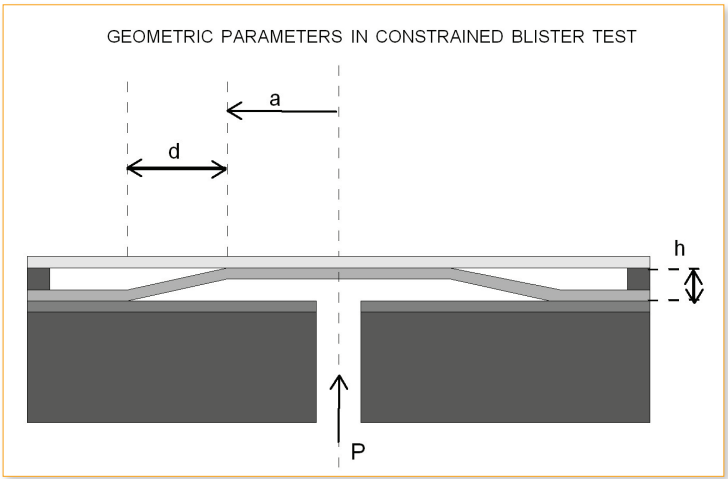


Figure 14—Details of constrained blister test for preventing film rupture in strongly adhered coatings.

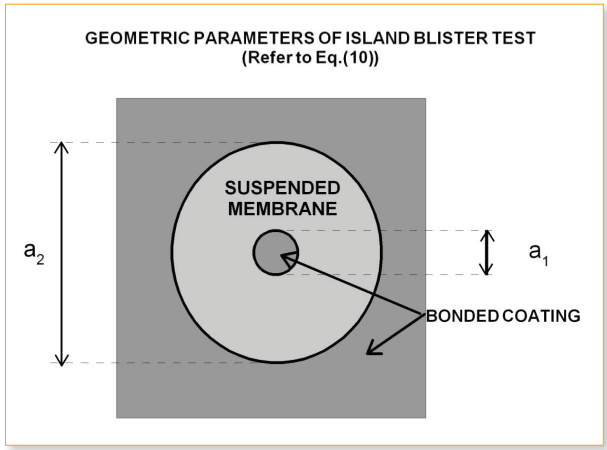


Figure 15—Details of island blister test used for avoiding film rupture for strongly adhered coatings. The driving force for delamination is much higher at the central island than on the peripheral edge, thus requiring much lower pressure to initiate delamination.

adhesive tape. The interfacial fracture energy was determined by noticing at what combination of spacer height h and applied pressure p the onset of delamination occurred. The interfacial fracture energy could then be computed from the following simple formula:

$$\gamma = (hp)_{threshold} \qquad (8)$$

where it is to be noted that the pressure p in equation (8) is that which just causes blister delamination to progress. The dissipative coefficient could then be obtained from blister area vs time data. Plotting the log of both sides of equation (7) a straight line is obtained, the slope of which gives β knowing γ from equation (8). Liang et al. give a very interesting application of the constrained blister test as applied to electropolymerized polymer coatings on copper substrates. They improve significantly on the work of Napolitano et al. mentioned above by bringing to bear advanced image analysis methods implemented on a powerful modern workstation. With this advanced hardware and software, they are able to measure in real time the critical blister growth front parameters and thereby analyze their data using a fracture mechanics result for the strain energy release rate derived by Liang et al.[37] given by the following formula:

$$G = ph\left[1 - \frac{d}{2a} + \left(\frac{d}{3a} - \frac{1}{2}\right)\left(\frac{\partial d}{\partial a}\right)\right] \qquad (9)$$

In this equation, G is the strain energy release rate, p the applied pressure, and the dimensional parameters are explained in *Figure* 14.

