Development of Low-VOC Waterborne Coatings

Derived from Polyurethane Dispersions based on Natural Oil Polyols using High Throughput Methods

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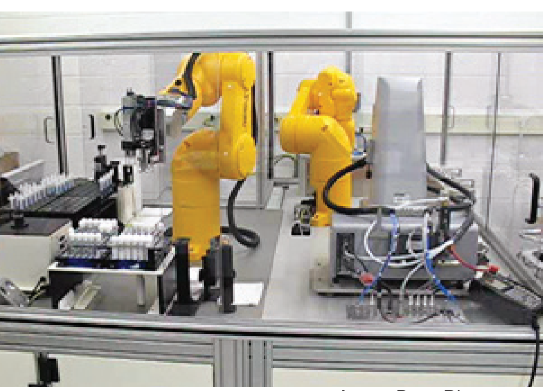
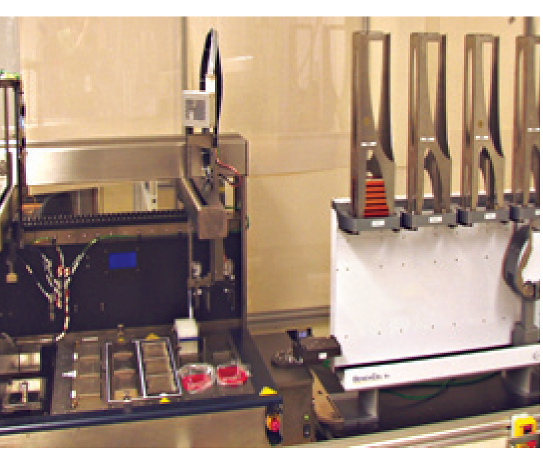
Formulation Robot


Anton Paar Rheometer


Automated Coating Station

INTRODUCTION

Today's coatings market exerts multiple pressures to successfully develop and introduce new coating products. Improving the environmental profile of these new products is a large driver that often requires significantly different formulation strategies. These complex coating formulations offer an excellent opportunity to use the strengths of high-throughput (HT) research[1-3] to understand how interactions between coating components affect final properties.[4,5] Dow has invested considerable effort to develop HT capabilities as a means for developing coatings including waterborne architectural, 1K air-drying, and 2K reactive industrial coatings.[6]

Waterborne polyurethane dispersions (PUDs) derived from natural oil polyester polyols (NOPs) have been developed.[7,8] Coatings made from the NOP-based PUDs have good toughness, abrasion resistance, hydrolytic stability, and acid resistance. They also exhibit superior water uptake (less) relative to competitive PUDs, due to the hydrophobic nature of NOPs.[9,10] Due to emerging VOC regulations such as the South Coast Air Quality Management District (SCAQMD), Dow has recently focused on developing low-VOC PUD coatings for concrete and wood. The basic steps are to develop solvent-free NOP-PUDs that allow formulators to add good cosolvents to produce low-VOC PUD coatings with enhanced properties at a VOC level of <100 g/L. To reach the goal, both the design of solvent-free NOP-PUDs with high performance and the formulation of them with good cosolvents are required. Good cosolvents enable the formation of crack-free films at ambient temperature and enhance end-user properties of PUD coatings at low VOC levels. In addition, solid understanding of mutual interactions between solvent-free PUD properties and solvents provides great flexibility in the design and development of low-VOC PUD coatings.

This article describes how HT research (HTR) capabilities have been utilized for the development of low-VOC NOP-based PUD coatings for wood and concrete applications. The HTR capabilities include statistically designed experiments, HT formulation, coating application, and characterization tools as well as informatics for data visualization, extraction, and modeling. This article begins with a brief introduction of these HTR capabilities and then concludes with use of these capabilities for development of low-VOC NOP-based PUDs.

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Photos courtesy of Dow Coating Materials, Dow Chemical Company.

