CSM Instruments
Advanced Mechanical Surface Testing

APPLICATIONS BULLETIN

Special Issue: Characterisation of Polymers

Quality Control of Minidisk polymer topcoat with Nano Scratch Tester and Tribometer

Within the large range of magnetic recording media presently available on the market, most utilise a thin protective coating of some kind on their read/write surfaces. In the case of magnetic hard disk drives, for example, the protective coating is usually DLC with a thickness of only a few nanometres (see Applications Bulletin No. 11, May 1999). On the other hand, *Minidisk* surfaces have a thin polymeric coating as their protection against scratches incurred during production and subsequent use. The *Minidisk* surface tested in this example had a polycarbonate surface film of thickness 1.2 µm and was characterised using the Nano Scratch Tester and the pin-on-disk Tribometer.

By using two different instruments to characterise such a surface enables adhesion data (scratch testing) to be combined with frictional and lifetime data (pin-on-disk testing) which together give a better overall picture of how the coating will perform in service conditions. Fig. 1

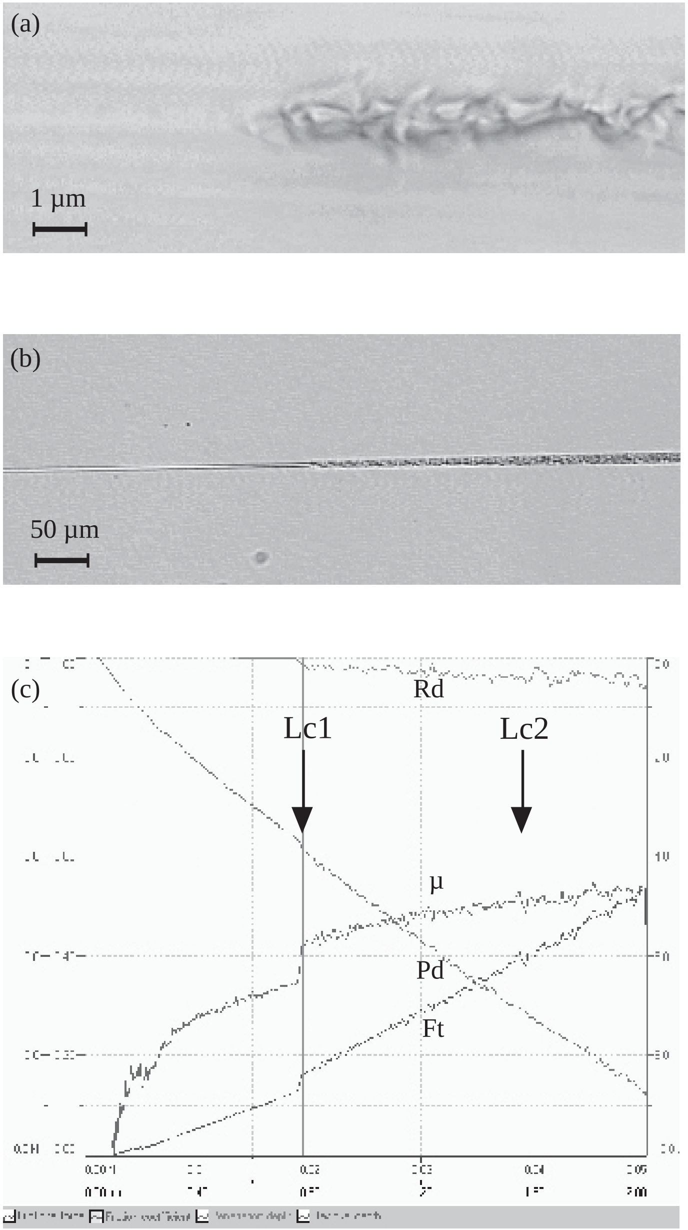

Figure 2 : Nano Scratch Tester results for a 1.2 µm polymer coating on the surface of a *Minidisk*. Complete results are shown in (c) including the frictional force, friction coefficient, penetration depth and residual depths. The first critical failure point (Lc1) corresponds to an applied load of 19.6 mN (a) whereas total delamination (Lc2) occurs at 38.7 mN (b). A spherical diamond indenter of radius 2 µm was used with a loading rate of 150 mN/min. over the range 0 - 50 mN.