An elementary analysis of the island blister test has been given by Allen and Senturia.[38] By assuming that the coating can be treated as a membrane (i.e., so thin that it has no unsupported stiffness) and that the major component of the driving force is due to residual stress, they come up with the following simple formula for the surface fracture energy of adhesion:

$$\Upsilon_a = \frac{(p_c a_1)^2}{32\sigma_0 t}\left[\frac{\beta^2 - 1}{32\sigma_0 t} - 2\right]^2 \qquad (10)$$

where:

γ_a = Surface fracture energy

p_c = Critical pressure for delamination propagation

σ_0 = Residual film stress

t = Film thickness

$\beta = a_1/a_2$

a_1, a_2 = Geometric parameters shown in *Figure* 15

Allen and Senturia also give an interesting comparison of the island blister test with the standard version and demonstrate why the former gives a much higher driving force for delamination on the inner island than the latter can achieve on the outer circumference of the suspended membrane.

Advantages of the Blister Test

As can be ascertained from the above discussion, the blister test has a number of advantages, with the main one being that it is the first test discussed up to this point which lends itself readily to a fully quantitative analysis based on fracture mechanics methods. This is due mainly to the fact that this test imposes relatively low strains on the coating material, thus avoiding the complex nonlinear visco-plastic behavior which greatly complicates methods such as the peel test. However, like the peel test, the blister test also concentrates the maximum stress at the delamination front, therefore constraining the failure crack to be close

to the coating/substrate interface of interest. Also, given the fact that a number of different versions are available, as shown in *Figure* 13, this test gives the user great flexibility in testing coatings with varying levels of adhesion.

Disadvantages of the Blister Test

Whereas the blister test lends itself fairly readily to quantitative analysis, this advantage is purchased at the price of ease of sample preparation. It always seems in the realm of adhesion testing that nothing comes free. If you gain an advantage in one quarter, you pay for it in another. The main impediment comes with drilling the hole at the center of the blister through which the pressurizing gas enters. This can be accomplished in a number of ways, but the most popular is the use of etchants which will erode away the substrate material and not attack the coating. For coatings on silicon substrates, all the methods of microelectronic lithography are available to etch holes in the silicon and construct the various structures required for tests such as the island blister configuration. However, to use these methods, a wafer fabrication facility must be available to carry out the involved series of steps needed to construct the desired structures. This work also requires the use of very nasty etchants, such as buffered hydrofluoric acid. In addition, the blister test is limited to fairly flexible coatings such as polymer base paints and soft metals. Hard brittle coatings will tend to crack before forming a blister under the influence of the applied pressure.

Finally, this test will have severe problems with coatings under high compressive stress since this will cause the coating to buckle as soon as it is lifted from the supporting substrate.

Summary and Recommendations

The blister test is most suitable in situations where a fully quantitative analysis of the adhesion strength of a coating to a particular substrate is required. Great flexibility is available in the types of samples which can be used and a number of investigators have provided a detailed analysis which can be used to analyze the data in a fully quantitative fashion.

As mentioned earlier, sample preparation is far more cumbersome for this method than many other techniques. Thus, the blister test is not recommended for situations where only qualitative or semiquantitative data are required as many other simpler methods are available for this type of work.

