Automated Dynamic Testing

for Drying, Hardness, and Adhesion of Paints, Coatings, and Adhesives

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Characterization of dry and cure is very important in the development of paints, coatings, and adhesives. It can be challenging to assess dry and cure of these products on a quantitative, non-biased basis.

Although there are many different techniques utilized to assess drying, curing, and performance, some are often qualitative at best. It would be useful to have quantitative techniques available to access these properties. In this paper, we introduce a novel automated dynamic dry time recorder (ADDTR) device that measures dry and cure of coatings similar to mechanical dry time recorders that meet ASTM Method D 5895.

The novel device is capable of recording and graphically displaying the coating drying profile as it dries so that drying time events may be easily identified, archived, and analyzed, even for clear coatings. Such analysis allows easy and quantitative comparison between different coating systems, chemistries, driers, etc. In certain configurations, the tester may also be utilized as a hardness, toughness, and adhesion tester.

INTRODUCTION

The evaporation of solvent/water and subsequent dry of a finish impacts such properties as coating application (e.g., atomization in spray processes), air entrapment, solvent popping, flow and leveling, gloss and gloss uniformity, and dust-free, tack-free, and dry-hard times, print and block resistance, and hardness development, to name a few.

Further, reactive water-based and solvent-based adhesive processing and performance is impacted by its film building and drying time as it cures. A variety of methodologies are used to access drying and film formation of paints, coatings, and adhesives, of which some include visual assessment of flash-off, physical assessment of drying by touching with the finger, or scratching with the fingernail.

Other physical methods include measuring hardness by pencil hardness testing[1] or by using the König, persoz, or sward rocker[2]. Still other physical methods include measuring print or block resistance as a function of time[3]. Chemical methods for assessing state of curing include measuring MEK double rubs as a function of time, while instrumental methods include monitoring FTIR spectra[4], Evaporative Dynamic Oscillation[5], and adaptive speckle analysis.[6,7]

ASTM Method D 5895[8] is a common method utilized to assess drying time of paints, coatings, and adhesives. ASTM D 5895 describes a method for measuring times of drying or curing during film formation of organic coatings using mechanical recorders. The method defines four stages of coating dry: set-to-touch time, tack-free time, dry-hard time, and dry-through time.

Identifying each drying stage relies on a visual assessment of a "drying track" made in the film as a stylus or probe is moved linearly, or in a circular pattern, through the drying film. Such an assessment is qualitative at best but is particularly challenging when evaluating drying of clear films.

In this work, we describe evaluation of coating drying using an automated dynamic drying time recorder. Although visual assessment is still possible and useful, drying profile and drying characteristics of the coating or adhesive is followed by a sensor and data logged and graphed for further analysis.

Further, by changing the stylus and probe of the automated tester and dynamically controlling normal force imposed on the sample at the probe, other performance properties of the coating may be determined such as scratch hardness and/or toughness, or scrape adhesion of the coating or coating system.

The ADDTR has been described in detail elsewhere[9]. Briefly, the tester utilizes a control system and a plurality of sensors to sense and measure drying and frictional forces of a coating or coating system, while automatically controlling various functions of the equipment such as applied load and rate of testing. A key feature of the tester regarding evaluation of drying time is the ability to sense the

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change in height of the stylus or probe while in contact with the sample in a very sensitive manner as the sample is drying.

In the method utilized in this work, the probe remains stationary while the coating moves on a platform beneath the probe. Essentially, it is believed that as the coating dries, its viscosity and modulus increase and eventually the film consolidates. During the drying and consolidation process, coating freely flows around and/or under, and/or over the probe as the coating is moved relative to the probe. As the viscosity and/or modulus of the coating increases, coating begins to pile up in front of the probe and no longer freely flows back over the track left by the probe.

Eventually, the coating's viscosity and modulus increase to the point such that the normal force imposed upon the probe is no longer sufficient to "push" the coating forward and/or out of its path, and hence the probe is "pushed up and over" the "mountain," so to speak, that was built up in front of the probe.

If the coating drying is relatively fast, once the probe reaches the top of the semi-dry "coating mountain," the probe will drop rather precipitously onto the surface of the coating in its dry-hard state (resulting in a "peak" in the observed data) and continue on the surface of the film, leaving a track until the film consolidates to the point such that the vertical force imposed on the probe is no longer great enough to mar the surface of the coating, at which point the coating is considered to be dry-through.

However, if the consolidation of the coating is slow and the film remains tacky for an extended period of time, the probe remains in the extended peak state for a longer period of time, and the resultant data displays a broad peak and/or a series of peaks when graphed. When multiple peaks and/or a series of peaks are observed in the drying profile after observation of the tack-free time, these are considered characteristic of the drying properties of the coating or adhesive itself, displaying multiple stages of drying or film-formation events.

Hence, not only are the times for when the probe begins to rise and when it returns to the surface of the film obtained, but also the breadth of the peak characterizes the tackiness

FIGURE 1—Schematic of Drying Film Moving Under Test Probe; 1—Load; 2—Angle, Φ, between normal load and probe/stylus; 3—Probe and stylus; 4—Track left in drying liquid film as it is drying due to drying events; 5—Liquid film drying; 6—Substrate; 7—Substrate support; 8—Substrate support direction and velocity
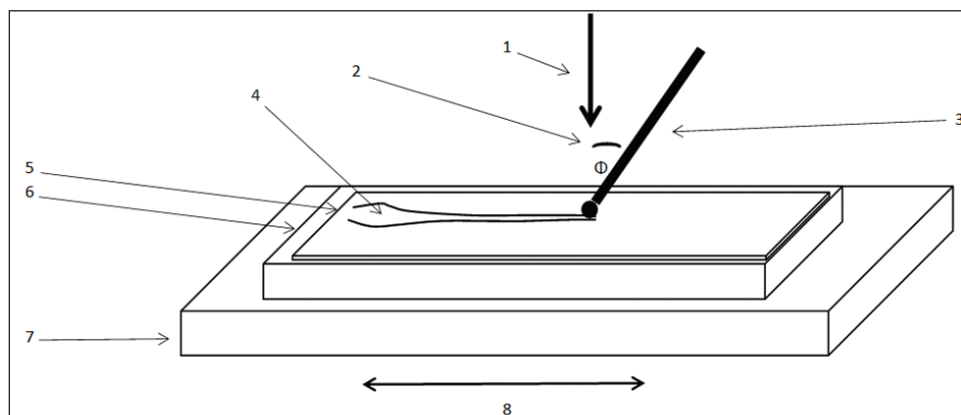
of the film as it is drying. *Figure 1* is a schematic drawing of a drying sample on a platform, both moving underneath a stylus and probe. *Figure 2* displays a proposed conceptual drawing of coating "piling up" in front of a Teflon probe as the wet film moves through and/or under the probe.

EXPERIMENTAL

All resins and polymers (including latices) and formulation constituents (including coalescent solvents) were used as received from the supplier. A variety of solvent-based and water-based coatings were evaluated for drying time. Typically, films were applied to 9 x 6-in. clear plate glass by bird bar or wire round rod utilizing a byko-drive automatic draw-down machine available from BYK Gardner USA, noting the actual time of drawdown.

The applied films were then placed onto the testing platform equipped with a 9.4 mm diameter Teflon probe attached to a stylus, and the testing platform having a plurality of sensors for measuring drying time events or controlling testing parameters. The drying-time-test duration determined the testing rate. For instance, a 2-hour test duration required a platform translation testing rate of 0.021 mm/s, while a 20-hour test duration required a platform translation testing rate of 0.002 mm/s.

Typically, a 10 gram normal force was applied to the probe in either a dynamic

or static manner and a 5-minute duration background scan was run on each glass substrate before coating application to the substrate. Under dynamic conditions, normal force load and probe height was monitored for each drying film as a function of distance and time. In this work, only probe height results are reported.

For scratch hardness testing, films were evaluated as a function of time from application or time after exiting an oven for force-dried samples. Films were evaluated on glass and other substrates for scratch hardness by a progressive load normal force technique, loading from 0 N to 110 N, with the maximum depending upon the substrate utilized. Coatings on wood and metal were evaluated up to 110 N maximum, while coatings applied to glass were evaluated at up to 80 N max.

For these scratch hardness and adhesion tests, the platform translation rate was 12.7 mm/s. Typically, progressive loading to 110 N was conducted over a distance of 130 mm with a normal force loading rate of 10.746 N/s. The testing probe consisted of a hardened stainless steel loop probe available from BYK Gardner USA attached to a stainless steel stylus. Surface scratch testing was conducted with a needle probe attached to the stylus, typically in a progressive load normal force load range of 0–1 N.

A typical progressive load scratch test was conducted over a distance of 60.04 mm at a platform translation rate

FIGURE 2—Proposed Conceptual Schematic of "Wet Film Pile-Up" in Front of Probe as the Drying Film is Moving Under Test Probe; 1—Load; 3—Probe; 4—Track left in drying liquid film as it is drying due to drying events; 5—Liquid film drying; 8—Substrate direction and velocity; 9—Wet Film Pile-Up
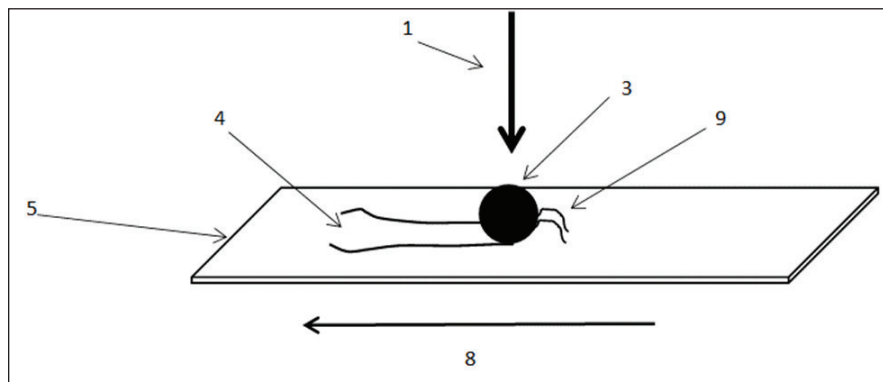
of 12.7 mm/s at a vertical force loading rate of 0.212 N/s. For scratch hardness, adhesion, and surface scratch testing, evaluations were conducted in at least duplicate or triplicate and the average failure load reported for each time-stamp evaluation (but sometimes higher duplication was used).

Scratch and adhesion results were determined visually, as well as by stereoscopic examination, and/or by a surface scan technique. Various failure modes were identified, depending on the test, and included load-to-surface mar, load-to-surface scratch, load-to-stick-slip, load-to-stomata crack, and load-to-complete failure.

