High-throughput Experimentation: A Modern Workflow for the Development of Waterborne Wood Coatings

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Introduction

Waterborne Radical Cure Technology

There are many advantages associated with radical cure of coatings: rapid rate of cure, significant energy savings, low/no VOCs, and one-component formulations. However, a disadvantage of solvent-based UV curable resins is their susceptibility to shrinkage, which leads to embrittlement. An interesting alternative exists in waterborne radical cure resins. In general, polyurethane dispersions (PUD) are highly valued for their superior mechanical properties. Coatings from non-functional, fully reacted PUDs tend to be less chemically resistant than solvent-based polyurethane coatings due to the lack of crosslinking. UV-curable PUDs (UV PUD) provide additional strength and chemical resistance from the crosslinking of acrylate functionality built into the urethane backbone. These UV PUDs do not exhibit shrinkage like the corresponding solvent-based radical cure systems can. Thus, they represent a well-balanced blend of mechanical properties and chemical resistance, with the previously mentioned advantages that radical cure offers.[1]

This property balance is important in the wood kitchen cabinet market. Coatings for this industry require resistance to both food ingredients and cleaning products. The appearance of the film is critical; a clear, non-yellow film is required to show the aesthetics of the wood grain. The coating must have the durability to stand up to everyday wear and tear. Acrylic latex formulations are a popular choice for waterborne wood formulations. These resins are typically inexpensive, but generally lack the excellent mechanical properties provided by a PUD. Since both the physical properties and price are important to the formulator, a blend of UV PUD and acrylic latex could offer an ideal solution.

High-Throughput Experimentation

High-throughput experimentation allows the coatings' chemist to screen more combinations than would be possible in a traditional workflow. High-throughput methods in material science[2,3,4] and coatings' laboratories[5,6,7,8] are fast becoming a tool of choice when rapid turnaround and speed to market are desirable. Combined with statistical analysis, a high-throughput screening (HTS) can provide trends and suggest optimal formulations for further consideration.[9]

In this example, the high-throughput screening of UV PUDs and acrylic latexes allowed for the study of multiple blend ratios which would have been difficult using traditional means of analysis. The experimental space consisted of four UV PUDs from Bayer MaterialScience and four commercial acrylic latexes. Five blend ratios were used, thus 56 unique formulation blends were prepared. Each waterborne blend was assessed for four different properties: chemical resistance, appearance, hardness, and mustard staining. Including replicates, over 1,700 measurements were taken during the course of this study.

Results and Discussion

All samples were diluted to 40% solids by the addition of water drop-wise while stirring. The following blends of UV PUD and acrylic latexes were prepared (UV PUD: acrylic latex based on volume): 100/0, 75/25, 50/50, 25/75, and 0/100.

After casting films with liquid handling technology onto various substrates, the samples were allowed to air-dry in a dark place for 15 hours. Once the water was removed, the samples were UV cured with 800mJ/cm^2 of energy from a mercury bulb.[10] After UV irradiation all samples were stored for 24 hours to allow for any post-cure that might occur.

Chemical Resistance

A library of coatings, each doped with a fluorescent dye, was assessed for chemical resistance using liquid handling technology.[11] The chemical resistance of the dye-doped films was determined by swelling the cured films with ethanol/water. The dye escapes into the extractant solution to a degree dependant upon the swelling of the film. The extractant solution exhibits high fluorescence intensity when the film has poor chemical resistance.[12]

Figure 1 below shows the average performance of each combination of UV PUD and acrylic. Several trends are immediately evident. Three of the four UV PUD materials showed superior chemical resistance. In general, the acrylic latexes were less resistant than the UV PUDs. Figure 1 suggests that the addition of certain UV PUDs into an acrylic latex can improve chemical resistance versus the straight latex. The amount of improvement was dependent on the UV PUD or acrylic chosen. A separate statistical analysis of the dataset[13] indicated that the most important variable for generating response variation was the composition of the UV PUD.