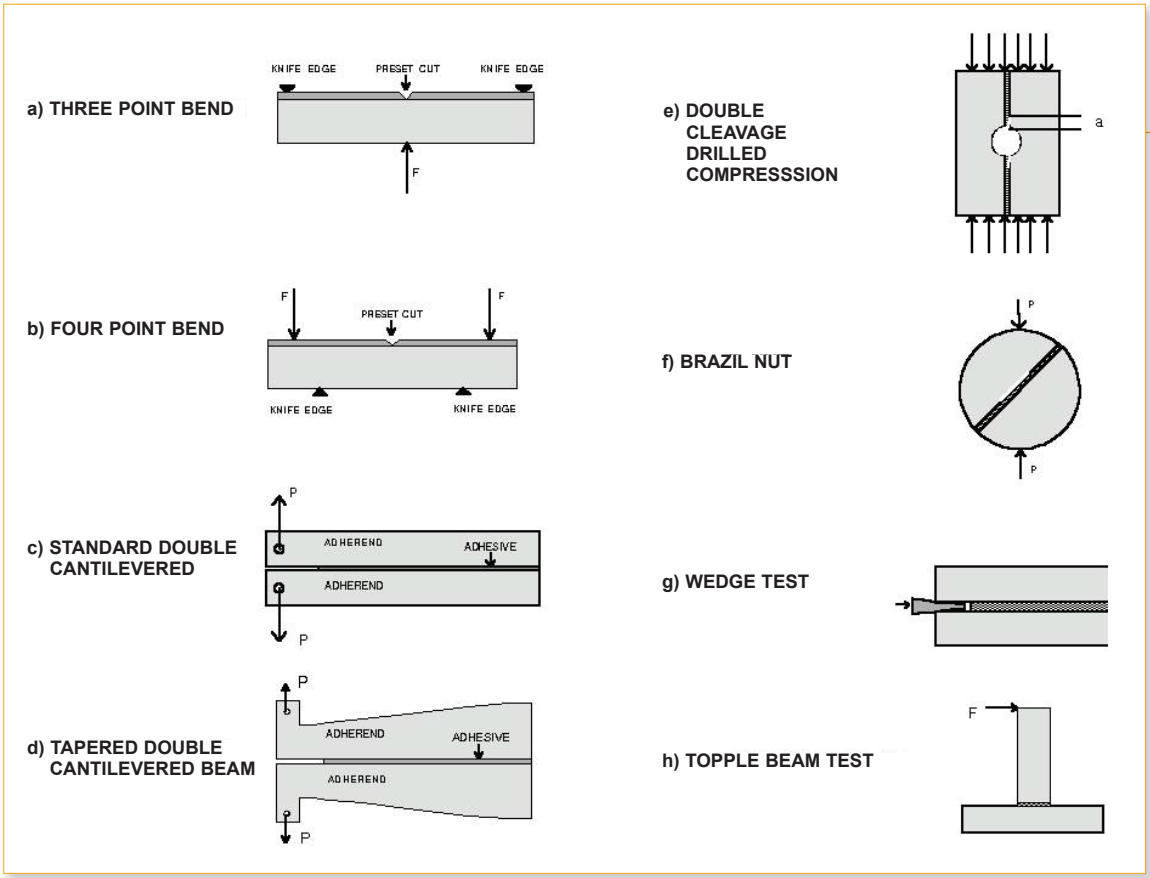


Figure 16—Several adhesion measurement methods that rely on the simplified mechanics of beam bending.

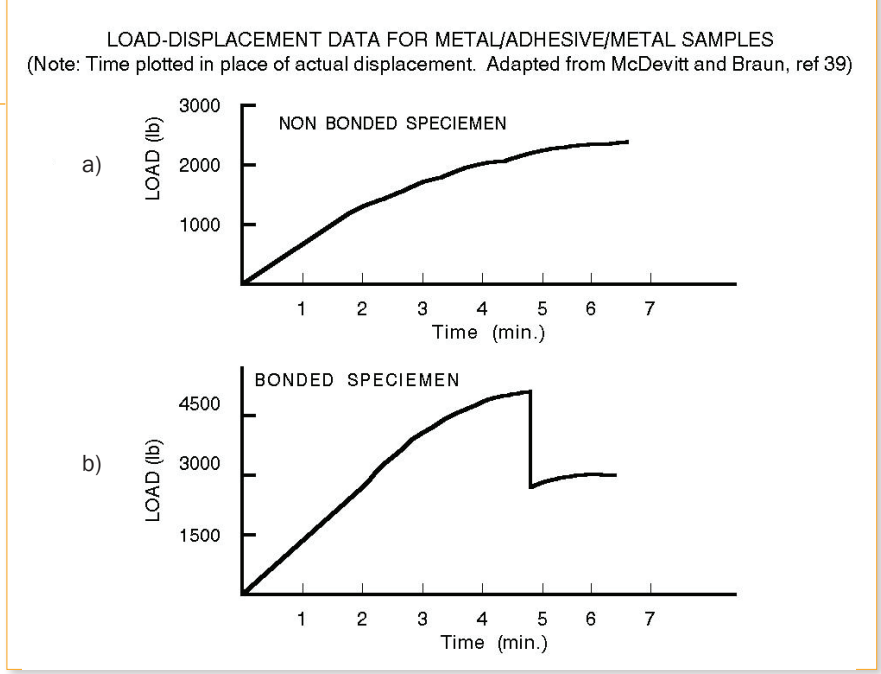


Figure 17—Sample data from three-point bend test for metal to metal sandwiches.