Load-to-complete failure, depending upon the substrate, included significant cracking/delamination of coating and/or removal of coating from the substrate.

Load-to-surface mar is that load where the surface of the coating begins to disrupt the surface either by a change in gloss or indention of the surface.

Load-to-surface scratch is that load where the surface is scratched, usually resulting in a slight cut into the surface of the coating film.

Load-to-stick slip is that load where there is a visible wave pattern left in the film where the probe has traveled; usually this wave pattern appears as a series of concentric "V"s in the film when viewed under grazing angle light through a low-power stereoscope.

Load-to-stomata crack is that load where small cracking begins to be seen in the track left by the probe; usually these cracks appear as mouth-shaped circles that appear, at least at the macro scale, as the shape of open stomata cells in tree and plant leaves and stems.[10] In plants, stomata cells are responsible for releasing moisture from the leaves of the plant and absorption of carbon dioxide from the atmosphere during the transpiration process.

Load-to-complete failure, depending upon the substrate, is that load where the coating is either completely removed from the substrate and/or there is a high density of film cracking, and/or stomata cracking has extended from small individual cracks to areas where large amounts of coating is removed from the substrate.

Progressive loading tests by this method, whether scratch hardness, adhesion, or scratch testing, is conducted under kinetic conditions. That is, testing is conducted with minimum static load imposed on the sample at the beginning of the test, by only initiating the test just after initiation of the platform holding the substrate and surface to be evaluated. Typically, platform initiation begins within about 20 microns of the probe from the sample surface, resulting in a platform translation of approximately ≤ 7 mm before test and activation at 0.1 N normal force.

Evaporative Dynamic Oscillation Tests (EDOT)[11] of films were conducted at room temperature and humidity conditions utilizing a 25 mm EDOT probe attached to a MCR 301 research grade rheometer from Anton Paar GmbH, Graz, Austria. Briefly, films were cast onto a bottom plate having a diameter of 60 mm and a well depth of 150 microns. Typically, the EDOT probe was positioned approximately 15 microns under the surface of the film for water-based samples, or 120 microns from the bottom of the well for solvent-based samples.

Actual depth of water-based samples was determined separately by systematically adjusting the height of a 25 mm aluminum plate-based measuring system until the face of the aluminum plate made complete contact with the surface of the sample. In this manner, water-based coating depths were determined within about 10 microns. Dynamic oscillation storage moduli, loss moduli, complex viscosity, and loss tangent of the drying films as a function of time were evaluated at a 0.1% strain rate, and frequency of 10 rad/s.

RESULTS AND DISCUSSION

Drying Time Determination– Solvent-Based Coatings

Figure 3 displays an image of a drying trace left by a Teflon probe after testing a VT-modified alkyd formulation. The drier package for the formulation consisted of 0.0005% Co, 0.001% Ca, 0.001% Zr, Metal on total resin solids (TRS). The drying trace was obtained over a period of 20 hours.

FIGURE 3—20-hr Drying Trace of VT-Modified Linseed Oil Alkyd; Drier package for the formulation consisted of 0.0005% Co, 0.001% Ca, 0.001% Zr, Metal on TRS; Solvent composition is Xylene; Image Ref. B53P192#30_20hr-cal-mark
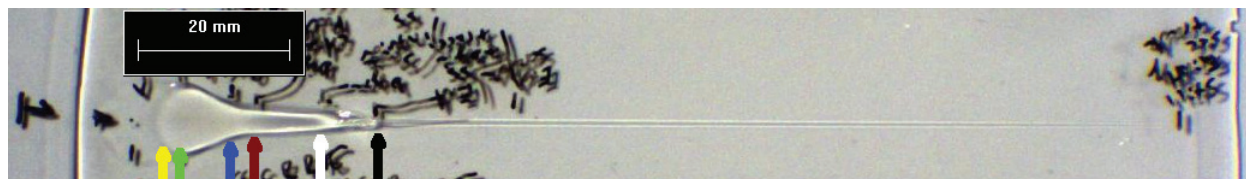
In the image, the starting point for the drying scan is consummate with the left of the 20 mm calibration mark. *Figure 4* displays a drying profile of the sample drying events in terms of distance as determined by the automated dynamic dry time recorder.

In *Figure 3*, a pear-shaped depression appears at about 3.7 mm (yellow arrow) with the widest portion of the pear-shaped depression occurring at about 6.4 mm (green arrow). According to the ASTM D 5895 test method, appearance of the pear-shaped depression represents the set-to-touch time. The noted 3.7-mm distance corresponds to about 0.6-hour drying time, while the 6.4 mm distance corresponds to about 1-hour drying time.

It is challenging to distinguish the tack-free time for the sample as defined by ASTM D 5895. According to the method, the tack-free time is reached where the continuous track in the film ceases, and the stylus starts to tear the film or leave a discontinuous cutting of the film. It is seen in *Figure 3* that the pear-shaped depression narrows significantly at about 13.3 mm (1.77 hours) (blue arrow), and at about 16.5 mm (2.25 hours) (red arrow), a groove appears in the track where the probe appears to be depressed into the drying film, but there is no discontinuous tearing of the film. However, stereoscopic examination shows that at this 16.5 mm distance, there is the appearance of an edge-pull at either side of the track edge.

The next significant drying event appearing under the stereoscope occurs at about 25.2 mm (3.52 hours) (white arrow). Here, a faint wave pattern appearing as a series of concentric "greater-than" signs—">"—appear in the drying track, which we call a stick-slip phenomenon. At about 32.4 mm (4.6 hours) (black arrow), there is a hump in the sample shaped as an inverted chevron (e.g., ">"), where the track groove ends and the stylus then begins to mar or scratch the surface of the film. There is a "dried resin string" extending to the right of the 32.4-mm mark and does not represent cutting of the film by the probe.

According to ASTM D 5895, where the stylus begins to scratch or mar the surface of the film is the dry-hard time of the film. The film continues to leave a visible track on the film for the balance of the test, (20 hours); therefore, in this

FIGURE 4—Automated Dynamic Drying Time Profile for VT-modified Linseed Oil Alkyd, 20 Hour Test
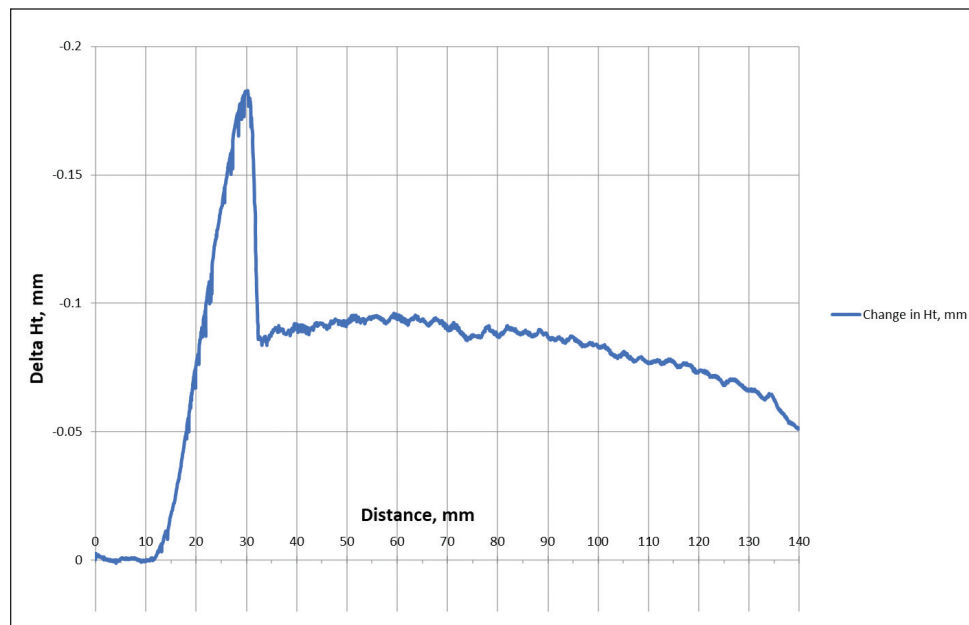
particular test, the film does not reach dry-through time by the end of the test.

Figure 4 shows that some of the drying time events are easily distinguished with the drying profile recorded by the ADDTR. The profile shows that at about 13 mm, the probe begins to rise as the coating begins to dry and force the probe to try to go over the coating that has "built-up" in front of the probe.

In the vicinity of 16 mm to 20 mm, there appears to be some indication of a stick-slip phenomenon in the sample. At about 30 mm, the probe appears to have reached the crest of the built-up and drying coating "mountain." Between about 30 mm and 32.5 mm the probe precipitously drops to the surface of the dry-hard film.

In this test and for this specimen, it appears that the rise in the probe at about 13 mm corresponds to the tack-free time of the film (about 1.77 hours). At the crest of the peak at 30 mm, the coating film appears to have completely dried to the point that the coating is no longer "sticky" and the precipitous drop of the probe onto the surface of the film represents the dry-hard time of the film.

The breadth of the peak shown in the drying profile represents the "stickiness" of the drying sample. The broadness of this peak shows that the viscosity and/or molecular weight of the sample increased sufficiently to

overcome the 10 gram normal force imposed on the probe, forcing the probe to rise over the built-up drying film.

The coating has not cured or dried sufficiently to resist the probe, pushing the sample along the track or adhesively pulling uncured sample along the track. After the dry-hard time, probe height is due to a combination probe penetration into the sample surface, film thickness, and shrinkage of the sample with time.

Figure 5 displays a drying profile for a 2-hour drying test for this same VT-modified linseed oil alkyd, while *Figure 6* displays an image of the drying trace. Although the dry-hard-time stage is not reached within 2 hours, this shorter dry time allows improved visualization of early drying events for the sample.

Figure 5 displays a very broad peak between about 12 mm and 76 mm, reaching a maximum at about 50 mm. *Figure 6* shows that at about 50–54 mm (roughly corresponding to about 39–40 minutes), the drying trace begins to narrow compared to the widest part of the trace near the beginning.

It is hypothesized that perhaps this drying time event corresponds to the set-to-touch time. At the very least, it may represent the end of the evaporative controlled drying process of the xylene solvent in the sample and the onset of a diffusion-controlled drying process.