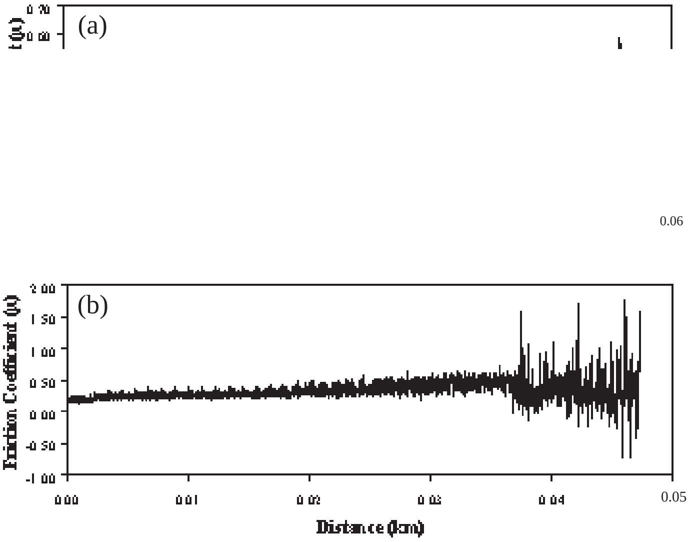

Figure 1 : Friction coefficient vs. distance traces for two different *Minidisk* surfaces. Note the critical rise in friction after 54 m (a) and 37 m (b). Tests were carried out with a 100Cr6 steel ball as the static partner, applied load of 1 N and speed 20 cm/s.

Nano Scratch method developed as reference test for polymeric automobile topcoats

Industrial automotive polymeric coatings, or varnishes, are often exposed to harsh environmental conditions yet they are expected to maintain a high gloss finish for at least five years. Following a strong demand from the automobile industry, their customers and suppliers (paint manufacturers), a project was set up to evaluate new test methods for characterising polymeric topcoat materials in terms of significant parameters.

One of the primary functions of industrial polymer coatings is to protect the underlying substrate material. Automotive coatings are subjected to daily and seasonal fluctuations of temperature and humidity and are exposed to environmental contaminants such as acid rain and salt. Additional hazards include car washes, road grit and gravel.

Mar resistance (also featured in Applications Bulletin No. 7, April 1998) characterises the ability of the coating to resist damage caused by light abrasion. The difference between mar and scratch resistance is that mar is related only to the relatively fine surface scratches which spoil the appearance of the coating. Mar resistance depends on a complex interplay between viscoelastic or thermal recovery, yield or plastic flow, and fracture. Polymers are challenging because they exhibit a range of mechanical properties from near liquid through rubbery materials to brittle solids. The mechanical properties are rate and temperature dependent and viscoelastic recovery can cause scratches to change with time.

Previous work [1-2] has focussed on the problems involved with characterisation of such complex coatings, but a dedicated instrument designed for standard testing has not previously existed. To this end, a project has now been underway for some time between all interested parties and after extensive testing and development, the outcome has been that the Nano Scratch Tester (NST) has been accepted as the preferred method for assessing scratch resistance of automobile coatings. This application note features some of the most interesting results from this project and shows the versatility of the NST in measuring the mechanical properties of a range of topcoats.

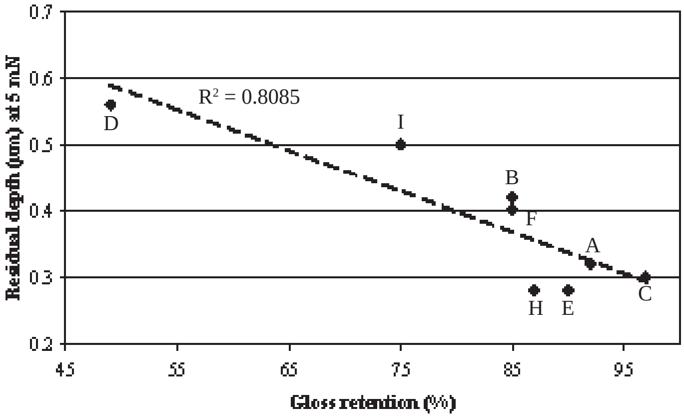

Figure 2 : Residual scratch depth (corresponding to an appied load of 5 mN) measured as a function of gloss retention for a series of unweathered topcoat samples. The level of gloss was measured with a glossmeter.

The study consisted of selecting 10 different materials which are all high bake (140°C) polymer topcoats. They consist of a pigmented basecoat (thickness = 12 µm) which is applied first, followed by the clearcoat (thickness = 45 - 50 µm), after which both are baked together. Two different colours were selected for the basecoat pigment (red and black) in order to investigate whether this had any influence on the scratch performance.