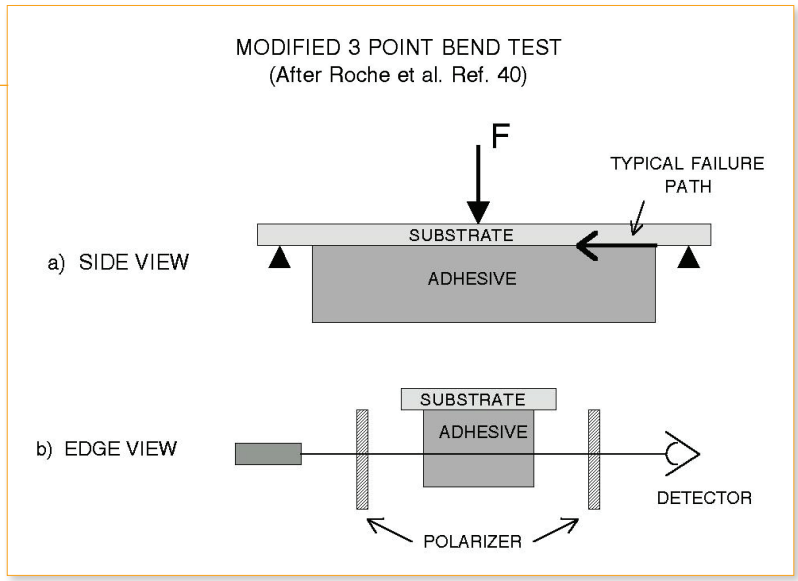


Figure 18—Variation of the three-point bend test allowing observation of the stress distribution in the adhesive layer.

Beam Bending Tests

There are a variety of tests for measuring adhesion that rely on the relatively simple mechanics of the elastic beam to simplify the required analysis for the stress intensity factors and the strain energy release rate which drive the delamination process. The most attractive feature of the bend test is the fact that the stress field induced by the bending operation is comparatively quite simple and can be analyzed by elementary methods. *Figure* 16 illustrates several of the most popular adhesion tests which rely on the mechanics of a bending beam. The following sections will discuss several of the more important ones.

Three-Point Bend Test

A standard configuration for the three-point bend test is shown in *Figure* 16a. McDevitt and Baun[39] carried out one of the earliest studies on metal to metal adhesive joints using the three-point bend test. These investigators found the curious result that apparently the three-point bend test was more sensitive to interfacial weaknesses than other tests they were performing, such as the T-peel, the wedge test, and the lap shear test. Load verses deflection data were gathered on metal/adhesive/metal sandwich samples as depicted in *Figure* 17. The top curve in this figure represents a nonbonded sample where a cured strip of adhesive was simply laid between two metal layers with no apparent bonding other than simple friction. This load-displacement curve thus serves as a baseline for a completely nonbonded joint. *Figure* 17b shows the case where the metal/uncured adhesive/metal sandwich was cured in an oven to achieve maximal bonding between all the layers. Note that this sample achieves a much higher load

level before yielding. In addition, the authors attribute the break in the curve to failure at the metal/adhesive interface. With basic calibration data in hand for completely bonded and unbonded specimens, the authors then proceed to test bonded samples that have been subjected to a variety of thermal and environmental stress conditions.

Roche et al.[40] have investigated an interesting variation of the three-point bend test which is also sensitive to conditions at the adherend/substrate interface. The basic configuration is depicted in *Figure* 18. At a high enough load, the adherend will detach from the substrate starting from the edge and proceed to the center as shown in the figure. With the configuration shown in *Figure* 18, the stress distribution in the adherend can be monitored using the photoelastic setup shown in *Figure* 18b. In a typical experiment, the sample stiffness and stress distribution are monitored as the load is increased. An important piece of information is the load at which delamination of the adherend just begins. This number is shown to be sensitive to the detailed substrate preparation procedure before application of the adherend. It is clearly shown that this technique can be a powerful tool for investigating the effect of different surface preparation procedures and adhesive formulations on the adherend/substrate adhesion strength. Making multiple identical samples also allows one to study the effect of thermal cycling and other environmental stress factors on the durability of the adhesive bond.