HTR CAPABILITIES FOR DEVELOPMENT OF COATING FORMULATIONS

HTR developed at Dow is an integrated set of advanced capabilities in hardware and software that allow many more experimental variables to be explored and understood than could be achieved with traditional approaches. Hardware includes material-handling robots (formulation and coating) as well as automated stations for measuring key properties of intermediates and final products to provide the key information for identifying promising products. Software includes HT experimental design, robotic control, data collection, processing, storage, visualization, analysis, and modeling (*Figure* 1).

In coatings, the basic steps are to formulate the materials, make the coatings, and test the dried films. The HTR formulation capabilities cover most coating materials including solids and liquids over a broad range of viscosities. Each coating is coated on various substrates including Leneta paper, steel, aluminum, and wood that are placed in a substrate holder and tracked based on a unique experimental ID attached to the substrate holder via a barcode. The dried films are tested using automated HTR tools, including color, gloss, thickness, tack, friction, scrub resistance, stain resistance, block resistance, and low-temperature coalescence. In addition, wet formulations are tested for pH, colloidal stability, freeze-thaw stability, viscosity, and rheology.

WATERBORNE POLYURETHANE DISPERSIONS DERIVED FROM BIO-RENEWABLE NOPS

Natural oil polyester polyols are prepared from chemically modified fatty acid methyl esters (FAMEs) derived from soy oil. The FAMEs are hydroformylated to the corresponding aldehydes intermediates and subsequently hydrogenated to the primary hydroxyls. The soy monomers are transesterified with a suitable glycol to increase molecular weight and generate the NOPs. The NOPs used in this study possess an average hydroxy functionality of two.

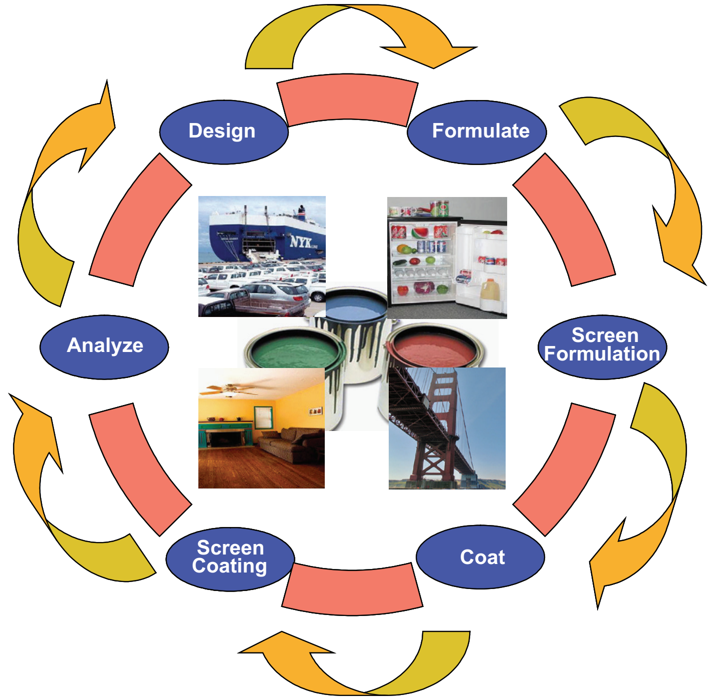

Figure 1—Schematic illustration of HTR coating workflow developed at Dow.

PUDs derived from NOPs are prepared by polycondensation reactions of polyisocyanates and polyols. *Figure* 2 illustrates the structure of NOP-PUDs. Polyols include NOPs, acid-containing diols such as 2,2-bis(hydroxymethyl)propionic acid (DMPA), and optionally short chain diols (SCDs) to enhance the hard segments. To facilitate PU prepolymer synthesis, high boiling point solvents such as Proglyde™ DMM and N-methylpyrrolidone (NMP) or low boiling point solvents such as ketones are often used. They can reduce the viscosity of PU