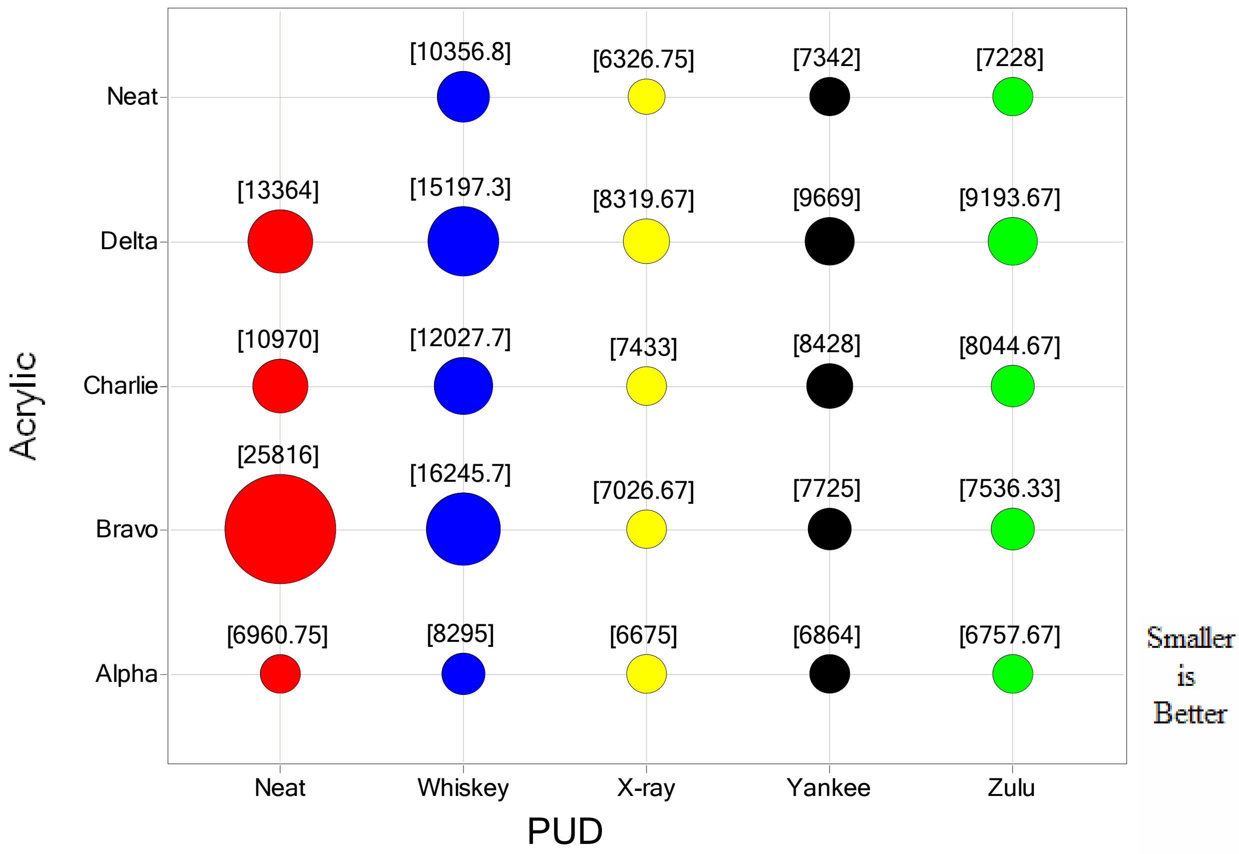

Figure 1 Average Chemical Resistance of UV PUDs, Commercial Acrylic Latexes, and Their Blends. The numbers above the markers indicate the average fluorescence of formulations with the composition indicated. A lower value suggests a better performance. The "neat" column consists of the straight acrylic latexes, and the "neat" row consists of the straight UV PUDs.

Figure 1 also suggests that the acrylic latex with the least chemical resistance is acrylic Bravo. A more detailed look at blends with this particular acrylic latex is shown in Figure 2. As the amount of UV PUD was increased, the chemical resistance of this acrylic latex improved. The level at which this improvement levels out was dependent on the UV PUD chosen. The composition of the UV PUD also determined the amount of improvement.