Four-Point Bend Test

The standard configuration for this test is shown in *Figure* 16b. *Figure* 19 shows the typical failure modes of the coating/substrate system as the bending load is increased. Note that there are two basic failure modes for this experiment.

In the one case, failure is by clean elimination of the coating from the substrate. It can also happen that after propagating a short distance an initial delamination will dive into the substrate, initiating a cohesive failure. Experiments and theory confirm that the crack will dive to some fixed depth below the interface and then propagate parallel to the interface. The precise depth of penetration is determined by the elastic properties of the coating and the substrate.

The four-point bend test is favored largely by those interested in obtaining fully quantitative information on the adhesion strength of coatings by taking advantage of the relatively simple beam mechanics involved in the fracture mechanics analysis of this problem. In particular, Evans and coworkers have used this test extensively to study the adhesion of a variety of metals to alumina (Al_2O_3) substrates. This work has recently been summarized by Evans.[41] A synopsis of their results is given in *Table* 2). The basic conclusion from this work was that interfaces that were clean and free from contamination were inherently tough and ductile. Failure occurred either by rupture of the ceramic or ductile fracture of the metal. Moisture was observed to cause stress corrosion effects which greatly weakened some of the interfaces.

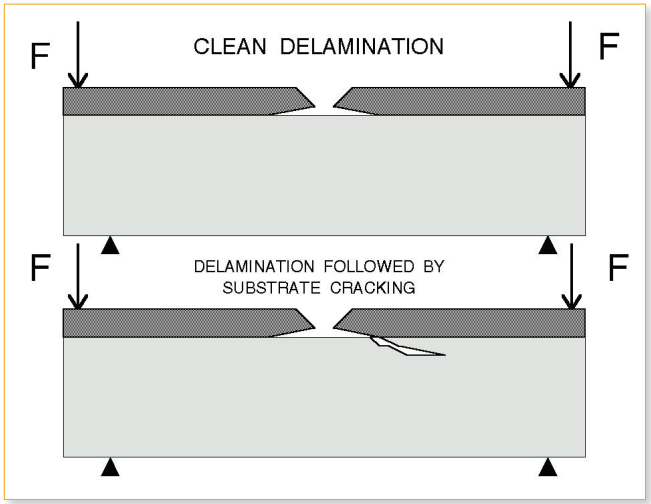


Figure 19—Failure modes of four-point bend test.

Table 2—Summary of Adhesion Strength of Various Metals to Alumina (Al_2O_3) Substrates

Metal	Conditions	Range of Adhesion Strength (Joules/M^2)	Comment
Nickel	High humidity	4-8	Impurity segregation at interface
γ-Nickel (Cr)	Dry air	>100	Failure in metal or Al_2O_3
Gold	High humidity	1.5 -2.5	Impurity segregation at interface
Gold	Dry air	>200	Failure in metal or Al_2O_3
Aluminum	All conditions	>50	Al_2O_3 rupture above 300 J/m^2
Copper	All conditions	>150	Failure in metal or Al_2O_3

Self-Loading Tests

It is well known that the internal stress in a coating can cause it to spontaneously delaminate from the underlying substrate. This effect is commonly seen in old paint coatings on wood trim and other artifacts where shrinkage stresses in the coating cause it to peel back from the edges and internal cracks. The idea naturally suggests itself to set up an adhesion measurement experiment where the driving force for delamination is derived solely from well-controlled internal stresses in the coating to be tested. The task of the experimenter

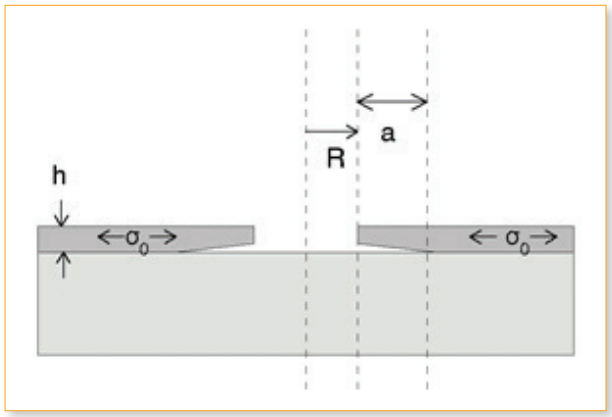


Figure 20—Schematic of circle cut test whereby delamination is driven by a known intrinsic stress in the coating.

is then reduced to monitoring the propagation of the delamination front at a known fixed level of internal stress. A number of experiments along these lines will be discussed in the following.