Figures 5 and *6* show that another significant drying event occurs at about 77 mm (roughly about 60 minutes). Tack-free time is reached at about 90 mm, about 71 minutes. Comparison to *Figures 3* and *4* show that the tack-free time is reached sooner for the more rapid test. It seems reasonable that the faster 2-hour test may result in a shorter drying time response when we consider that the shorter test is conducted at a higher shear rate, and thus it is expected that the viscoelastic sample will respond to this increased shear rate in a "stiffer" manner. We also note that for longer duration tests, the drying film remains wetter around the probe longer, which would also result in longer measured drying times.

Figure 7 displays a repeat drying trace of the VT-modified linseed oil alkyd shown in *Figure 6*. As can be seen in the image, the traces are similar overall. However, the trace of *Figure 7* displays more drying event activity in the drying trace than in *Figure 6*, especially after the tack-free time is reached.

FIGURE 5—Automated Dynamic Drying Time Profile for VT-modified Linseed Oil Alkyd, 2 Hour Test
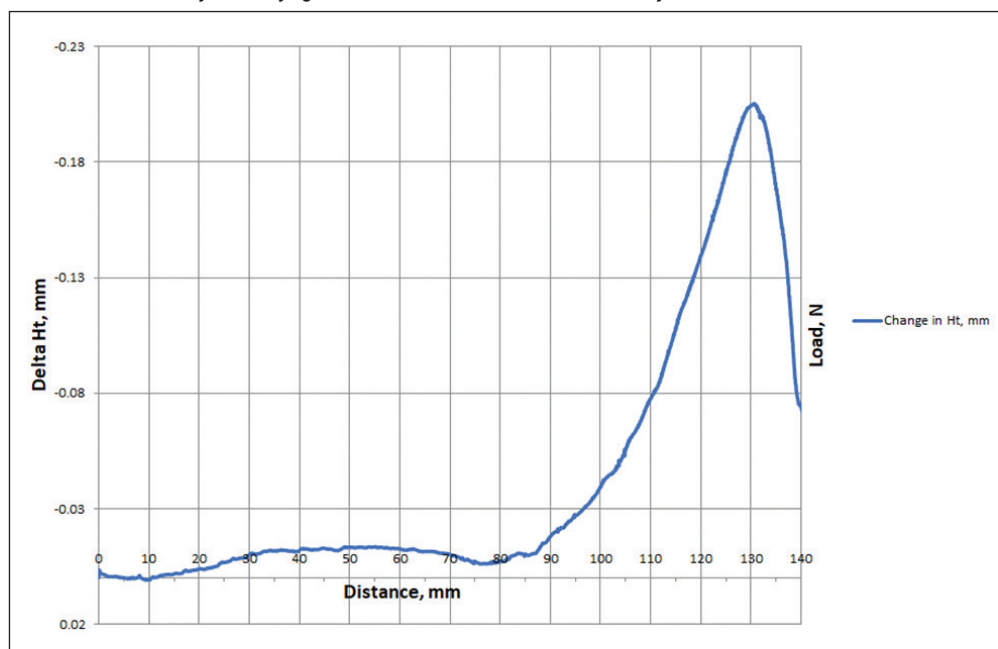

FIGURE 6—2-hr Drying Trace of VT-Modified Linseed Oil Alkyd; Drier package for the formulation consisted of 0.0005% Co, 0.001% Ca, 0.001% Zr, Metal on TRS; Solvent composition is Xylene; Image Ref. B53P193#31_2hr_Opt-Sen-mark
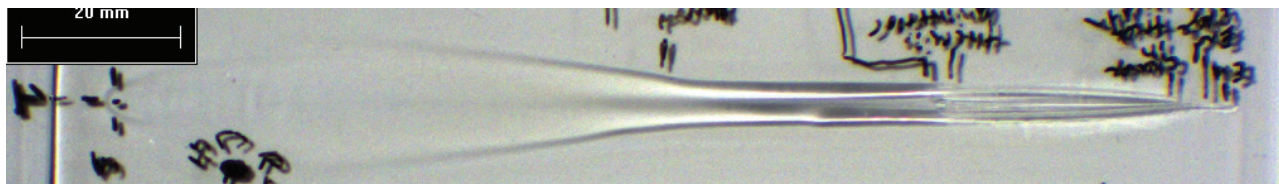

FIGURE 7—2-hr Drying Profile of VT-Modified Linseed Oil Alkyd; Drier package for the formulation consisted of 0.0005% Co, 0.001% Ca, 0.001% Zr, Metal on TRS; Solvent composition is Xylene; Image Ref. B53P192#29_2hr-Mark
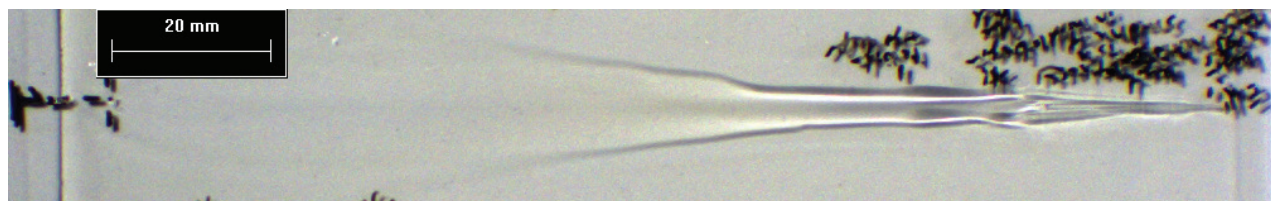
Figure 8 is the automated drying time recorder profile of the drying trace. Comparing this to *Figure 5*, overall, the two traces are similar. However, the increased drying event activity noted in *Figure 7* is detected by the ADDTR instrument. Further, *Figure 8* seems to show some of the stick-slip phenomenon previously shown in *Figure 4*. *Figure 9* is an overlay of the two ADDTR traces from *Figures 5* and *8*.

Figure 10 is an overlay of a 48-hour evaporative dynamic oscillation test (EDOT) of the VT-modified linseed oil alkyd discussed in *Figures 3–9* (red curves) with the 20-hour automated dynamic drying time test (green curve) for this same formulation. The EDOT test displays storage modulus (square symbols), loss modulus (triangle symbols), complex viscosity (circle symbols) and tan delta (diamond symbols).

The EDOT test also shows a blue symbol designating the crossover point between storage and loss modulus, or at tan delta equals 1. This crossover point is the sol-gel point of the drying film and is where the material transitions from a more liquid state to a more solid state and is calculated to occur at about 132.6 minutes drying time.

Interestingly, the first derivative of the ADDTR drying curve (green curve), after smoothing, results in a maximum at about 141 minutes drying time. We have noted above that this area of the curve may correspond to the tack-free time in the drying profile, and it appears to roughly correlate with the sol-gel time of the EDOT curve. It is reasonable that these two times correlate because at the tack-free time, the coating is transitioning from a more liquid state to a more solid state.

Further analysis of the ADDTR curve results in a curve maximum occurring at about 255 minutes, and an initial curve minimum after the maximum, corresponding to the dry-hard time of 288 minutes. At this time, the coating displays a tan delta value of approximately 0.772. This value may be useful for characterizing dry-hard times of solvent-based alkyd coatings by the EDOT method. Necessarily, a tan delta value of 0.772 is not adequate for dry-through time, and the coating will need to display a lower tan delta value before the dry-through characteristic may be

reached. When the ADDTR test was ended at 19.55 hours, it still could not be characterized as reaching dry-through according to ASTM D 5895, as there was still a slight trace left on the surface of the film. A tan delta of approximately 0.574 was measured at this

time. Thus, a tan delta less than 0.574 may be required for a dry-through film for this solvent-based alkyd. It is noted that after 48 hours, a tan delta of 0.415 was measured for the coating film, so it appears that the coating continues to cure with time.

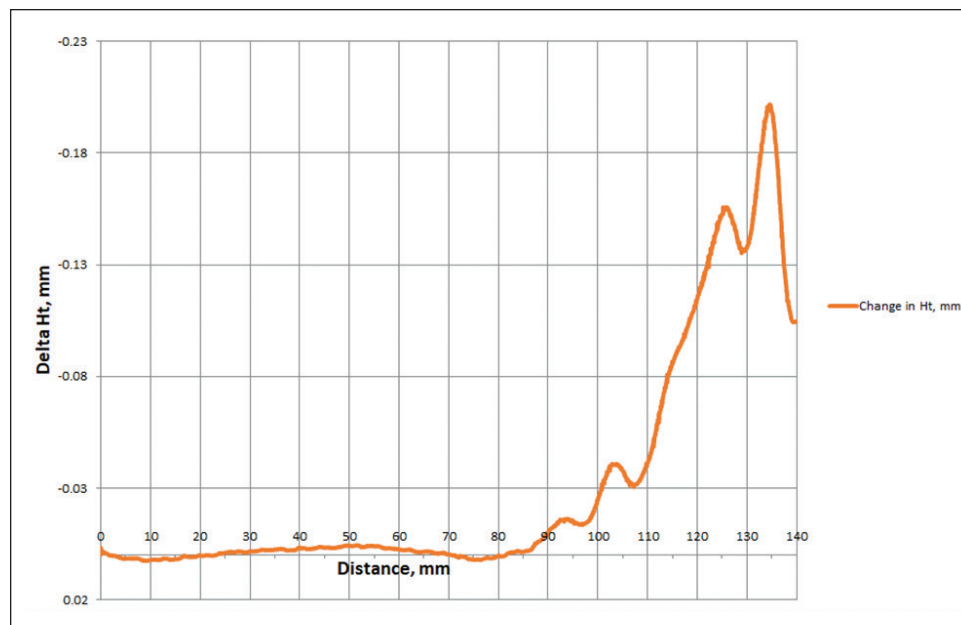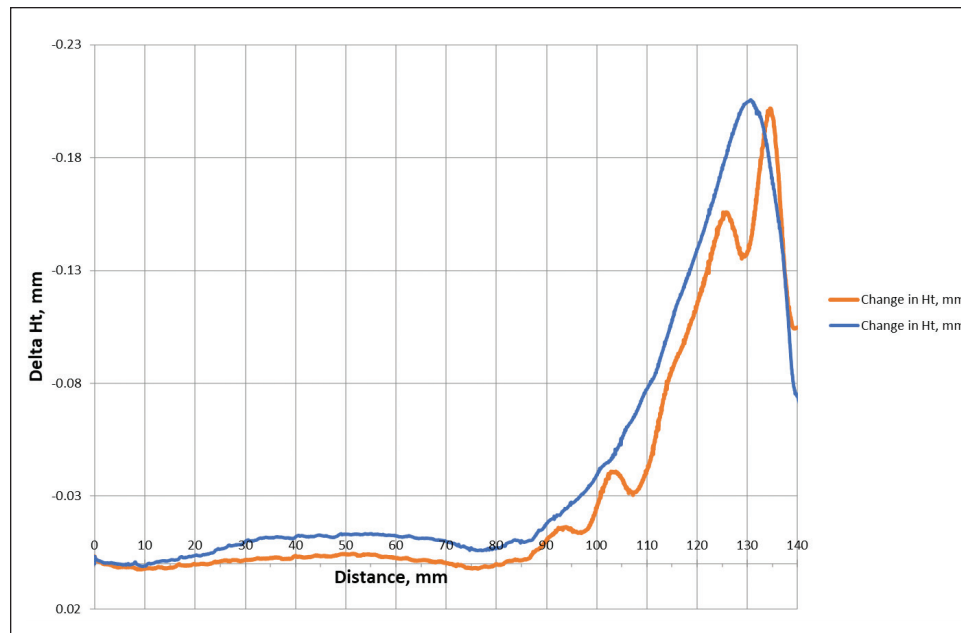FIGURE 8—Automated Dynamic Drying Time Profile for VT-Modified Linseed Oil Alkyd, 2 Hour Test