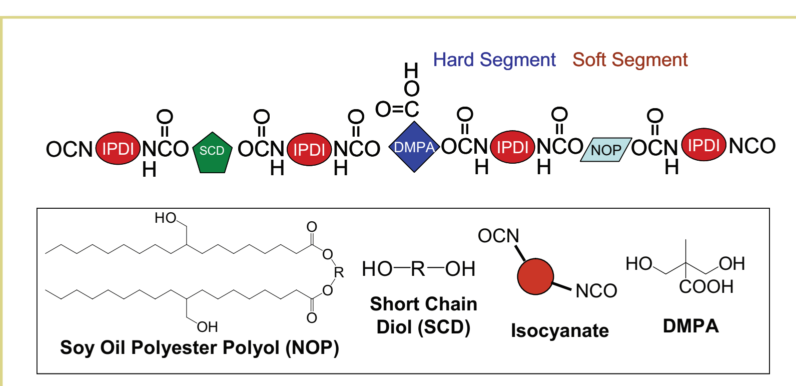

Figure 2—Schematic illustration of the structures of NOP-PUDs.

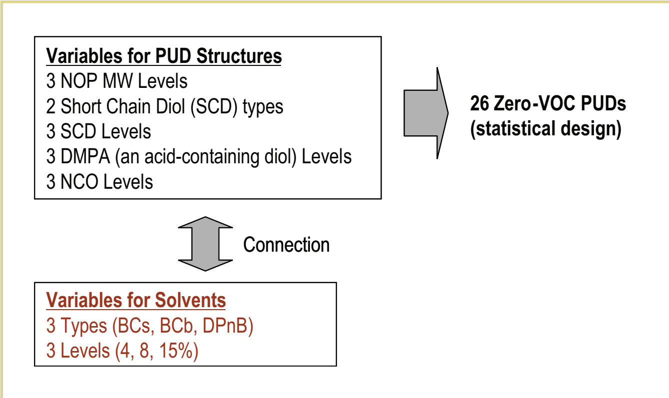

Figure 3—Variables for solvent-free PUDs and solvents in the DOE.

prepolymers and dissolve solid DMPA in reaction mixtures. Sequential steps including neutralization, dispersion, and chain extension yield stable NOP-PUDs with a diameter of 50–150 nm.

EXPERIMENTAL

Scope of HTR Designed Formulation Experiment

Figure 3 illustrates the variables for PUD structures and solvents examined in the statistically designed experiment. Five variables for PUD structures include NOP molecular weight (MW), short chain diol (SCD) type and level, DMPA level, and NCO level. A total of 26 statistically designed solvent-free NOP-PUDs were prepared. For the designed HTR formulation experiment, three types of solvents at three levels (4, 8, and 12 wt% based on PU solids) were tested. Butyl Cellosolve™ Solvent (BCs), Dowanol™ DPnP Glycol Ether (dipropylene glycol n-propyl ether, DPnP), and butyl Carbitol™ Solvent (BCb) are good solvents for NOP-PUDs, having different evaporation rates (*Table* 1). Using the statistical design, a total of 144 DOE formulations were designed, which requires a total of 1488 formulations based on a full-factorial design method. In addition, a PUD with known properties (PUD-Control) was used as a control for the HTR experiment to assess reproducibility of test methods on PUD coatings.

Designs of solvent-free NOP-PUDs and HTR formulations for low-VOC PUD coatings were created using the D-optimal design strategies, in which the number of experiments was minimized to require the fewest experiments possible but yet still be able to study effectively the effects of the input variables of interest. The actual experimental conditions included in the design were chosen based on an algorithm in which an objective function relative to the expected analysis model was optimized. In addition, replicate experiments were added to the plan to enrich the data for statistical analysis and modeling purposes. Once the proposed set of experiments was finalized (including "Controls" and replicates), the suggested experimental runs (144 suggested input conditions) were assigned to the HT library plates in a statistically-friendly way, such as 24 formulations for each library plate. These experiments were assigned to the HT plate positions in such a way as to minimize the amount of potential confounding between the effects of the input variables of interest and any effects associated with HT related variables. This would assure that the results are much less likely not to be biased by other extraneous (blocking) variable effects.