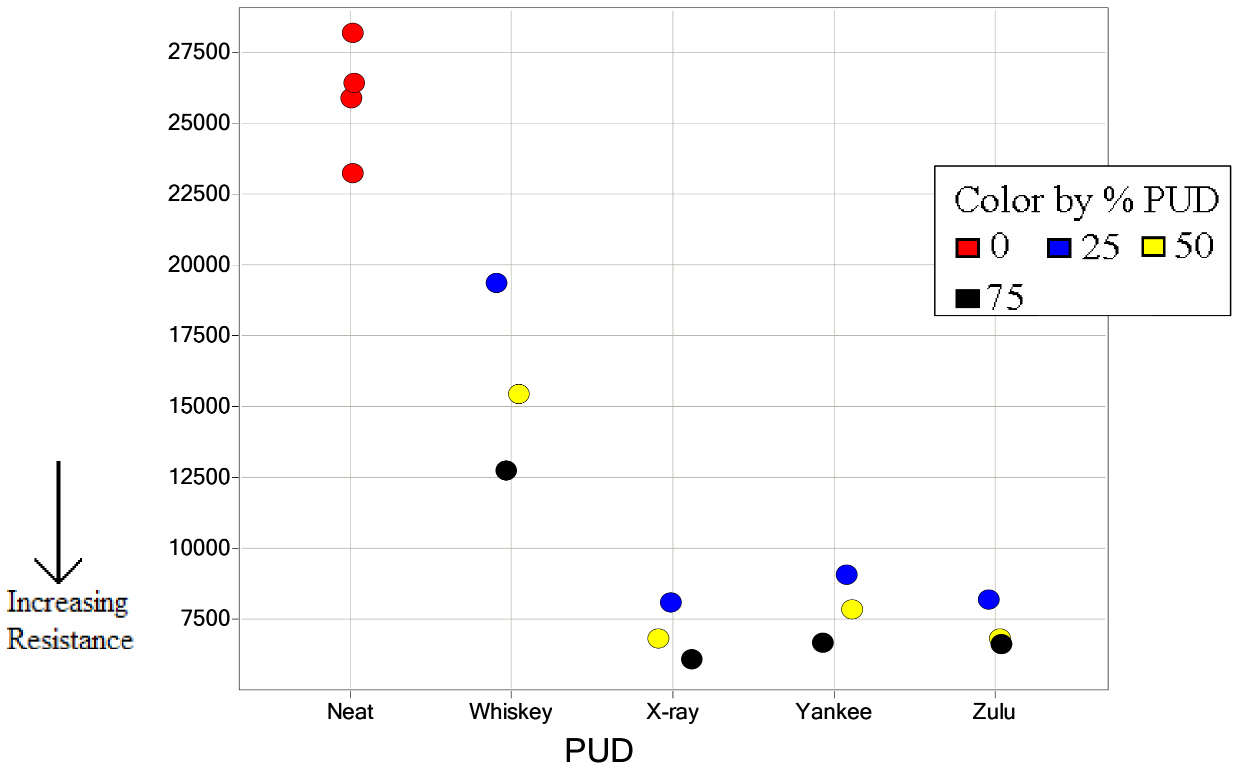

Figure 2 Chemical Resistance for Acrylic Bravo as a Function of UV PUD Type and Amount. The y-axis is the fluorescence intensity in the extractant solution. A high value indicates poor chemical resistance. The x-axis is the UV PUD blend partner for Acrylic Bravo. The color of the marker reflects the amount of UV PUD in the blend as shown on the legend.

Appearance

Incompatibility between a PUD and acrylic latex can be quite common and will often manifest in hazy films. High-throughput light scattering was used to monitor for haze and resin incompatibilities.[14] A cloudy film scatters light, causing a reduction in percent transmittance through the film. The data in Figure 3 shows that most coating blends are clear, having a transmittance greater than 92%. Acrylic latexes Bravo and Delta when used alone with no cosolvent did not form good films. For these latexes, the addition of a UV PUD improved the appearance.