FIGURE 9—Overlay of Two Separate Automated Dynamic Drying Time Profiles for VT-Modified Linseed Oil Alkyd, 2 Hour Test

FIGURE 10—Overlay of EDOT and ADDTR Drying Curves for Solvent-based VT-Modified Linseed Oil Alkyd Film
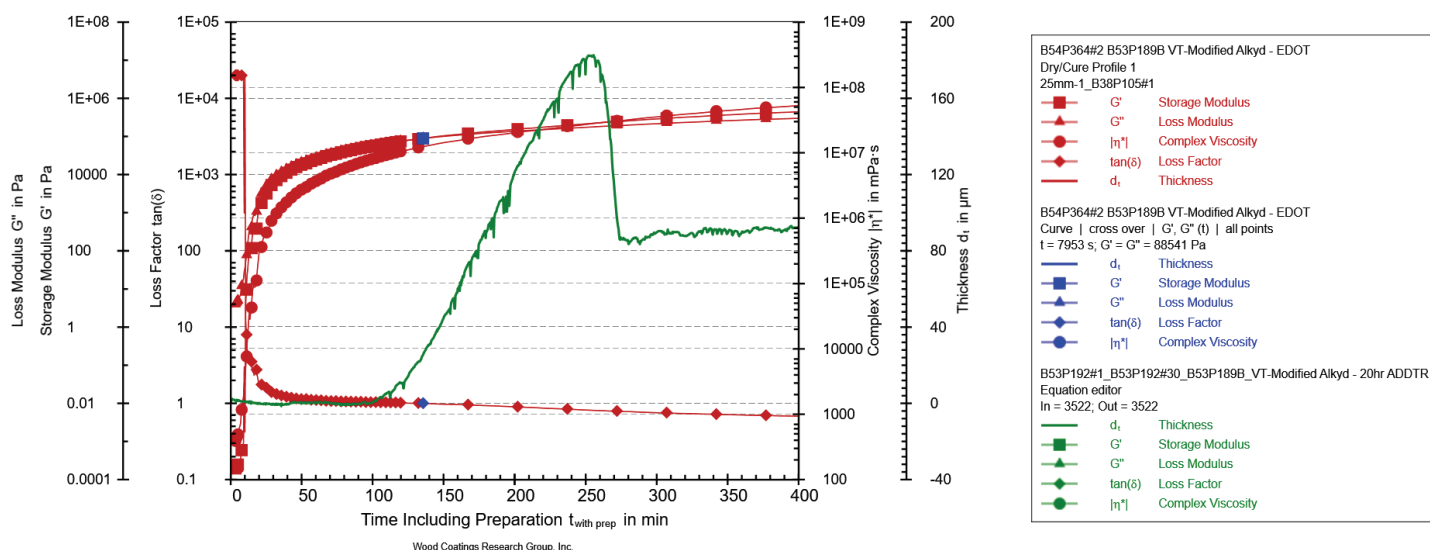

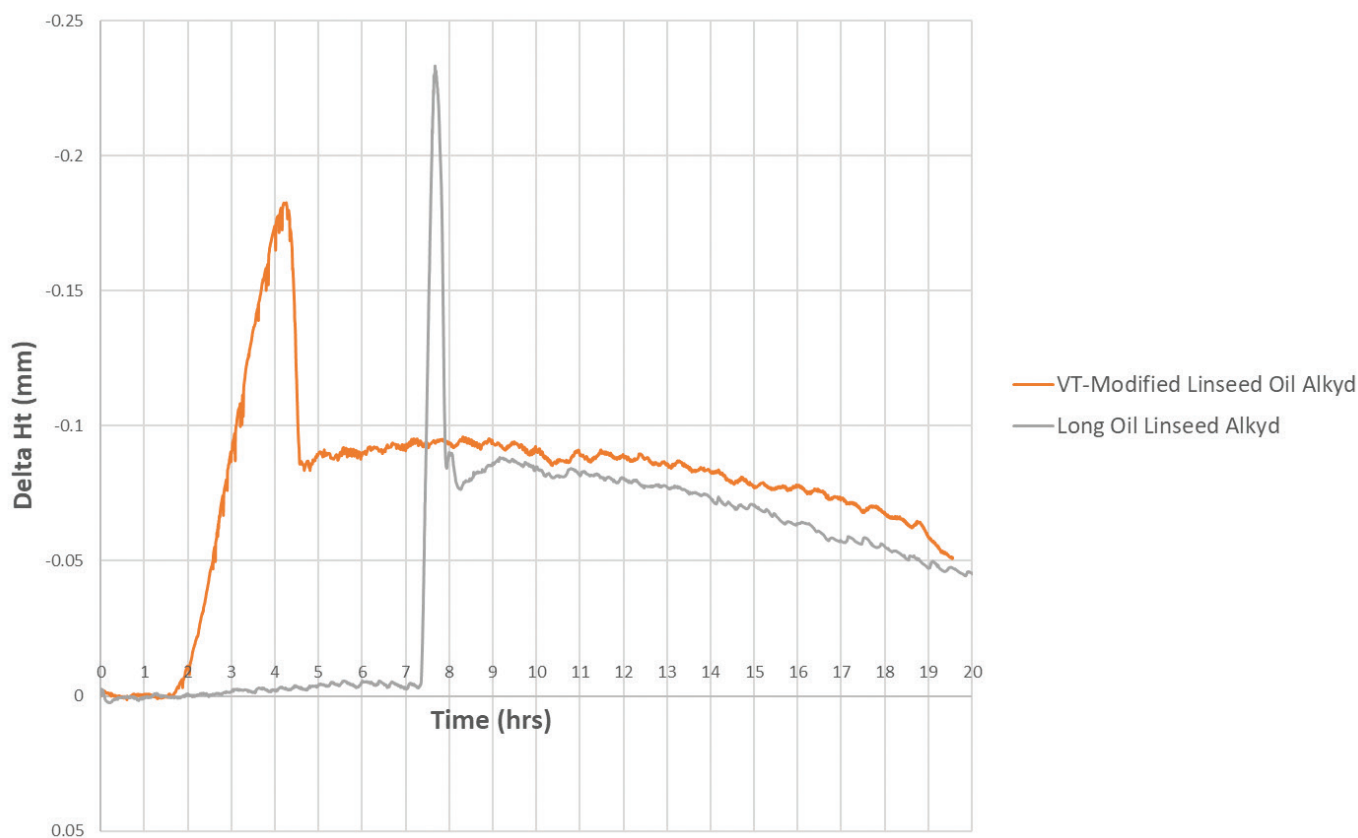Wood Coatings Research Group, Inc.

FIGURE 11—Comparison of Drying of VT-Modified Linseed Oil Alkyd vs. Long Oil Linseed Alkyd

The data of *Figures 3–10* indicate that for this solvent-based VT-modified alkyd formulation, it requires approximately 1 hour to reach set-to-touch, approximately 2.35 hours for the sample to reach a tack-free state, and another 2.45 hours for the sample to go from a tack-free state to a dry-hard state, or a total of approximately 4.8 hours. After approximately 19.5 hours, the sample has not reached a dry-through state. At 48 hours air dry, the sample displayed a tan delta of 0.415, and at that time the sample was found to display a glass transition temperature of ~20.1 °C by EDOT-DMTA; after 100 hours air dry, the sample resisted printing up to 4 psi pressure.

Figure 11 compares drying profiles of the VT-modified linseed oil alkyd to that of a very long oil linseed alkyd obtained by utilizing the ADDTR.

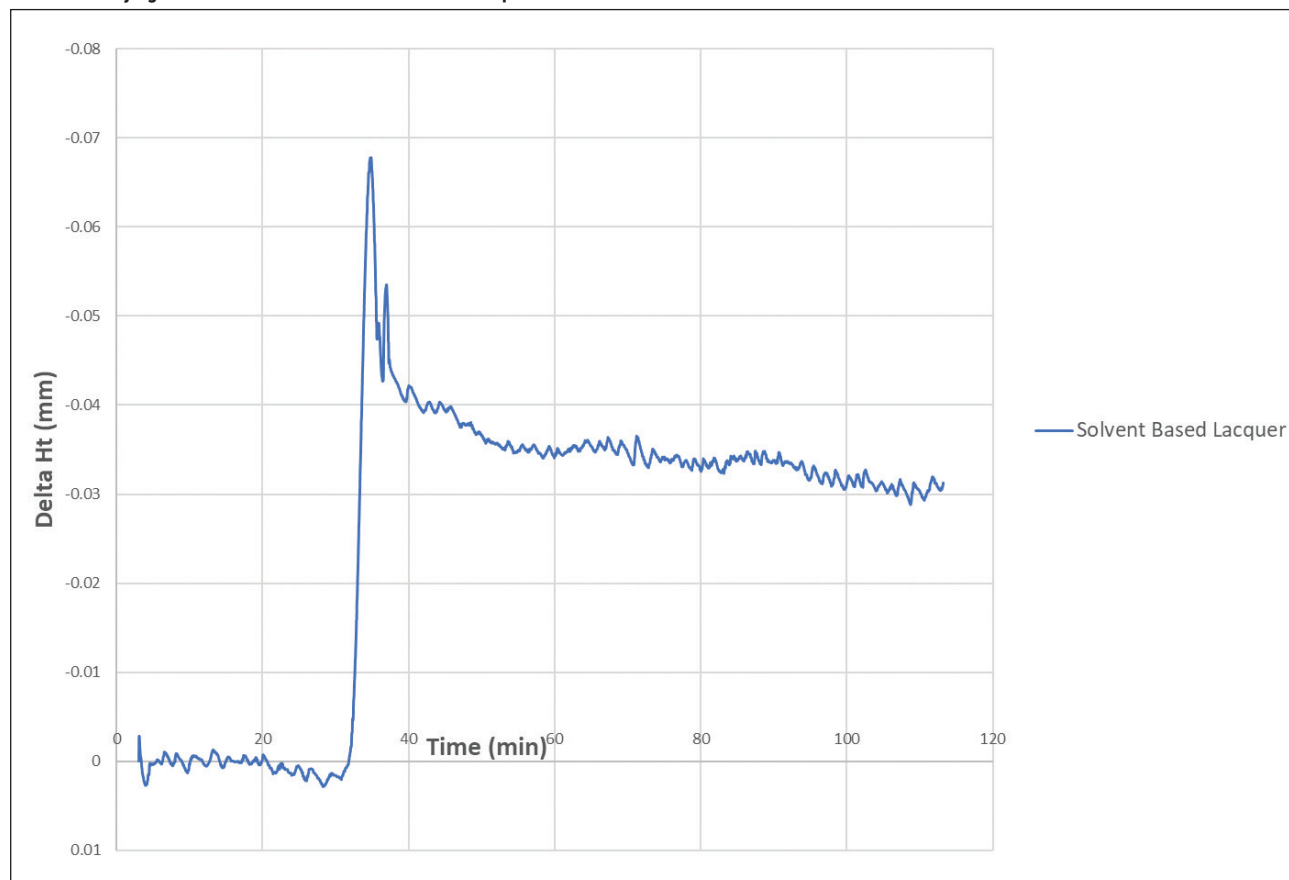**FIGURE 12—Drying Profile of Solvent-based Nitrocellulose Lacquer**