Synthesis of Solvent-free NOP-PUDs by MEK Process

A common process to produce solvent-free PUDs is to use a low boiling point, volatile solvent such as acetone and methyl ethyl ketone (MEK), which is removed from the dispersion by distillation after the completion of PUD synthesis (*Figure* 4). This technique is commonly referred to as the "acetone or MEK process." A drawback of this process is economics. Not only does equipment have to be explosion-proof, but the cost to distill and dry solvent before recycling for next batches or disposing of it by incineration is significant. Additional cost comes from reduction in production output since a significant part of reactor's volume is occupied with removal of solvents.

NOP-based PU prepolymers were first synthesized from polyols including NOPs, SCDs, DMPA, and MEK charged in a round-bottom flask under nitrogen. The mixture was immerged in an oil-bath preset at 70°C. When temperature reached 55–60°C, polyisocyanates were slowly added using a dropping funnel. The mixture was then stirred for 4–5 hr. Samples were taken periodically to measure %NCO and COOH level. When the target values were reached, triethylamine (TEA) was added to neutralize COOH groups of PU prepolymers. The resulting PU prepolymers were dispersed in water under high

Table 1—Characteristics of Glycol Solvents

Glycol Solvents		bp (°C)	Evaporation Rate (n-BuAc = 1)	Solubility in Water (wt%)
BCs	Butyl Cellosolve™ Solvent	170.7	0.079	∞
BCb	Butyl Carbitol™ Solvent	230.4	0.004	∞
DPnP	Dowanol™ DPnP Glycol Ether	213	0.014	19.6

shear, yielding a stable dispersion of PU prepolymers. Chain extender (generally diamine) was added and then MEK was stripped off under vacuum at 50–55°C. The resulting solvent-free NOP-PUDs were characterized with solids content, particle size, pH, residual NCO, viscosity, and minimum film-forming temperature (MFFT). The 26 solvent-free NOP-PUDs synthesized by MEK process had solids content of 30–43%, particle diameter of 60–110 nm, and MFFT of 0–40°C.

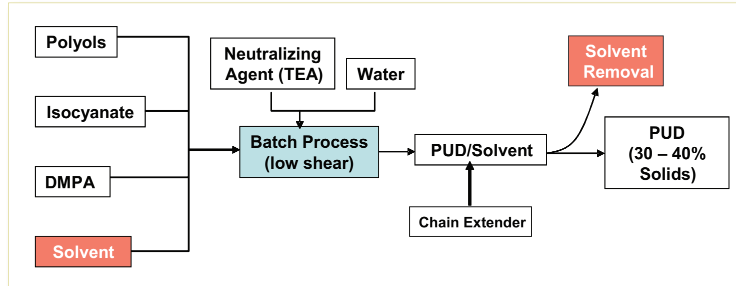

Figure 4—Schematic illustration of batch solvent process for synthesis of solvent-free PUDs using an MEK process.

HTR Workflow Including Formulation, Coating, and Test of Properties

Figure 5 illustrates the HTR workflow for PUD wood coatings used in the experiment. This workflow leverages existing HTR capabilities developed for waterborne architectural coatings and is augmented with manual-type ASTM test methods. The workflow includes the use of the HT Hamilton robot and a conventional shaker for the formulation of PUD coatings. The Hamilton robot was first calibrated for dispensing of all coating components including 26 solvent-free NOP-PUDs, three solvents, and water. The different components exhibited a linear relationship of actual versus target amount with R^2 values higher than 0.99. The resulting calibration file defines detailed aspiration/dispensing conditions, tip used, and calibration results including dispensed/requested weights for each liquid. A weighing robot was also used to determine the actual amount of components to be dispensed in the Hamilton.

Various coatings were applied on the Automated Coating Station using a doctor blade on Leneta paper, aluminum, and primed maple wood with a waterborne primer. Additionally, coatings were manually applied using a #50 drawdown bar (5 mil of wet film thickness) on steel panels.

The films on aluminum substrates were tested for thickness using the HTR Color-Gloss-Thickness (CGT) tool, pendulum hardness using Gardner pendulum hardness tester, universal hardness using HTR microindenter, and chemical resistance. Early water and chemical resistance were evaluated with 5: no effect, 4: slight trace of water, 3: blister, wrinkling, and bubble, 2: corrosion, and 1: coating failure. In addition, the manually prepared films on steel were tested for direct impact resistance using Gardner impact tester with falling weight.