The base ingredients of each sample material consisted of one or more components of acrylic, melamine, urethane, silane and carbamate. The samples can be considered as the present *state-of-the-art* in automobile polymeric topcoats and were sourced from three different suppliers.

The samples were evaluated as 'unweathered' and 'weathered', the latter consisting of 400 hours in a Xenon Arc weatherometer using borosilicate inner and outer filters. Such filters give a better equivalent spectra to sunlight and 400 hours is approximately equal to 3 months in service. This is also the period of time in which customers provide the manufacturer with feedback on the quality of their vehicles.

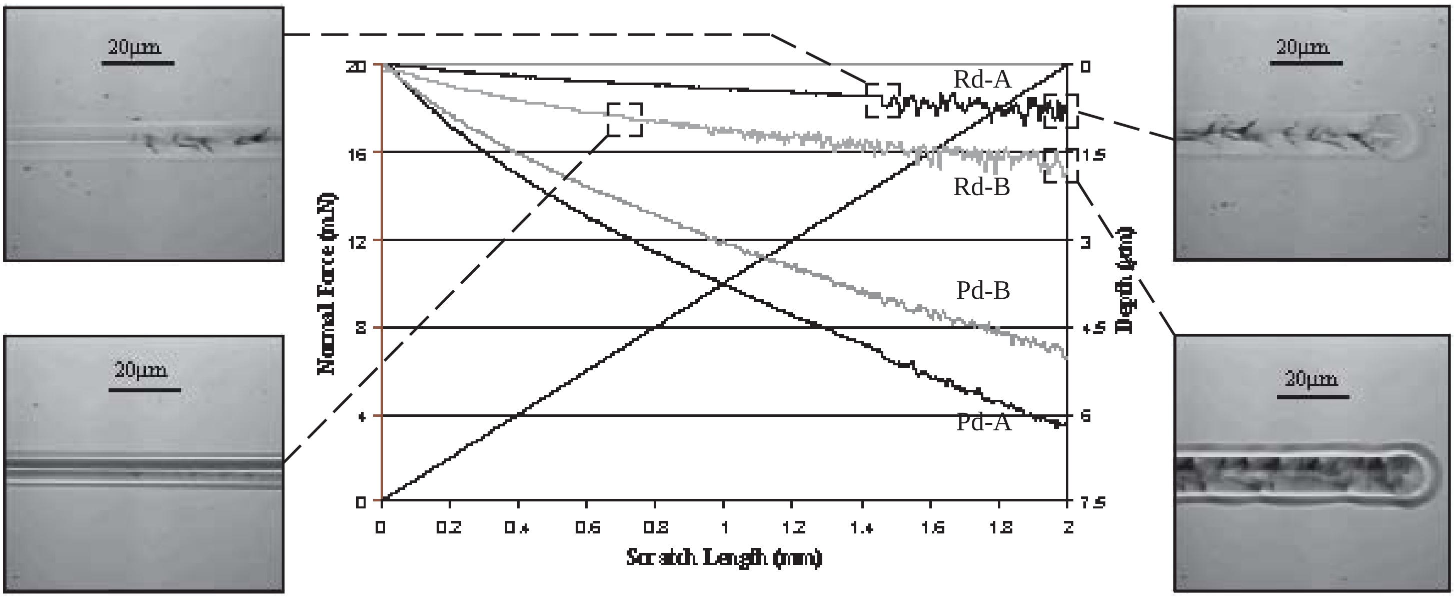

Figure 1 : Nano Scratch Tester results for progressive load (0 - 20 mN) measurements on two different polymer varnish topcoats (A and B). The penetration depth (Pd) during scratching and the residual depth (Rd) after scratching are presented for both samples. Optical micrographs show the onset of plastic deformation (left) and the extent of deformation at maximum load (right). Measurements were made with a 2 µm radius diamond stylus.