FIGURE 13—Impact of Wet Film Thickness on Drying Profile of Solvent-based Nitrocellulose Lacquer
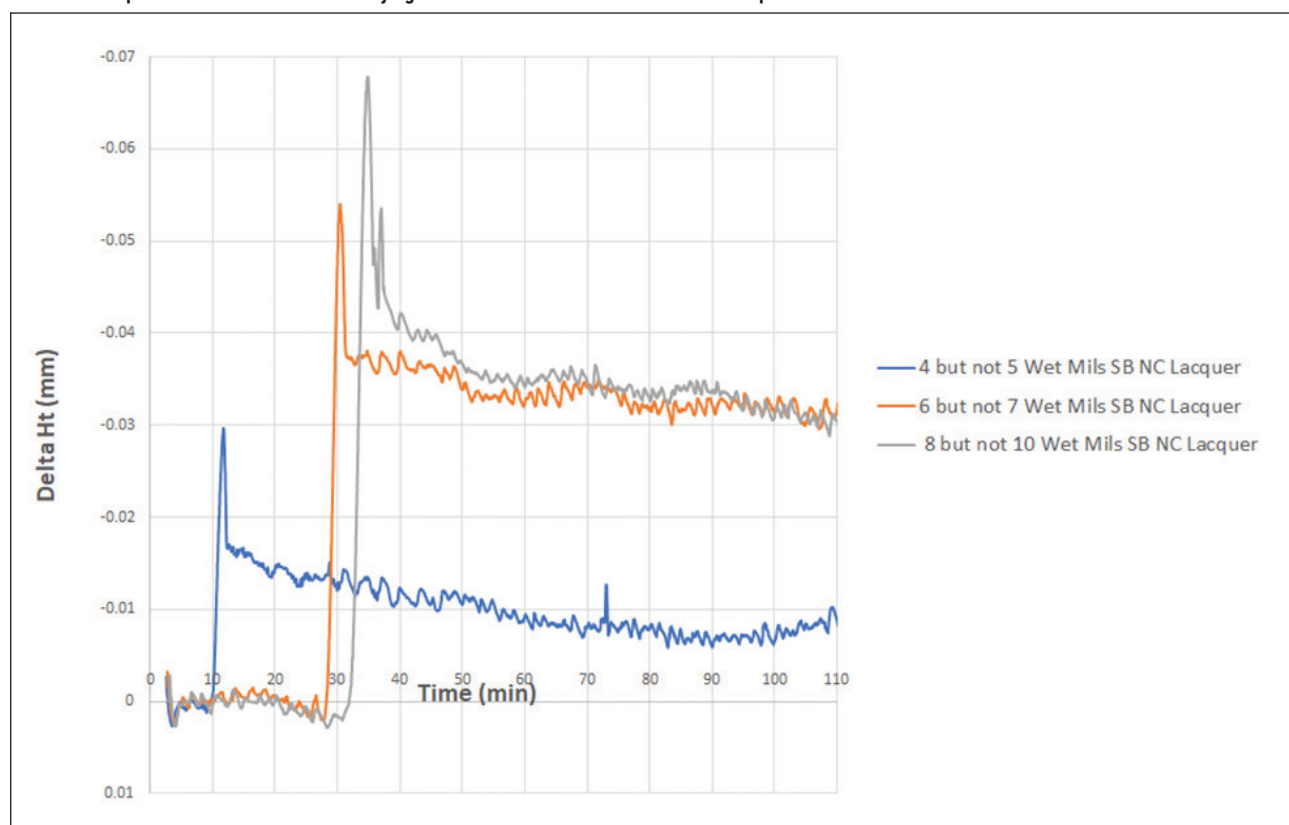
FIGURE 14—Impact of Catalyst Concentration on ADDTR Drying Curves for Solvent-based Acid Cure Varnish
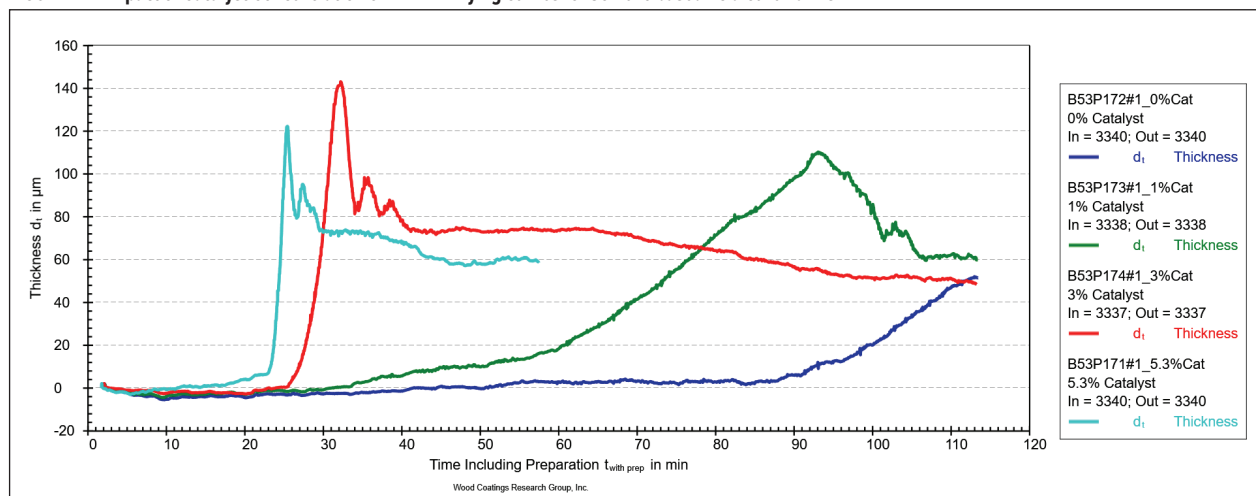

FIGURE 15—Impact of % Wt Catalyst Concentration on Drying and Curing of Solvent-based Acid Cure Varnish
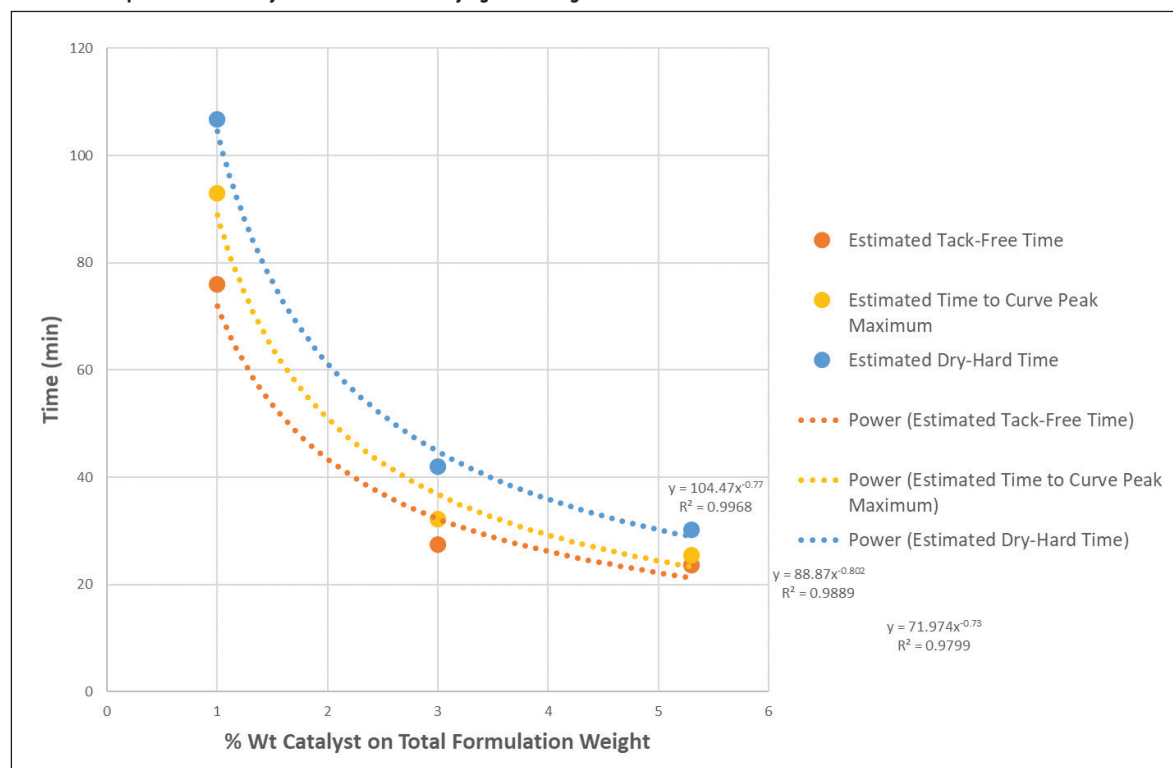

Figure 12 is a 2-hour ADDTR drying profile of a nitrocellulose lacquer applied with a 6 mil bird bar.