Circle Cut Test

In this experiment, one has a coating on a substrate with a uniform biaxial stress σ_0 which can be due to any number of factors such as deposition conditions, thermal expansion mismatch strains, shrinkage due to solvent loss, and so on. At time zero, a circular cut is made somewhere in the interior away from any edge, giving rise to the situation shown in *Figure* 20.

The act of generating a sharp edge creates a stress singularity at the edge of the cut in the interface between the coating and the substrate. If the adhesion of the coating is relatively weak, then the coating will delaminate from the substrate, forming an annular ring of delaminated material as shown in the figure. The radius of the cut and the radius of the delaminated annular region are then measured by optical or other means and this information can then be used along with knowledge of the stress level σ_0 in the coating and its elastic properties to calculate the critical surface fracture energy according to the following formula:

$$\gamma_c = \frac{h\sigma_0^2}{E}\left[\frac{2\beta}{\left(1+\beta\left[\frac{a}{R}\right]^2\right)^2}\right]$$

$$\beta = \frac{1-\nu}{1+\nu}$$

where:

R,h, and a = Coating and cut dimensions as shown in *Figure* 20

σ_0 = Residual stress in coating

E = Modulus of coating material

v = Poisson's ratio of coating

γ_c = Critical strain energy release rate

A convenient feature of this test is the fact that according to equation (11) the size of the annular delamination region will always be constrained since the driving force G decreases as the size of the delaminated region given by the parameter "a". Thus, unlike many other adhesion tests, at some finite delaminated size "a," the driving force for delamination will be too small to propagate the delamination further and the experimenter can make the appropriate measurements at leisure.

Farris and Bauer[42] have used this method to study the adhesion of polyimide coatings. This approach has a number of distinct advantages, including:

- Closely simulates the mechanism by which coatings tend to delaminate which is at high stress, low strain, and mixed mode conditions of tension and shear
- Relative ease of sample preparation
- Amenable to quantitative analysis

The main drawback is that since the driving force for delamination relies solely on the internal film stresses, there may not be sufficient strain energy in the coating to initiate a delamination if the level of adhesion is too high. This fact tends to limit this test to coatings with weak adhesion. However, since the driving force for delamination scales linearly with the coating thickness, one can always make thicker coatings until the level where delamination occurs is reached. This approach obviously entails much additional labor which is a further negative feature of this method.

MELT Test

In view of the limitation of the circular cut test to weakly adhering coatings, a related approach called MELT (Modified Edge Liftoff Test) has been explored by Hay et al.[43] The main innovation in this approach is the use of a layer of material on top of the coating to be tested which will drive up the total internal stress and thus give sufficient driving force to delaminate any coating. A schematic representation of this test is given in *Figure* 21.

As shown in the figure, complications can arise due to crack initiation in the substrate rather than at the interface of interest. Hay and coworkers exercised this technique on a multilayer sandwich consisting of epoxy/dielectric layer/silicon nitride/native oxide/silicon. They sidestepped the substrate fracture problem by using a hydrofluoric acid solution to etch out a large initial crack in the silicon nitride layer.

Additionally, they polished the edge of the sample with fine sandpaper to eliminate any flaws left behind by the wafer dicing operation. The thick epoxy top layer between 150 and 200 microns pro-

vided the driving force for crack propagation due to thermal expansion mismatch with the silicon substrate. Under these conditions, they observed clean delamination of the dielectric layer from the silicon nitride.