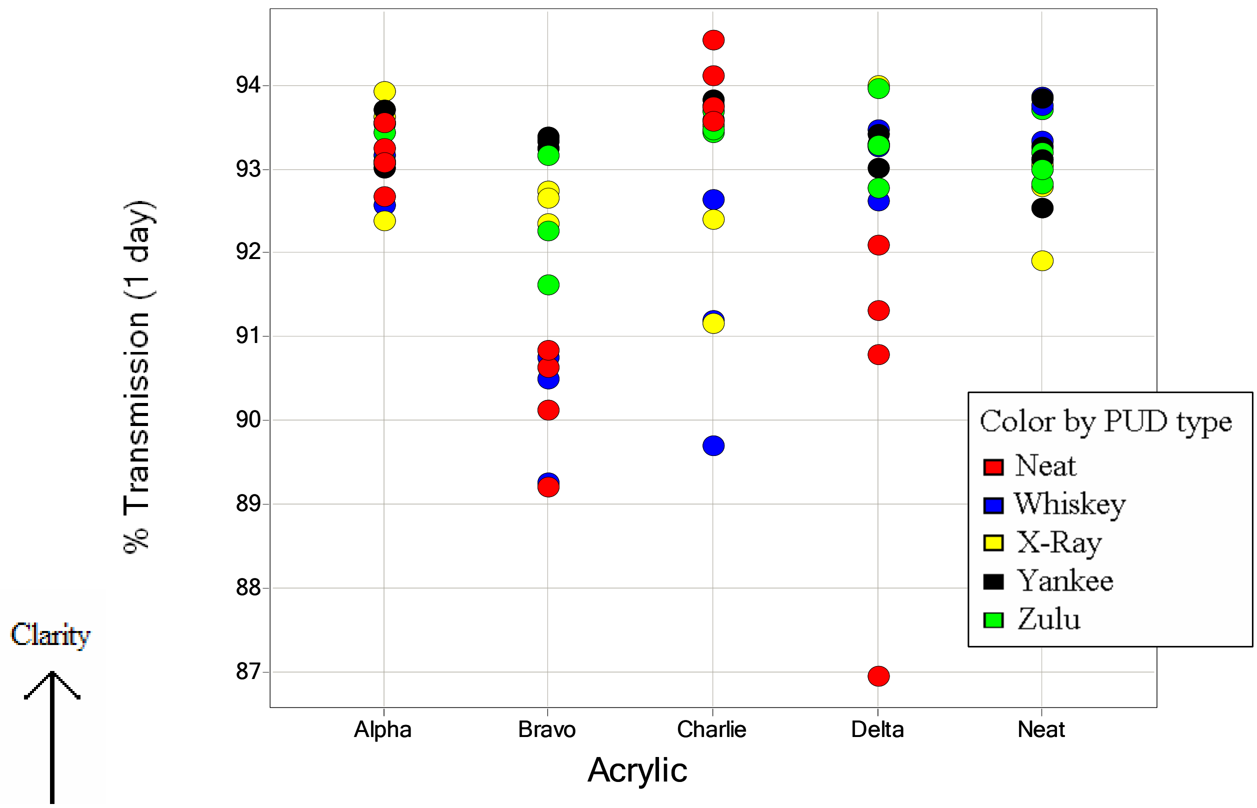

Figure 3 Percent Transmittance of Light Through UV PUDs, Commercial Acrylics, and Their Blends One Day After Preparation. The y-axis is the percent of light transmitted through the film to the detector. Values close to 100% are clear films. The color of the marker represents the PUD component of the blend, as shown in the legend above. The "neat" column consists of straight UV PUDs, and the "neat" red markers are straight acrylic latexes.

Radical cure formulations must contain photoinitiators which often absorb light in the visible spectrum. This can make these formulations yellow, particularly at high photoinitiator concentrations. The color of the cured films in this study was determined by high-throughput absorbance spectroscopy.[15] Figure 4 indicates that there were no yellow films prepared from these blend formulations. The only formulations with poor results are ones where film formation suffers.