RESULTS AND DISCUSSION

Formulations of Interest

Figure 6 schematically shows the broad distribution of pendulum, universal hardness, impact flexibility, and early water resistance of 128 experimental NOP-PUD coatings in the designed HTR experiment as a function of VOC level corresponding to solvent level. The figure also points to many formulations with enhanced properties at VOC level of <80 g/L desirable for low-VOC PUD wood coatings. They are comparable or superior to a prototype PUD Control formulated with Proglyde DMM at 250

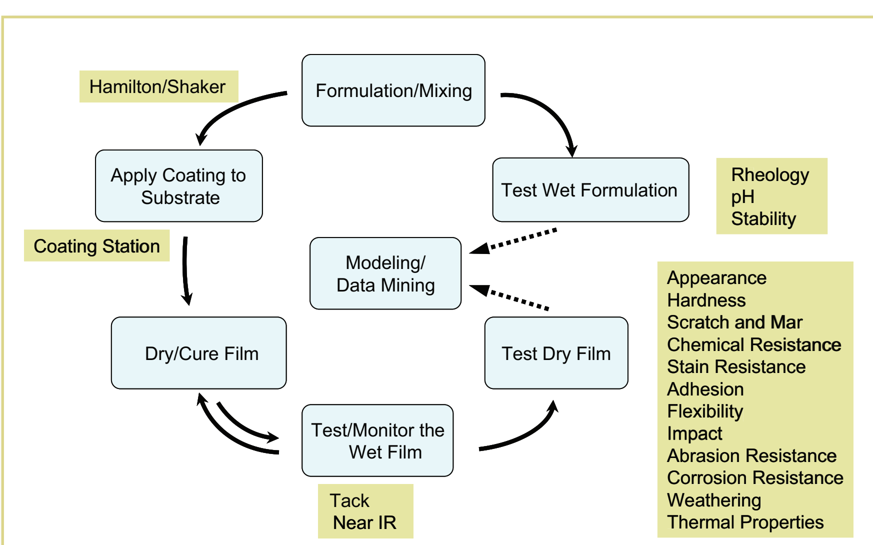

Figure 5—HTR workflow for PUD coatings.