The above workers noticed an interesting property of their epoxy loaded samples which seemed to contradict previous work that used chromium as a superlayer instead of epoxy. From the chromium work, it was noticed that the driving force for delamination depended on the size of the initial crack length and did not settle down to a constant value until the delamination length had reached at least 20 times the chromium layer thickness. With the epoxy loaded samples, there was no apparent dependence of the driving force for delamination on the initial crack size. A subsequent finite element analysis of the problem comparing the driving force for delamination for both the epoxy- and chromium-loaded systems indicated that indeed the behavior of the epoxy and chromium systems is very different. In the epoxy case, the driving force rises so sharply with crack length that it nearly resembles a step function. The chromium system rises much slower and essentially follows the rule of 20 times the chromium thickness before leveling off to a steady state.

Microstrip Test

The microstrip test is closely related to the MELT test in that the same principle of using a superlayer on top of the layer to be tested is used to get a sufficient driving force for delamination. A schematic of the basic sample configuration is shown in *Figure* 22. The version of the test described here was carried out by Bagchi et al.[44] and reviewed by Evans.[45] What is shown in the figure are the various layers of the adhesion measurement test structure. The substrate may be a block of ceramic or glass or whatever is the material of interest. On top of the substrate, narrow parallel strips of a release layer material are first deposited. *Figure* 22 shows one such layer. Next, the coating is applied as a blanket layer. On top of that, the superlayer is deposited as a blanket coating. A good candidate for this material when testing thin metal films is chromium which can develop internal stress levels up to 1 GPa. The blanket coatings are now etched into thin strips perpendicular to the release layer strips using photolithographic methods. The adhesion test begins after a thin cut is made down the center of the release layer strip using either etching or milling techniques. As the adhesion between the release layer is very weak by design, a delamination is immediately initiated starting from the cut to the edge of the release layer. Depending on conditions,

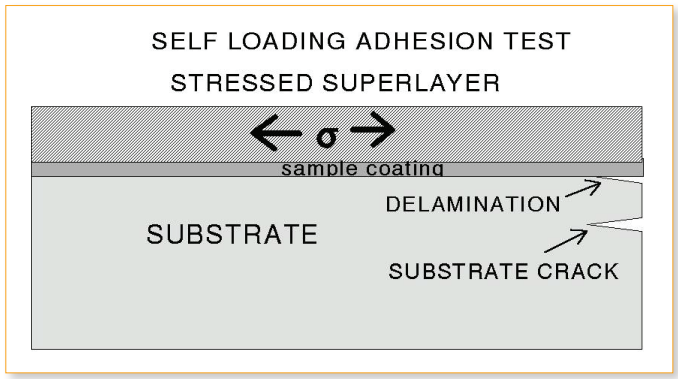


Figure 21—Schematic of MELT test devised to overcome the limitation of the circle cut test which is limited to testing weakly adhered films. Enhanced driving force for delamination is supplied by a well characterized superlayer.

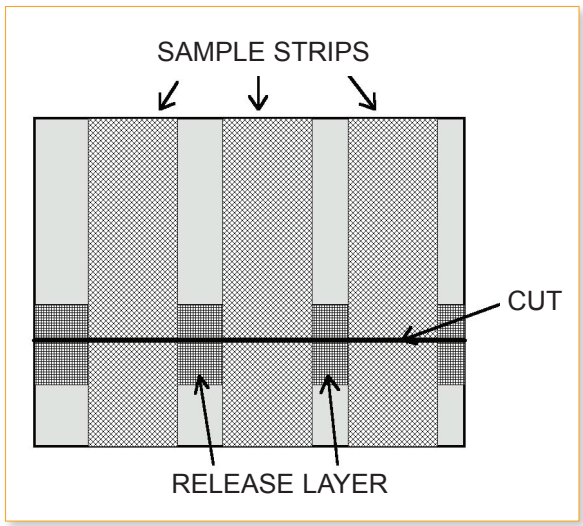


Figure 22—Schematic of microstrip test.

the delamination front will proceed past the edge of the release layer and into the interface between the coating and the substrate. If the delamination stops at the edge of the release layer, then clearly there is not enough strain energy in the chromium superlayer and a thicker layer of chromium needs to be applied. At a sufficient thickness of the chromium layer, the delamination will proceed at the coating/substrate interface or possibly proceed as a subcrack in the substrate, depending on how well adhered the coating is.