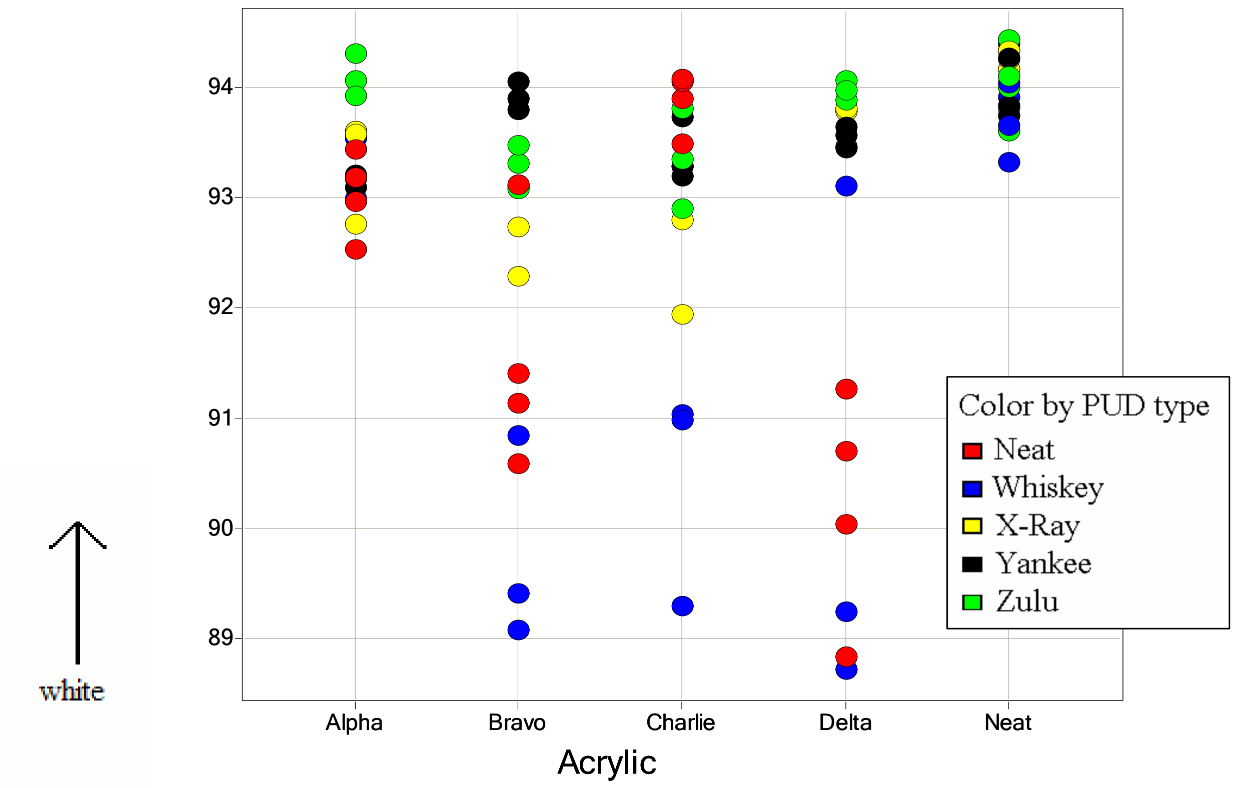

Figure 4 Yellowness Index of UV PUDs, Commercial Acrylics, and Their Blends. The y-axis is the colorimetric variable L, where L=100 for a white standard. The color of the marker represents the PUD component of the blend, as shown in the legend above. The "neat" column consists of straight UV PUDs, and the "neat" red markers are straight acrylic latexes.

Mustard Staining

High-throughput absorbance spectroscopy[11] was also used to examine the staining capability of yellow mustard. Yellow mustard is considered to be one of the most aggressive staining materials in food products on the market. In fact, the Kitchen Cabinet Manufacturer's Association (KCMA) requires testing for mustard staining in order for a cabinet to receive the KCMA certification seal.[16] To determine the stain resistance of the blend library, mustard was applied to each sample for 24 hours, then rinsed off the surface and toweled dry. The residual yellowness was calculated from the absorbance spectrum[17] immediately after the removal of the mustard (Figure 5) as well as 24 hours after removal (Figure 6). The immediate assessment shown in Figure 5 suggests that the UV PUDs are more susceptible to staining than the acrylic latexes. However, Figure 6 shows that most formulations become colorless again after 24 hours of aging. There were a few blend compositions with UV PUD Whiskey that appeared to have a problem with persistent mustard staining. On its own, this UV PUD did not suffer from persistent staining.