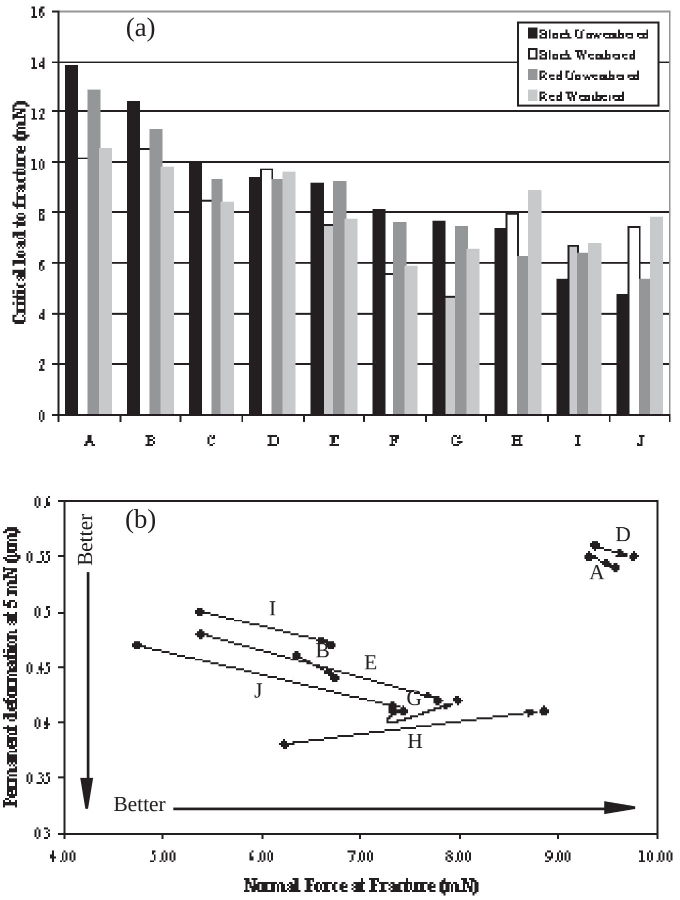

Figure 3 : Summary (a) of the critical fracture loads for the 10 tested samples. Note that four groups of measurements are included, namely before and after weathering and red/black colouration. In (b) the permanent deformation at 5 mN has been plotted as a function of fracture load; this example shows the samples whose scratch resistance improves after post aging (weathering).

The results presented in Fig. 1 show progressive load measurements over the range 0 - 20 mN on two different topcoats. The pre- and post-scan modes of the NST have been utilised in order to plot the penetration depths during the scratch tests and thus evaluate the level of viscoelastic recovery after the tests. Clearly, sample A shows a greater relaxation than sample B and much less plastic deformation along the sides of the scratch path. The greater the deformation, the more gloss is lost from the surface of the coating.

A typical correlation between residual scratch depth and gloss retention is shown in Fig. 2 where 8 of the tested samples appear to form a linear relationship for tests carried out at a constant load of 5 mN. Note that these results are for unweathered samples.

Fig. 3 (a) summarises the critical failure loads for the 10 tested samples, i.e., the load at which first fracture of the coating occurs. In each case, four points are plotted for each sample in order to compare the effects of weathering and colouration. A general trend is that the critical load is less after the weathering period although no real conclusion can be drawn regarding the colouration of the basecoats. In contrast, it was found that for some samples the scratch resistance improves after weathering (see Fig. 3 (b)). In this example, two points are plotted for each sample with an arrow denoting the transition after the weathering period; in certain cases (E, H and J) the applied load required for coating fracture is significantly increased. Such a phenomenon could be explained by a hardening of the coating as a result of the weathering process, or chemical modifications due to UV exposure.

A complete nano scratch test result is shown in Fig. 4 where a distinct change in the frictional force and penetration depth signals corresponds to first failure of the coating (seen as a rupture along the scratch path). This point corresponds to an applied load of approximately 21 mN and a scanning force microscope image of the resulting deformation is also shown. Note the significant viscoelastic relaxation after testing (the difference between the penetration and residual depth signals).

Mr Tom Dusbiber of Ford Motor Co. in Detroit is acknowledged for providing some of the results presented.