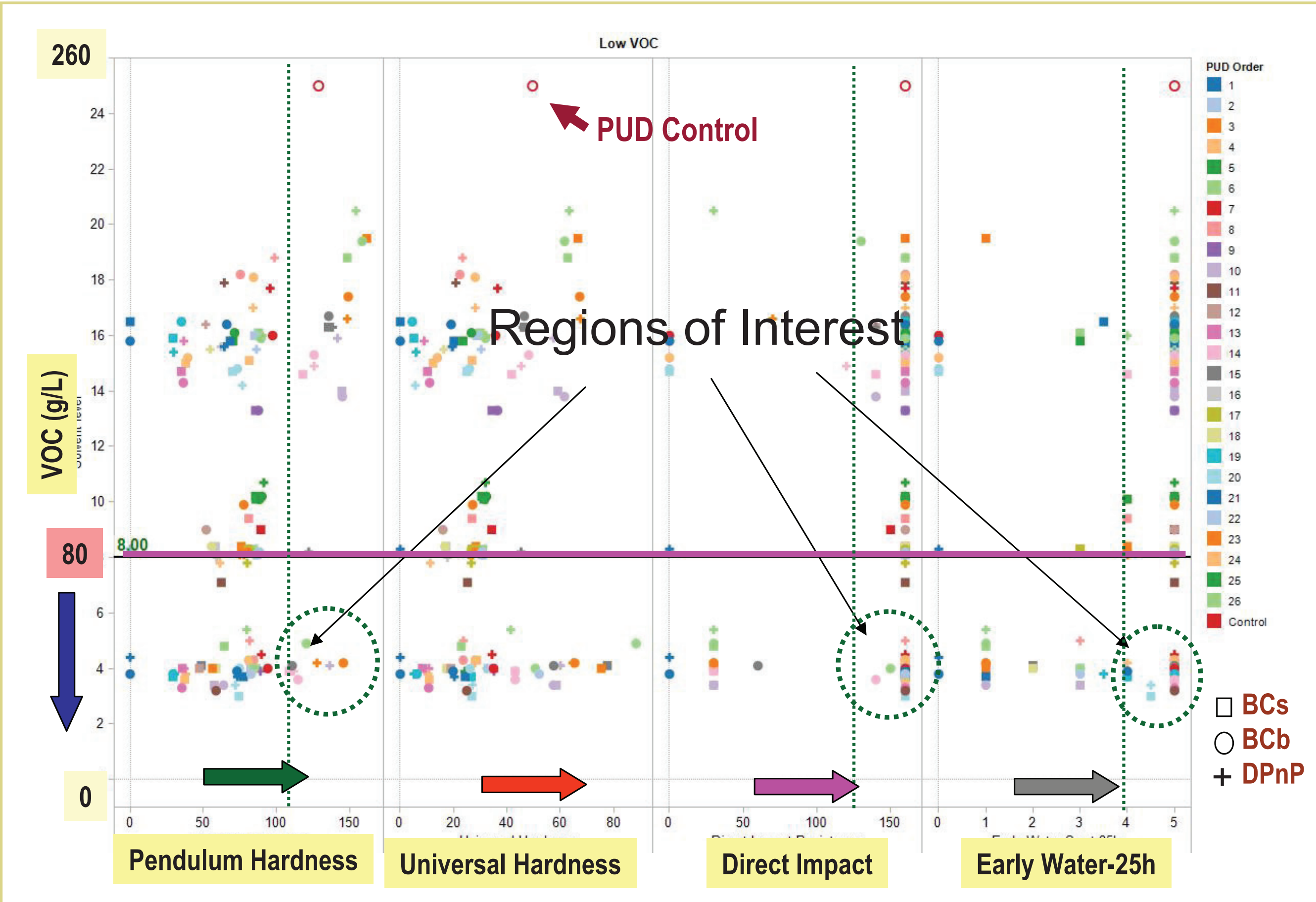

Figure 6—Visual presentation of pendulum, universal hardness, impact, and early water resistance of NOP-PUD coatings as a function of VOC level corresponding to solvent level (% of PU solids). TEA is not included in VOC calculation in the figure. Color represents each NOP-PUD and shape represents glycol solvents.

g/L VOC. The desired properties for wood coating applications include high hardness (>100 sec), good impact flexibility (>120 lb-in.), and good early water resistance (>4). The formulations in dotted circles could meet the requirements for wood coatings at low VOC level of <80 g/L.

Control Analysis: Reproducibility of Data and Test Methods

The designed HTR experiment includes two duplicates of a control (PUD-Control) in each library plate of 24 formulations. The data from the controls were analyzed to get an insight of the plate-to-plate reproducibility of data for the different screens. *Table* 2 summarizes the results. Pendulum hardness of PUD-Control ranged at 120–135 sec, with an average of 125.5 ± 5.6 sec. Universal hardness was 49.3 ± 2.8. In addition, direct impact resistance, early water resistance, chemical resistance of water, and mustard were equivalent ("pass") for the control across all plates. These results suggest that pendulum, universal hardness, direct impact, early water, and chemical (water and mustard) resistance are reproducible over the plates in the designed experiment. However, for betadine and 50% EtOH resistance, two data values out of the 16 control data set gave different results. These deviations are due to problems inherent in the test methods and lead to poor models from the data.

Modeling Using Statistical JMP Program

The data measured in the statistically designed HTR experiment were subjected to modeling using statistical software (JMP program).[11,12] Note that models are in forms of mathematical relationships of input variables, PUD structures, and solvents in the experiment. Models for continuous responses including pendulum hardness and universal hardness were created using a least square regression method to understand the potential correlations between the responses and input variables within this data.