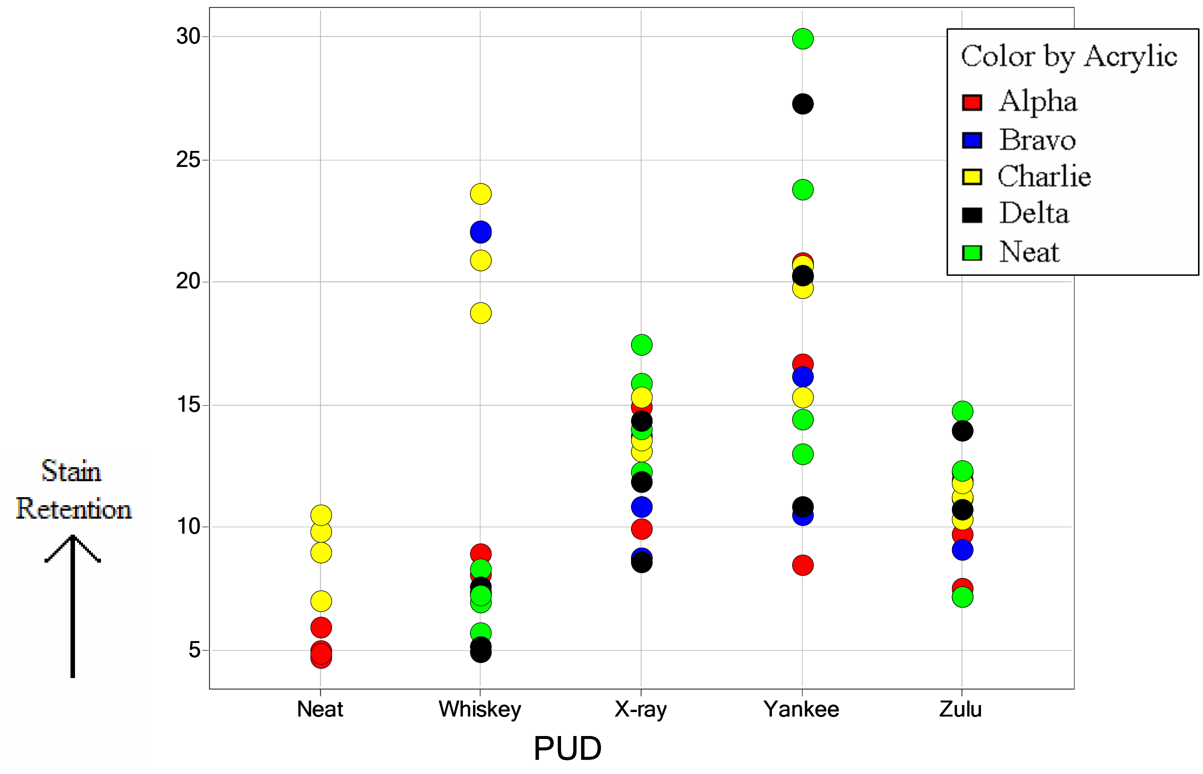

Figure 5 Yellowness Index UV PUDs, Commercial Acrylics, and Their Blends Immediately After Mustard Removal. The y-axis is a yellowness index, where lower yellowness index values are closest to colorless. The color of the marker represents the acrylic latex component of the blend, as shown in the legend above. The "neat" column consists of the straight acrylic latexes, and the "neat" red markers are straight UV PUDs.

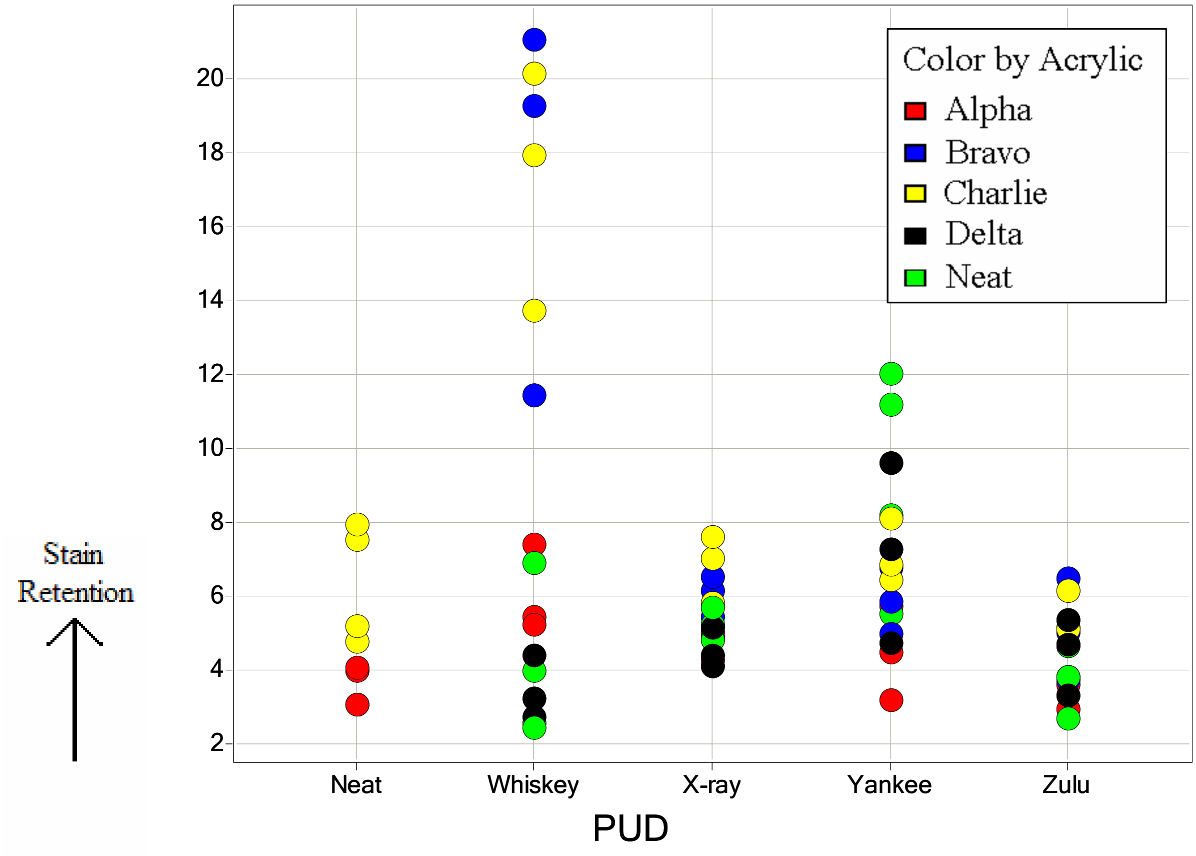

Figure 6 Yellowness Index UV PUDs, Commercial Acrylics, and Their Blends 24 Hours After Mustard Removal. The y-axis is a yellowness index, where lower yellowness index values are closest to colorless. The color of the marker represents the acrylic latex component of the blend, as shown in the legend above. The "neat" column consists of the straight acrylic latexes, and the "neat" red markers are straight UV PUDs. Note scale change from plot above.