The data of *Figure 11* indicates that the VT-modified alkyd reaches a tack-free time and dry-hard time faster than the long-oil linseed alkyd. However, the long oil linseed oil alkyd displays a shorter time between the tack-free state and the dry-hard state. Conversely, the nitrocellulose lacquer (shown in *Figure 12*) dries significantly faster than the VT-modified alkyd, reaching a tack-free time in about 30 minutes and a dry-hard time in about 40 minutes.

Figure 13 compares the impact of applied wet film thickness on the ADDTR drying profile of the nitrocellulose lacquer. In *Figure 13*, wet film thickness was evaluated using a Wet Film Thickness Gage available from Paul N. Gardner Company. Using this gage, measured film thickness is determined as a range, for example, at least 4 mils, but not 5 mils. Although the gage measures film thickness as a range, the data shows the expected trend that greater film thickness result in longer drying times. The data also shows that the ADDTR is capable of characterizing

drying of very fast-drying and thin wet-film-thickness samples.

Figure 14 compares the air-drying behavior of an acid-cure varnish as a function of para-toluene sulfonic acid catalyst concentration (% wt) added to the varnish formulation. *Figure 15* shows a power analysis of the tack-free time, time to curve peak maximum, and dry-hard time estimated from the drying profiles of *Figure 14*. The data indicates that for this product, increasing catalyst concentration significantly reduces air drying time of this sample.

FIGURE 16—4-hr Drying Trace of Acrylonitrile-Modified Core-Shell Polymer Film Coalesced with 35 PHR Butyl Cellosolve Coalescent; Image Ref. B53P265#43_#1_Coreshell_EB_4Hr-Crop-A
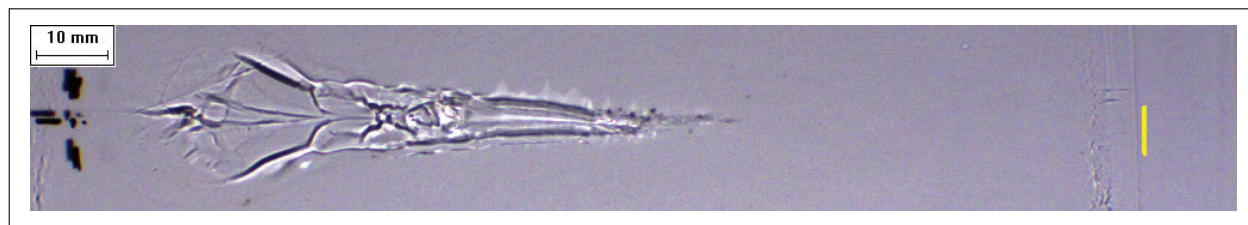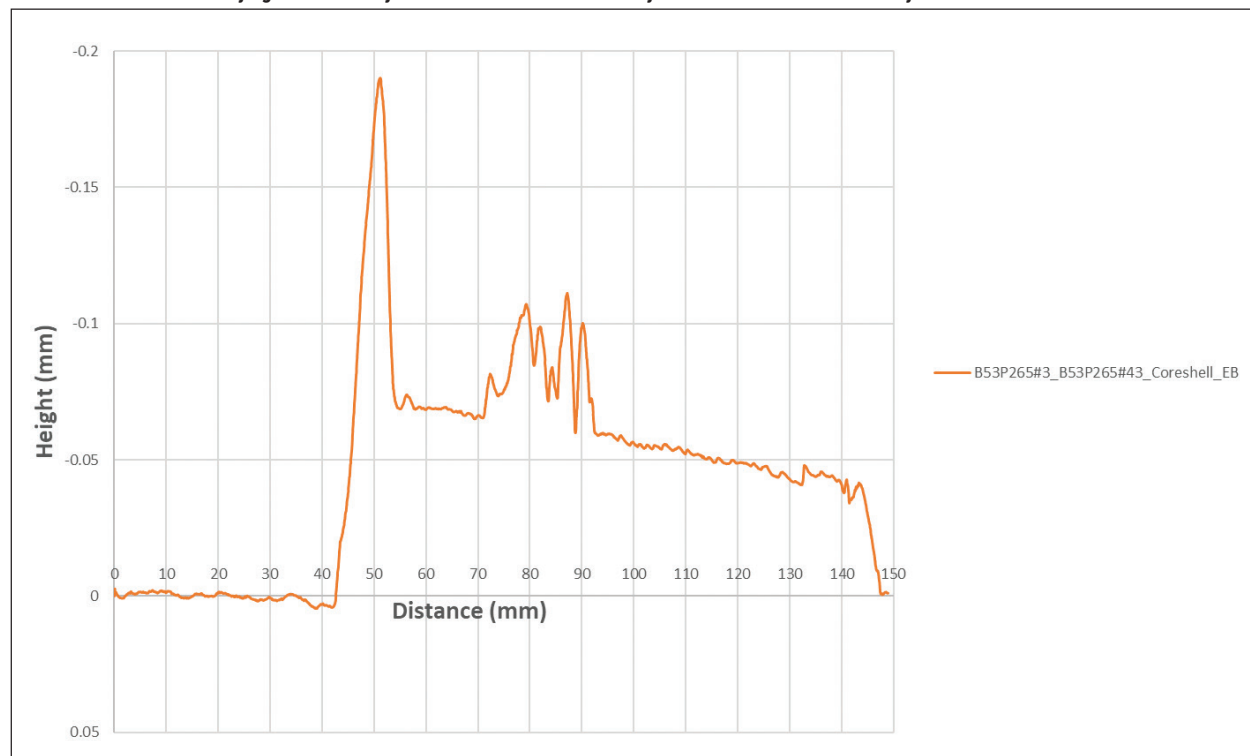

FIGURE 17—4-Hour ADDTR Drying Profile for Acrylonitrile-Modified Core-Shell Polymer Coalesced with 35 PHR Butyl Cellosolve Coalescent

Drying Time Determination— Water-Based Coatings

As with solvent-based coatings, water-based coatings may be evaluated using the ADDTR. However, we found the behavior of water-based coatings to depend upon the type of polymer and film formation process.

Figure 16 displays a 4-hour drying trace of coating film consisting of an acrylonitrile-modified core-shell polymer designed for wood applications, coalesced with 35 PHR ethylene glycol mono-butyl ether cosolvent. The trace displays a number of drying time events. Figure 17 displays the ADDTR drying profile for the drying trace of Figure 16.

The ADDTR drying profile confirms a significant number of drying time events in the film as it is drying. The fall-off between 140 mm and 150 mm in Figure 17 is where the probe transitions from the drying film to the surface of the glass substrate. The significant number of drying time events displayed in Figures 16 and 17 is likely due to the complexity of the film formation process of water-based coatings,[12-14] as well as the tenderness of the film in the early stages of drying. The film shows a significant drying time event at about 43 mm (~75 minutes), but does not dry hard until about 93 mm (~ 2 hours, 40 minutes). Figure 18 displays an overlay of the ADDTR drying profile (green curve) for this sample with the EDOT drying profile (blue curves and symbols).

In Figure 18, storage modulus is represented by the square symbols, loss modulus by triangles, complex viscosity by circles, and loss tangent by diamond symbols. Crossover between the storage modulus and the loss modulus is shown by the red symbols. Referring to Figure 18, whereas the crossover point appears to be associated with tack-free time for solvent-based coatings, this does not appear to be the case for this water-based coating.

Storage modulus-loss modulus crossover occurs at about 19.3 minutes, well before 75 minutes where the ADDTR shows the beginning of a peak-type drying event. It is further seen that the sol-gel point is associated with a dramatic rise in sample viscosity.

In water-based coatings, the crossover point can be associated with a change in rheology of the coating system; that is, a pseudoplastic rheology modifier may impact the rheology of the coating and hence the observed sol-gel point. In some cases, depending upon the coating composition (polymer, cosolvent, rheology modifier), the coating may not display a sol-gel crossover point at all since the measured storage modulus may always be greater than the loss modulus throughout the early coating drying times; clearly, the coating is not tack-free immediately after application in those cases. Hence, the ADDTR may give a better indication of tack-free time in those cases.

It is worth noting that the tan delta value displayed by EDOT at 75 minutes is about 0.488; tan delta at the dry-hard

time (approximately 2 hours, 40 minutes) is shown to be about 0.27 for this sample. These tan delta values are much lower for this water-based sample than for the VT-modified SB alkyd sample discussed previously. This is not entirely unexpected as the overall hardness of the water-based sample is greater than that of the solvent-based alkyd.

Also, separate visual analysis of a water-based drying film indicates that at about the 1 hour, 15 minutes timeframe, there appears to be a slight skinning of the sample and may be the reason the ADDTR profile shows multiple peaks in this region. Further visual examination of the drying

trace indicates a dry-through time of about 170 minutes (tan delta about 0.26).

Figure 19 compares the impact of coalescent hydrophobicity (from the standpoint of water solubility) on the film formation process of the acrylonitrile-modified core-shell lacquer, and hence drying profile, comparing the impact of 100% water, 35 PHR ethylene glycol monobutyl ether, 35 PHR propylene glycol butyl ether, and alkyl acetate 700.

Each of the coalescents have approximately equivalent relative evaporation rates. *Figure 19* shows that addition of coalescent shortens tack-free time relative to water, and that the more

hydrophobic the coalescent, the earlier tack-free time is reached. Assuming that the more hydrophobic coalescent in this case results in better film formation, the results indicate that better film formation led to earlier drying times.

Further, the data show that as the hydrophobicity of the coalescent increases, the number of drying time events, in terms of extraneous peaks in the drying profile, decrease. EDOT drying profiles for these films also show that as the coalescent hydrophobicity increases, the time-to-sol-gel transition (crossover) decreases and the time at which the complex modulus begins to increase also decreases.

Taking all these results together, it is hypothesized that the film formation process is actually further along at an earlier time, even before application of the wet coating, as the hydrophobicity of the coalescent increases. This is consistent with Taylor's[14] findings and postulate, that if the difference between ambient and T_g of a latex polymer-based film is > 50 °C, polymer interdiffusion is essentially complete before the onset of diffusion-controlled evaporation of the filming aid utilized in the coating.