[1] J. L. Courter, *Mar Resistance of Automotive Clearcoats: Relationship to Coating Mechanical Properties*, J. Coating Tech., 69 (1997) 57 - 63

[2] G. S. Blackman, L. Lin and R. R. Matheson, *Micro- and Nano-Wear of Polymeric Materials*, American Chemical Society Proceedings (2000) 258 - 269

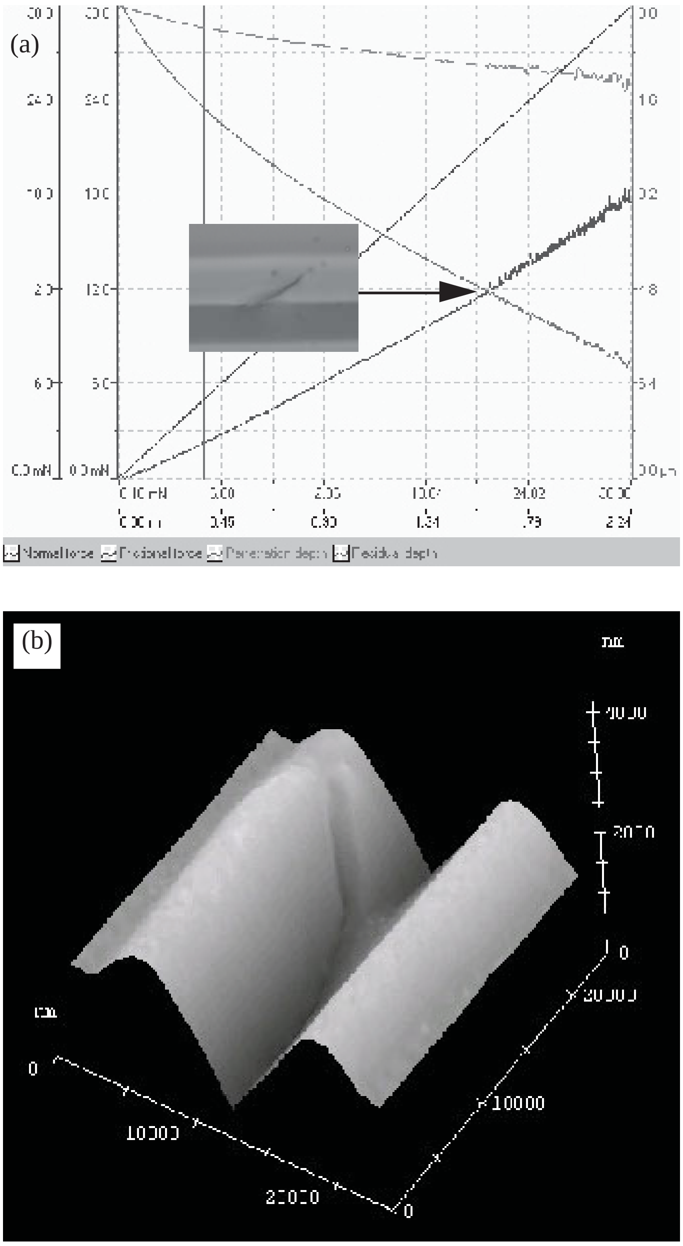

Figure 4 : Typical Nano Scratch test data for a progressive load scratch (0 - 30 mN) made on a polymer topcoat with a spherical diamond stylus of tip radius 2 µm. The scanning force microscope image in (b) corresponds to the (inset) optical micrograph of first failure in (a).

Failure properties of nail varnish investigated with the Micro Scratch Tester

In recent years, the mechanical properties of cosmetic coatings (such as nail varnishes and lipsticks) have become of high importance in satisfying the ever increasing demands of the customer. In the case of nail varnishes, many manufacturers are seeking to improve adhesion to the substrate whilst retaining adequate aesthetic qualities and longevity. An additional requirement is that the varnish retain sufficient viscoelastic properties so that small scratches will ‘recover’ completely after only a small period of time.

In this study, two different varnishes (A and B) were assessed with progressive load micro scratch testing to obtain information on the failure modes, viscoelastic properties and ease of delamination. A spherical diamond tip of radius 100 µm was used to perform tests over the range 0 - 3 N with a loading rate of 6 N/min. Both types of varnish were coated onto standard substrates of a material which resembles that of a human nail.

Complete results are shown in Figs 1 and 2 and it can be clearly seen that varnish A fails in a brittle manner with significant delamination occuring above the first critical load. A large amount of viscoelastic recovery (approximately 24 µm) occurs immediately after scratching. In contrast, varnish B fails at a much lower load with plastic deformation being the dominant mechanism and far less penetration than with varnish A. Note that the frictional force at maximum applied load is about the same for both samples.