Table 3 shows the summary of goodness of fit for the models. The model for pendulum hardness was statistically significant, with 99% of the total variation (R^2 value) in the response variable. No lack of fit or issues with model residuals was ob-

Table 2—Reproducibility of End-user Properties of PUD-Control in the Designed HTR Experiment.[a]

Responses (Properties) of PUD Coatings	Reproducibility
Pendulum hardness / sec	125.5 ± 5.6
Universal hardness / N/mm^2	49.3 ± 2.8
Direct impact resistance / lb-in. (↑120)[b]	150 ± 15 (all data passed)
Early water resistance (↑4)[b]	All passed (100%)
Water resistance (↑4)[b]	All passed (100%)
Mustard resistance (↑3)[b]	All passed (100%)
Betadine resistance (↑4)[b]	Two failed (13%)
50% EtOH resistance (↑4)[b]	Two passed (13%)

[a]Total of PUD-Control tested in the DOE is 16.
[b]The nominal scale in parenthetic represents to be passed of each response.

Table 3—Goodness of Fit for Least Square Regression Models

	Pendulum Hardness	Universal Hardness
Significant model	Yes	Yes
R^2 value	0.985	0.957

served. The model for universal hardness was also significant with 96% of the total variation.

The rest of the responses including direct impact, early water, and chemical (water, 50% EtOH, betadine, and mustard) resistance were measured on nominal scales of 1–5. Logistic regression modeling was used to develop models for the categorical responses to predict the probability of getting a "pass" classification related to the various other attributes available within this data. Logistic regression is similar to regular regression except that the model predicts the probability of falling into one category versus another. *Table* 4 shows the summary of goodness of fit for the logistic regression models. All models are statistically significant with no lack of fit or issues with model residuals. "Correct Classification Rate" in *Table* 4 assesses how well each model does at predicting the correct categories. It was determined based on information obtained from the model fit diagnostics. All logistics regression models fitted the data very well, and thus they could be used to predict the probability of achieving desirable results (i.e., "pass" instead of "fail").

Investigation of Mutual Interactions between PUD Structures and Solvents

For the construction of significant models, input variables include NOP MW, SCD type and level, DMPA level, NCO level, solvent type, and level as single variables as well as their interaction variables. Consequently, the created models allow for better understanding of mutual interactions between the variables of PUD structures and solvents. For example, *Figure* 7 shows scaled estimates of significant variables to pendulum hardness of NOP-PUD coatings. The figure indicates the order of single variables that significantly affect pendulum hardness. The scaled estimate indicates how significantly variables affect pendulum hardness. For example, the variables with positive scaled estimate increase pendulum hardness, including variable 1 and 2. However, the variable 3 with negative scaled estimate decreases hardness. In addition, the model for pendulum hardness suggests that mutual interactions of these single variables are significant. Of course, these mutual interactions are observed with other models of direct impact, early water, and chemical resistance. Ultimately, these significant models and solid understanding mutual interactions of variables for the responses can be useful for design and development of target low-VOC PUD coatings.

Validation of Created Models

To test how reliable the created models are in predicting low-VOC PUD formulations, three formulations with an emphasis on nature and amount of solvents were predicted using the created models. The three formulations were then prepared and tested on manual benchtop. *Table* 5 summarizes the results of validation experiments. The measured results of pendulum, universal hardness, direct impact, early water, and chemical (water, mustard, and betadine) resistance were well

Table 4—Goodness of Fit for Logistic Regression Models

	Direct Impact Resistance	Early Water Resistance	Chemical Resistance			
			Water	50% EtOH	Betadine	Mustard
Significant model	Yes	Yes	Yes	Yes	Yes	Yes
Lack of fit	No	No	No	No	No	No
Correct classification rate	Very Good	Excellent	Excellent	Very Good	Excellent	Excellent

Table 5—Validation of Models with Three Predicted Low-VOC PUD Coatings on Benchtop