It is expected that the more hydrophobic the filming aid utilized here, the more it lowers the T_g of the polymer. An interesting result (not shown) is that during initial drying, up to about 20 to 30 minutes, complex modulus (considered a measure of stiffness) of the films as shown by EDOT, follows the order: alkyl acetate 700 > water ≈ PnB > EB. Water quickly transitions to the greatest complex modulus at about 40 to 45 minutes drying time, followed by PnB while the film modified with alkyl acetate 700 transitions to the film with the lowest complex modulus at about 70 to 75 minutes. After about 23 to 24 hours air dry, the order of complex modulus is water ≥ PnB > EB > alkyl acetate 700.

The results indicate that PnB displays an interesting combination of early water release, early film formation, with good final film stiffness.

Hardness Testing of Films

Hardness and/or toughness of films may be evaluated by changing the stylus and probe of the ADDTR and adding the capability to progressively control and load a normal force to the sample. For these tests, the instrument was equipped with a loop stylus at an angle of 45-degrees from normal. A progressively loaded normal force was applied to the sample approximately over the tip of the stylus at a controlled rate of

FIGURE 20—Hardness Development of Long Oil Linseed Alkyd as a Function of Time
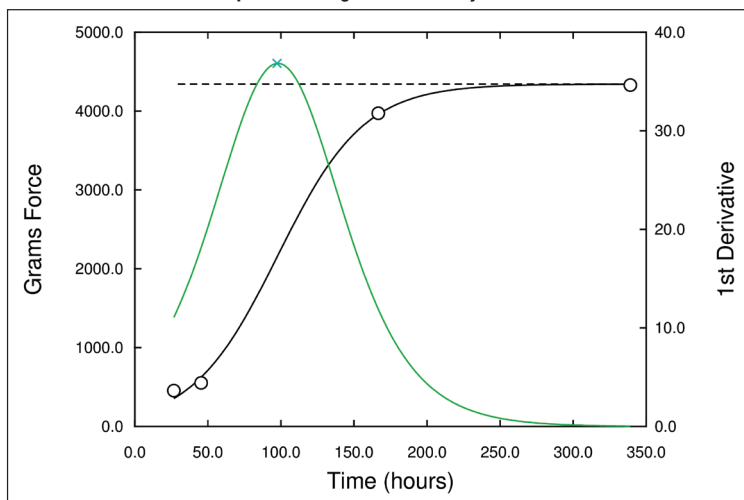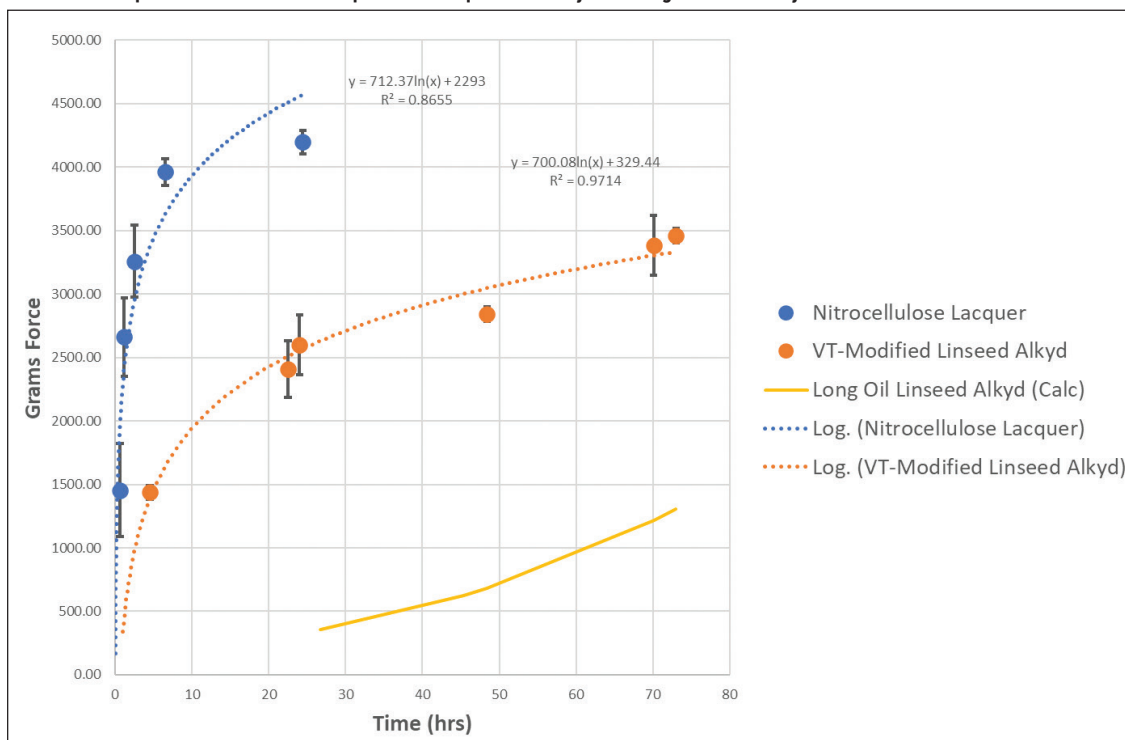

FIGURE 21—Comparison of Hardness Development NC Lacquer vs. VT Alkyd and Long Oil Linseed Alkyd

loading. Any deviation of the stylus distance from the position of the normal force load was accounted for to calculate a calculated load applied to the sample.

However, in these tests we did not account for any change in stylus distance due to bending of the stylus and probe under load. We found the stylus and probe to bend as much as 0.505 ± 0.025 mm at 50.228 ± 0.011 N actual load, whereas the stylus alone was found to bend 0.422 ± 0.008 mm at 50.309 ± 0.007 N.

The net result of stylus bending in the methodology utilized is a very slight decrease in calculated loads. The sample was moved relative to the probe such that probe simulates being pulled across the sample surface rather than being pushed across the sample surface. Although the direction of testing may be reversed, the stated configuration mitigates the probe digging into the surface

of the sample, especially should one be testing on a wood substrate.

Figure 20 displays hardness measurements as a function of time on the long oil alkyd previously referenced in *Figure 11* utilizing the ADDTR in progressive mode hardness testing with the loop stylus. The circle symbols represent the average of two runs per test, utilizing complete failure/removal of the film as the failure criteria. The solid black line is a logistic growth curve fit of the data.

A freely available program called Simfit was used to fit the growth model. Simfit is a simulation, fitting, statistics, and plotting software created by Dr. W.G Bardsley of the University of Manchester, UK, and is available at *https://simfit.org.uk*[15]. The equation fit to the data is $F(x) = A/(1 + B \exp(-kt))$ (r2 = 0.9989); the horizontal dashed line is the maximum predicted force asymptote, A (4343.6 grams force);

$B = A/(S_0-1)$, (27.732), where S_0 is the predicted initial force (157.6 grams force); t is time and k is the rate constant (0.033933).

The green curve is the first derivative and the cross indicates the maximum in the first derivative curve. $t_{1/2}$ for the sample is found to be 97.9 hours. Essentially the data indicates that it requires about 14 days cure for the coating to reach its minimum hardness growth rate. We used the equation for the long oil alkyd to predict hardness development for this product at short timeframes so a hardness development comparison as a function of time could be made to the nitrocellulose lacquer and the VT-modified alkyd referenced in *Figures 11* and *12* (all from the standpoint of complete removal failure criteria).

The result is displayed in *Figure 21*. Error bars in *Figure 21* are ± standard deviation for each measurement. As can be seen from the data, the VT-modified alkyd develops initial hardness much faster than the long oil alkyd; however, the regression equation still predicts that it will require about 12 days for the VT-modified alkyd to reach a hardness of about 4300 grams; conversely, as expected, the nitrocellulose lacquer is most rapid in its rate of hardness development, appearing to reach its full cure in less than 24 hours.

Figure 22 displays hardness testing results of a commercial acid catalyzed varnish as a function of time out of the cure oven. The results are displayed as a function of two failure criteria, stick-slip (black circle symbols), and failure by cracking of the finish (green diamond symbols). Each data point displayed is the average of two progressive load test. Stick-slip failure was fitted to a monomolecular growth model (solid black line), while cracking failure was fitted to a Gompertz plus constant growth model (green dashed line); the lavender dash-dotted line represents the asymptote for the cracking failure model but happens to be that for the stick-slip model as well.

The representative models and calculated parameters for the curves of *Figure 22* are shown in *Table 1*. As can be seen in the figure, stick-slip failure occurs before cracking failure and may indicate the linear viscoelastic limit of the sample. The difference between the two curves may indicate a ductile limit failure envelope before catastrophic failure by cracking.

FIGURE 22—Hardness Development of Acid Cure Varnish as a Function of Time Out Oven
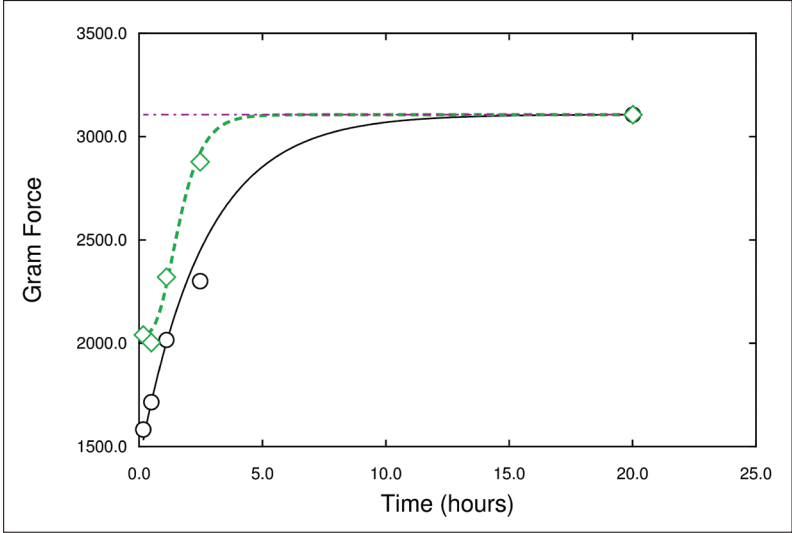
TABLE 1—Calculated Parameters for Representative Models of *Figure 22*

Failure Criteria Evaluated	Model Fitted	R²	Parameter	Parameter Value	Calculated Parameter Standard Error	Max. Observed Growth Rate	Time when Max Growth Rate Observed
Stick-Slip	S(t) = A/(1 - Be⁽⁻ᵏᵗ⁾); B = 1-(S₀/A)	0.9866	A	3107.6	1.3	596.4	0.17
			B	0.54	0.0085		
			K	0.38	0.032		
			t-half	0.20	0.024		
Cracking	S(t) = Ae⁽⁻ᴮᵉ⁽⁻ᵏᵗ⁾⁾ + C B = log(A/S₀)	0.9938	A	1069.4	13.1	542.1	1.11
			B	7.73	5.50		
			K	1.50	0.55		
			C	2037.4	12.7		

It can be seen that eventually, stick-slip and cracking approach the same failure load at some point in the cure profile. According to *Figure 22*, the varnish develops properties very rapidly once it exits the force dry cure cycle which consisted of 5 minutes at 95 °F followed by 5 minutes at 150 °F air temperature. Before exposure to the oven, measurement of the sample resulted in a value of ~395 gram force. Including this data point and modeling the data relative to "Time of Drawdown" resulted in both the stick-slip and cracking data sets being fit by a Richards model with m < 1 (not shown).