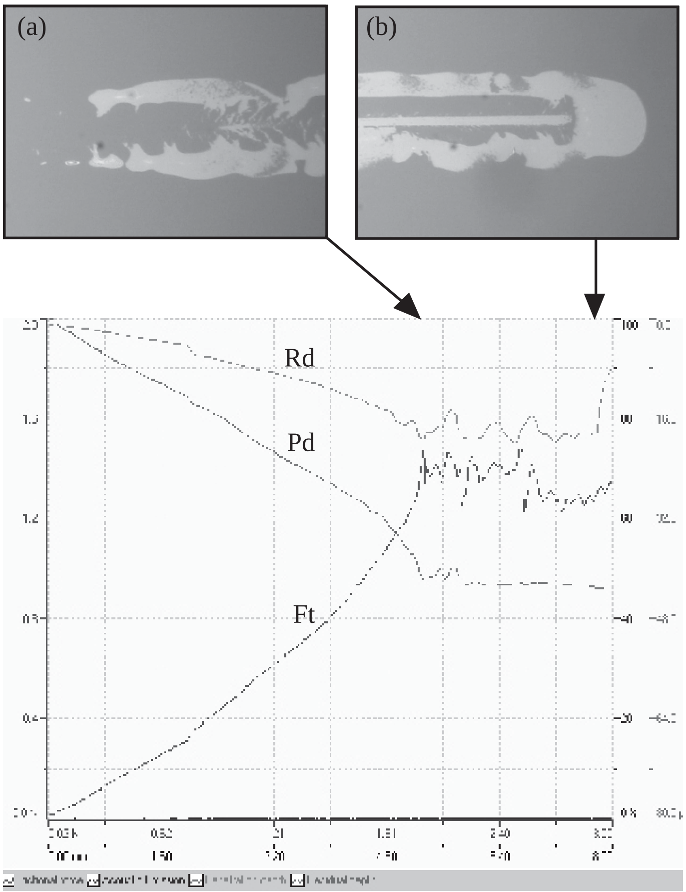

Figure 1 : Micro Scratch Tester results for varnish A showing (a) first failure at 1.94 N and (b) complete delamination at 2.86 N. Note the rapid increase in frictional force (Ft) and the viscoelastic relaxation (seen as a difference between Pd and Rd).

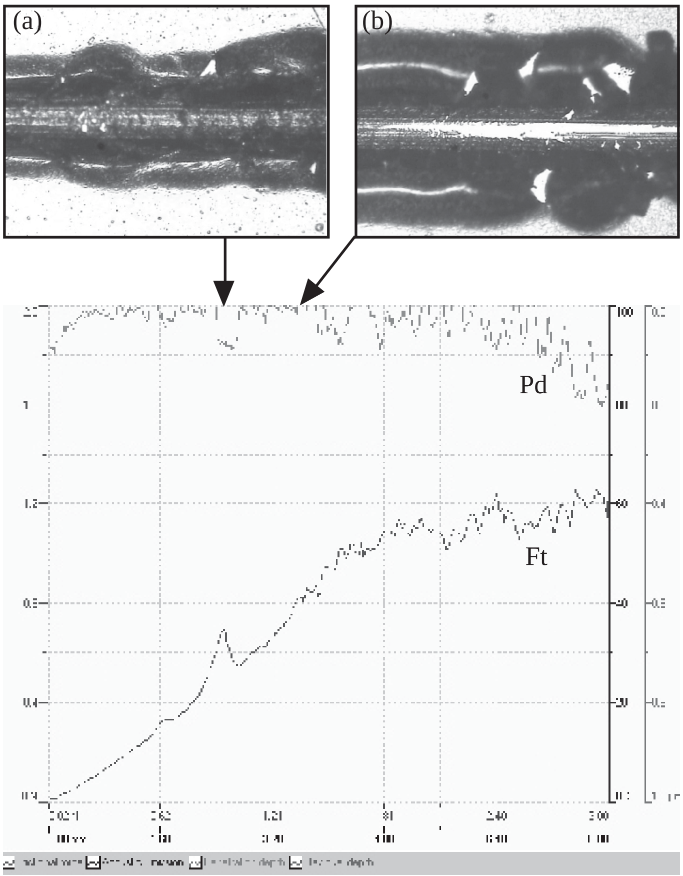

Figure 2 : Micro Scratch Tester results for varnish B showing (a) first failure at 0.95 N and (b) complete delamination at 1.36 N. Note the negligible change in penetration depth (Pd) and the small peak in the frictional force corresponding to the onset of cracking.

CSM Instruments

This Applications Bulletin is published quarterly and features interesting studies, new developments and other applications for our full range of mechanical surface testing instruments.

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