Screens		PUD-V1	PUD-V2	PUD-V3
Pendulum hardness (sec)	Predicted	97.2	93.1	136.6
	Measured	95	93	131
Universal hardness (N/mm^2)	Predicted	35.9	37.7	55.6
	Measured	39.1	40.5	52
Direct impact (lb-in.) (↑120) [a]	Desirability	0.961	0.928	0.992
	Measured	pass	pass	pass
Early water resistance (↑4) [a]	Desirability	0.999	1	0.968
	Measured	pass	pass	pass
Chemical–water (↑4) [a]	Desirability	0.957	0.773	0.999
	Measured	pass	pass	pass
Chemical–Mustard (↑3) [a]	Desirability	0.861	0.819	0.991
	Measured	pass	pass	pass
Chemical–Betadine (↑4) [a]	Desirability	0.815	0.847	0.96
	Measured	pass	pass	pass
Chemical–EtOH (↑4) [a]	Desirability	0.072	0.321	0.574
	Measured	pass	fail	fail

[a]The nominal scale in parenthetic represents to be passed of each response.

consistent with predicted ones, indicating that the JMP-assisted models for those responses are valid. However, 50% EtOH resistance was not validated. The plausible reason could be related to the ability of EtOH to dissolve PUD films and its volatility to be evaporated from films. Interestingly, PUD-V1 had good 50% EtOH resistance, indicating that it would be one of the good candidates for low-VOC PUD wood coatings.

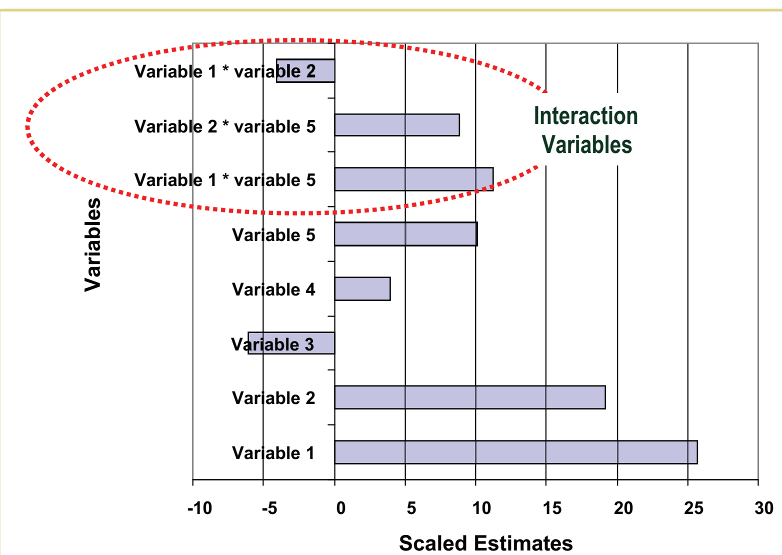

Figure 7—Significant variables of PUD structures and solvents that affect pendulum hardness.

Modeling for Mechanical Properties and Scratch Resistance of Solvent-free NOP-PUDs

The 26 solvent-free NOP-PUDs in the designed experiment were characterized with mechanical properties using dynamic mechanical spectroscopy and scratch resistance using tribometer. Twenty-five percent of Proglyde DMM based on PU solids was post-added to form crack-free films as well as to minimize the effect of residual solvents in dried films on the properties. Significant models for storage modulus (E') at room temperature, tan δ (loss/storage modulus, E''/E'), and scratch resistance were constructed. Combined with the models for properties (hardness, flexibility, early water, and chemical resistance) of NOP-PUD coatings, they can be utilized in prediction of low-VOC PUD coatings for wood and concrete.

CONCLUSIONS

HTR methods were proven to be an effective tool to screen coating formulations for product developments by exploration of mutual interactions of main variables. Validated statistical models for hardness, flexibility, early water, and chemical (water, mustard, and betadine) resistance were created for the development of low-VOC PUD coatings with enhanced end-user properties at VOC of <100 g/L. Combined with the statistical models for mechanical properties and scratch resistance of solvent-free NOP-PUD coatings, they allow for optimizing low-VOC NOP-based PUDs with target properties in response to existing and new customers. In addition, the complete development of automated HTR tools for industrial coatings will provide quick and right solutions to various coatings markets.

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