Hardness

Automated microindentation was used to determine coatings' physical properties. With microindentation a diamond-head indenter contacts the film's surface with a known force in the z-direction.[18] The microhardness is determined from the applied force versus penetration area profile. Figure 7 shows the average hardness for all blend compositions. It was not possible to measure the hardness of straight acrylic latexes Delta and Bravo since film formation without cosolvent was problematic. For the particular components in this study, the UV PUDs tended to be harder than the acrylic latexes, with the exception of UV PUD Yankee. A statistical analysis of the dataset[13] indicated that the most important variable for generating response variation was the identity of the UV PUD.

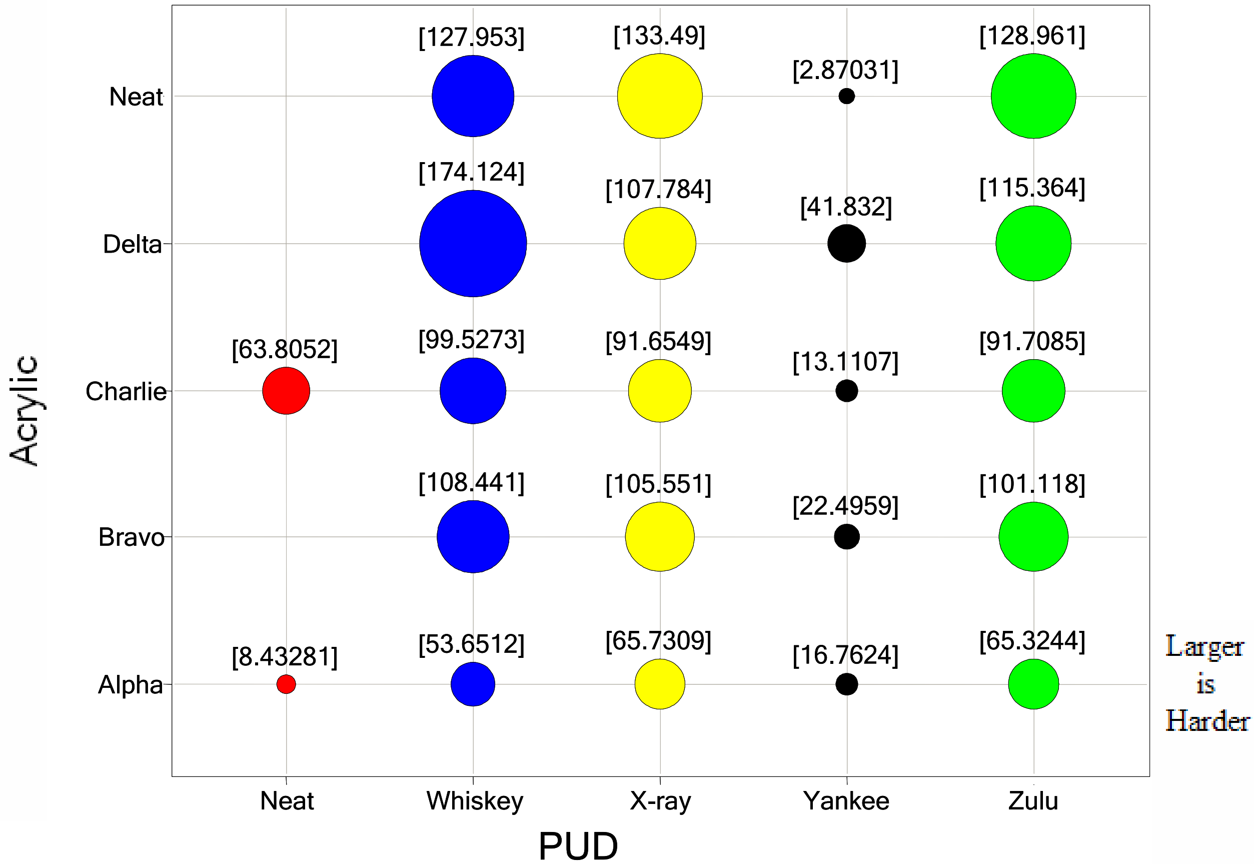

Figure 7 Average Hardness of UV PUDs, Commercial Acrylic Latexes, and Their Blends. The numbers above the markers indicate the average hardness of formulations with the composition indicated. A higher value suggests a harder film. The "neat" column consists of the straight acrylic latexes, and the "neat" row consists of the straight UV PUDs.