Figure 23 compares hardness development determined by the ADDTR in progressive loading mode for the nitrocellulose lacquer referenced in *Figures 12* and *13*, versus the water-based acrylonitrile-modified core-shell polymer referenced in *Figures 16–19*.

It is clear from examining the data of *Figures 12, 13, 16,* and *19* that the solvent-based lacquer dries faster than the water-based products. Further, the data of *Figure 23* shows that the solvent-based lacquer (black circle symbols) has the fastest hardness development by this method.

Although the butyl glycol modified water-based lacquer (green square symbols) shows good initial hardness development, the data indicates that its hardness development does not increase substantially over the 24-hour period.

We found the film based on butyl glycol to display some cracking phenomenon during drying, and during testing, the film displayed tearing. Because the test evaluates a combination of hardness, toughness, and adhesion, its performance is poorer due to presumed poorer film formation and hence poor film integrity, and/or a weak film.

The water-based lacquer modified with PnB filming aid (inverted blue triangle symbols) shows the next fastest hardness development, with its ultimate hardness slightly surpassing that of the solvent-based lacquer. Overall, the PnB-modified film behaves most like the solvent-based lacquer.

Finally, the alkyl acetate 700 cosolvent (red half-triangle symbols) displays the slowest initial hardness development, but its final overall film integrity appears to be greater as it yields the greatest gram force at 24 hours air dry.

FIGURE 23—Hardness Development of Solvent-based Lacquer vs. Water-based Lacquer Modified with Various Filming Aids
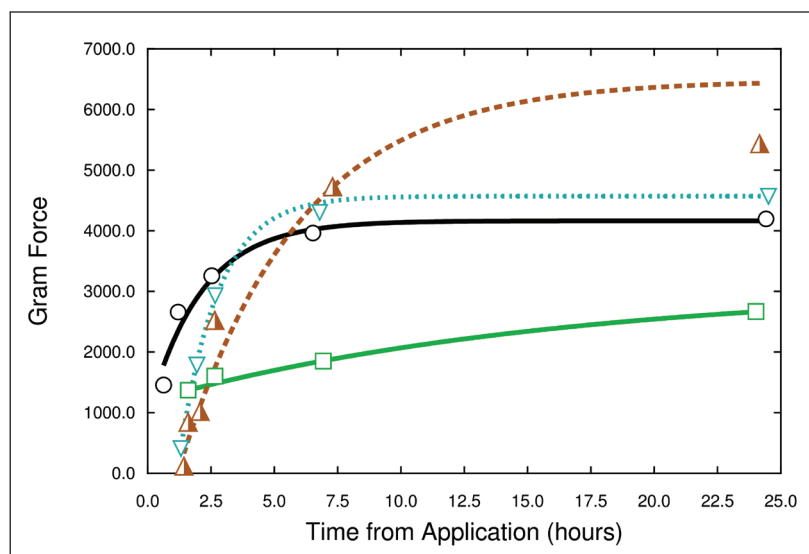
This result indicates an overall greater quality of film formation for this sample. Each data set was evaluated with complete removal of the sample from the substrate as the failure criteria, and modeled utilizing a monomolecular growth model of the form

$$S(t) = A/(1 - Be^{(-kt)})$$

$$\text{Where } B = 1-(S_0/A)$$

All the data is modeled reasonably well by this growth model for each of the samples except for the alkyl acetate 700 modified water-based lacquer, which resulted in the poorest correlation coefficient. *Table 2* details the model parameters for each of the fits.

Figure 24 displays scrape-adhesion results of four commercial coating systems on maple veneer or solids utilizing the ADDTR in progressive normal force loading mode as described above. The results are displayed as the average of several runs.

The number of runs and respective coefficient of variation for the testing is as follows: for the failed acid cure system, n=12, COV=7.3%; for the non-failed acid cure system, n=3, COV=1.3%; for the roll coat UV system, n=5, COV=24.4, and for the precatalyzed lacquer system n=5, COV=9.1%. Error bars are ± standard deviation for each measurement result. The results show that the UV system has the poorest adhesion while the non-failed acid cure, and the precatalyzed lacquer systems, display the best adhesion.

CONCLUSIONS

The method presented here holds promise to directly and systematically evaluate the impact of formulation variables on film formation, drying, curing, hardness development, toughness, and adhesion.

The ADDTR appears to be a versatile instrument that can be utilized to characterize drying, curing, hardness, toughness, and adhesion of paints, coatings, and adhesives.

For example, the drying time recorder may be used to analytically characterize tack-free times and dry-hard times of coatings. In terms of drying time, the instrument is based on the principle that as the coating is drying, the viscosity and complex modulus of the drying film changes.

A probe, having been inserted into the wet film pushes the wet film in front of its path. While the film is wet, the wet film flows back over the path of the probe. At some point in the drying process, the viscosity and modulus of the film increases to the point where the film "piles up" in front of the probe; when the viscosity and modulus reaches a point that the film can no longer be piled up in front of the probe, the height of the probe is forced up the built-up pile, and eventually when the film reaches the dry-hard state and is no longer "sticky" the probe descends over the back side of the built-up pile onto the surface of the dry-hard film.

TABLE 2—Calculated Monomolecular Growth Model Parameters for Each of the Samples of *Figure 23;* **Failure Criteria— Force at Complete Removal of Film from Substrate**

Sample	Symbol, Fit Line Type, and Color	R^2	Parameter	Parameter Value	Calculated Parameter Standard Error	Max. Observed Growth Rate	Time when Max Growth Rate Observed
Solvent Based NC Lacquer	Black Circle; Solid Black Line	0.9586	A	4165.1	90.9	1142.3	0.63
			B	0.77	0.14		
			K	0.48	0.14		
			t-half	0.91	0.25		
Butyl Glycol Modified Water Based Lacquer	Green Square; Solid Green Line	0.9899	A	3099.3	439.3	106.4	1.60
			B	0.62	0.049		
			K	0.062	0.022		
			t-half	3.36	2.44		
PnB Modified Water Based Lacquer	Inverted Blue Triangle; Dotted Blue Line	0.9981	A	4571.5	36.6	2749.8	1.31
			B	2.16	0.058		
			K	0.66	0.021		
			t-half	2.22	0.029		
Alkyl Acetate 700 Modified Water Based Lacquer	Red Half-Triangle; Dashed Red Line	0.9544	A	6483.7	2755.2	1310.4	1.43
			B	1.29	0.33		
			K	0.21	0.18		
			t-half	4.44	2.57		

FIGURE 24—Scrape Adhesion Results for Several Commercial Coating Systems Determined with ADDTR in Progressive Loading Model
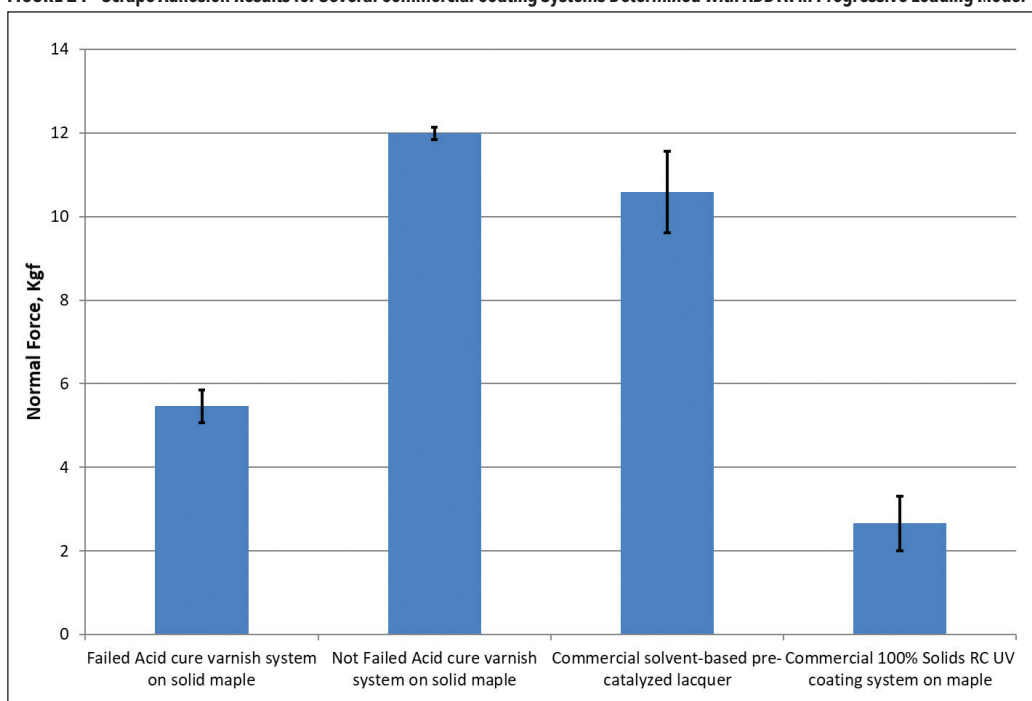
The instrument monitors the height of the probe as a function of time and travel distance, and the drying process just described results in a "drying event peak." Further, the breath of the peak indicates the "stickiness" of the sample after the tack-free time. Data on solvent-based alkyds, solvent-based acid cure varnish, and solvent-based nitrocellulose lacquer demonstrate that the instrument characterizes drying of these coating systems.

Water-based coatings may be characterized as well. In fact, it is shown that coalescent has a dramatic impact on the drying process and that more hydrophobic filming aids appear to coalesce the film quicker. It is also found that the drying profile produced by the ADDTR may represent a drying "fingerprint" of the sample.

Changing the probe and stylus and utilizing the instrument in a progressive, normal force-loading mode allows the hardness and/or toughness and adhesion of a drying coating system to be evaluated as a function of time. The adhesion of a finished coating system may also be evaluated.

Because this test takes less than 12 seconds per run and because each run utilizes a very small area per run, multiple runs may be made and statistics obtained, and almost any substrate may be evaluated. ❖

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