Assuming that the delamination proceeds at the coating substrate interface, it will go for a certain distance and then arrest. In this test, all of the test strips are of a finite length and the driving force for delamination decreases toward zero as the crack front nears the end of the strip. Therefore, the delamination front must arrest and the remaining ligament is therefore indicative of the adhesion between the coating and the substrate.

Advantages of Self-Loading Tests

Self-loading tests come very close to mimicking the conditions under which real coatings delaminate in terms of strain level and mode mixity and this is their main advantage as adhesion tests. This is especially true for microelectronic structures where intrinsic stress is one of the major causes of device failure. In addition the self-loading tests lend themselves readily to quantitative analysis since the strain level at failure is typically quite low and linear elastic theory suffices to carry out the required fracture mechanics evaluation of the strain energy release rate.

When being used to evaluate microelectronic devices, the test structures required to carry out the adhesion measurements can be fabricated using equipment that is nearly identical to that used in the production line. Thus, although sample preparation is fairly involved, it does not require resources beyond what should already be available in the existing manufacturing facility. Finally, the test structures can be integrated into the actual manufacturing process as diagnostic probe sites capable of giving near real-time quality control and monitoring information on real manufacturing parts. Of all the adhesion tests discussed so far, the self-loading tests come the closest to being an ideal adhesion measurement method.

Disadvantages of Self-Loading Tests

The main disadvantage of the self-loading tests is the need to know the internal stress and mechanical properties of the coating being tested. The problem of determining the internal stress in a coating is a rather large subject in itself and would require another full article to do it justice. Further complications arise if the internal stress level is insufficient to cause delamination and one of the superlayer methods must be implemented, thus greatly increasing the work required for sample preparation. Finally, the trajectory of the delamination crack front may deviate from the interface into either the substrate or the coating, depending on conditions. This will significantly complicate the fracture mechanics analysis involved. In essence, the self-loading tests share the common problems of all fully quantitative tests in that they inevitably involve much more work than the simply qualitative or semiquantitative methods.

Summary and Recommendations

The self-loading adhesion tests will find their most suitable application in situations where quantitative data is required to support numerical modeling simulations of the structures being fabricated. Multilevel wiring structures from the microelectronics industry are a prime example of an application which can benefit greatly from this type of test. Such structures are replete with interfaces between dissimilar materials that are subject to numerous manufacturing processes which can introduce high levels of internal stress. As a specific example, consider the use of organic insulators as dielectric layers in multilevel wiring schemes. Among the most popular materials for this application are the polyimides. These materials are typically coated as a viscous liquid using either spin or spray coating methods. The resulting film must be cured at an elevated temperature generally above 300°C to achieve the correct electrical and mechanical properties required of it. Cooling back to room temperature will induce a large internal thermal expansion mismatch strain in the coating if the underlying substrate is either silicon or a ceramic material since most polyimide materials have thermal expansion coefficients 10 to 30 times larger than either silicon or most ceramics. An elementary calculation using the principles of continuum theory shows that the resulting stress level in the coating can come to nearly 50% of the yield stress of the polyimide itself. In cases such as this, appropriate stress modeling supported by fully quantitative adhesion data are required to carry out the type of engineering design analysis necessary to support fabrication and manufacture of a useful device. The large amount of work involved in implementing the self-loading methods will quite likely limit them to this type of application.

CODA AND MORE TO EXPLORE

As pointed out in the beginning, this article is a major condensation of a much larger work.[1] The whole problem of determining the stress level in coatings had to be omitted altogether and the important topics of continuum theory and fracture mechanics were covered in the barest detail. In addition, many topics of great importance to the coatings industry such as surface modification, contamination, and cleaning and details of surface chemistry were well beyond the scope of this article. The author would therefore like to refer the interested reader to two further sources of information on these important topics. One is the MSTC short course on The Chemistry, Physics and Mechanics of Adhesion Science and the second is a symposium series covering many of the recent advances in these important topics. Both may be readily accessed online at www.mstconf.com. CT

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