Figure 8 shows a more detailed view of blends with the UV PUD X-Ray. This UV PUD increased the coating's hardness in all acrylic blends. Figure 8 also suggests that there may be a point of diminishing returns where further UV PUD addition did not confer additional hardness. This point was dependent on the particular UV PUD and acrylic latex in the blend.

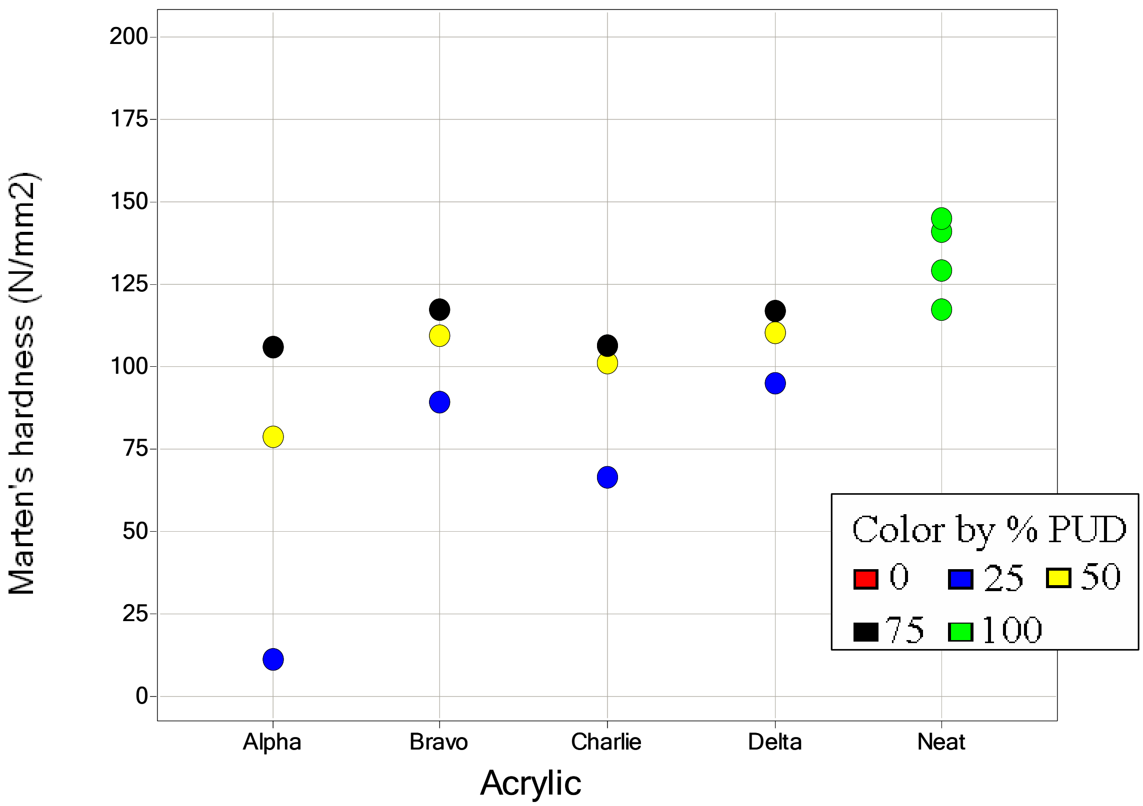

Figure 8 Hardness for PUD X-Ray as a Function of Acrylic Type and Amount. The color of the marker reflects the amount of UV PUD in the blend as shown on the legend. The "neat" column consists of straight UV PUDs, and the "neat" red markers are straight acrylic latexes.

Conclusions

A high-throughput screening workflow made it possible to screen UV PUD/acrylic latex blends for performance in the wood kitchen cabinet market. Information obtained in this experiment can be used to tailor the desired material characteristics to fit within a certain price range. For every application, the required property set is different. The visualizations above are helpful to the coatings' formulator in the search for optimum resin and cost combinations.

Within this range of products it was noted that the addition of a UV PUD to an acrylic latex typically increased the hardness and chemical resistance over the straight acrylic. It was the UV PUD component that most affected these properties in blended formulations. The appearance of the blends was typically satisfactory. For those acrylic latexes that formed poor films by themselves, the addition of UV PUD aided coalescence. Some UV PUD/acrylic blends did show a tendency to stain on exposure to yellow mustard, but the stains faded rapidly after removal of the mustard in almost all instances.

Acknowledgements

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15 With ColorEye® XTH from GretagMacbeth®, Ltd., www.gretagmacbeth.com.

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17 ASTM Standard E313-98.

18 With FISCHERSCOPE® H100C XYp, www.fischer-technology.com.