Effects of Additives on the Performance of Two-Component Waterborne Polyurethane Coatings

Sharon Xudong Feng, Phil Lunney, and Rebecca Wargo—Bayer Corporation*

The effects of various additives and solvents on a coating's performance in a two-component waterborne polyurethane coating system are studied using a statistical experimental design method. Using a blocked arrangement of fractional factorial design matrices, six different independent variables, including the use of different additives, catalysts, as well as solvents at different levels, were examined for their effects on various coating performance parameters, such as gloss, hardness, viscosity, and chemical resistance.

Statistical analysis revealed several significant effects of these additives on the coating performances. Most importantly, several two-factor interactions between additives were also found to significantly influence the performance properties of the coating. These interactions could be very difficult to detect using traditional one-at-a-time experimental approaches. The information obtained from this study could be used for designing coating systems with superior performance properties.

BACKGROUND

Mandated by both increasing environmental concern and higher performance requirements, tremendous efforts have been devoted to the development of high performance, low formaldehyde, or formaldehyde free water-based coatings. Two-component waterborne polyurethane coating systems have been an important part of this development effort.[1-5] However, the ever increasing popularity of waterborne coatings presents a continuing challenge for formulators. Compared to traditional solventborne coatings, formulators working with waterborne systems have to deal with much higher surface tension due to the fact that water, the majority of its "solvent," has a surface tension of 72.5 dynes/cm versus a typical surface tension of <30 dynes/cm for most organic solvents. To modify the surface properties of waterborne coatings so that the desired flow/leveling and other surface performance requirements can be achieved over a low surface tension substrate, formulators often have to use additives. In addition, waterborne systems frequently require the use of various thickeners to obtain the unique rheological properties for application. The availability of many new waterborne additives today on the market has enabled formulators to tailor waterborne coating systems with a much higher degree of sophistication in terms of both aesthetics and performance. The presence of these additives as well as their interactions, however, inevitably has profound impacts on the properties of the coatings. These effects are usually not fully understood. This study uses statistical experimental design as a tool to investigate the relationship between the presence of various additives as well as solvents in two-component waterborne polyurethane coating systems and the performance of the coatings when applied on wood.

APPROACH

The effects of five different additives and one solvent are studied for their impact on coatings performance. Statistical correlations between some of the performance parameters are also explored.

The independent variable choices are as follows:

Additive/Solvent	Variable Choice
Flow aid	Low or high
Thickener	A or B
Defoamer	Present or absent
Catalyst	Present or absent
Down gloss aid	Present or absent
Polar solvent	Present or absent

Presented at the 26th International Waterborne, High-Solids and Powder Coatings Symposium, February 10-12, 1999, New Orleans, LA.
*Coatings and Colorants Division, 100 Bayer Rd., Pittsburgh, PA 15205-9741.

Table 1—Design Matrix

Trial	Flow Aid	Thickener	Defoamer	Down Gloss Aid	Solvent	Catalyst
1	Low	A	Absent	Absent	Present	Absent
2	Low	A	Absent	Present	Absent	Present
3	Low	A	Present	Absent	Absent	Present
4	Low	A	Present	Present	Present	Absent
5	Low	B	Absent	Absent	Absent	Absent
6	Low	B	Absent	Present	Present	Present
7	Low	B	Present	Absent	Present	Present
8	Low	B	Present	Present	Absent	Absent
9	High	A	Absent	Absent	Present	Present
10	High	A	Absent	Present	Absent	Absent
11	High	A	Present	Absent	Absent	Absent
12	High	A	Present	Present	Present	Present
13	High	B	Absent	Absent	Absent	Present
14	High	B	Absent	Present	Present	Absent
15	High	B	Present	Absent	Present	Absent
16	High	B	Present	Present	Absent	Present

EXPERIMENTAL

Materials

The two-component waterborne polyurethane system used in this study contains an OH-functional acrylic emulsion and a water-dispersible polyisocyanate. The characteristics of the resins are as follows:

	OH-Functional Acrylic Emulsion	Polyisocyanate
Solid content (wt%)	42	100
NCO content (wt%)	—	17.1
OH number	18	—
Viscosity, cps	50-500	1000-5000
Equivalent weight (as supplied)	3100	245

The additives and solvents used in this study are as follows:

Additive/Solvent	Name	Manufacturer
Flow aid	BYK 346	BYK Chemie
Defoamer	Tego Flow 425	Tego Chemie
Catalyst	FASCAT 4224	Elf Atochem
Thickener A	Acrysol RM-825	Rohm and Haas
Thickener B	Borchigel LW44	Bayer, Wolff Walsrode
Down gloss aid	Pergopak M3	Lonza
Polar solvent	N-methyl-2-Pyrrolidone	

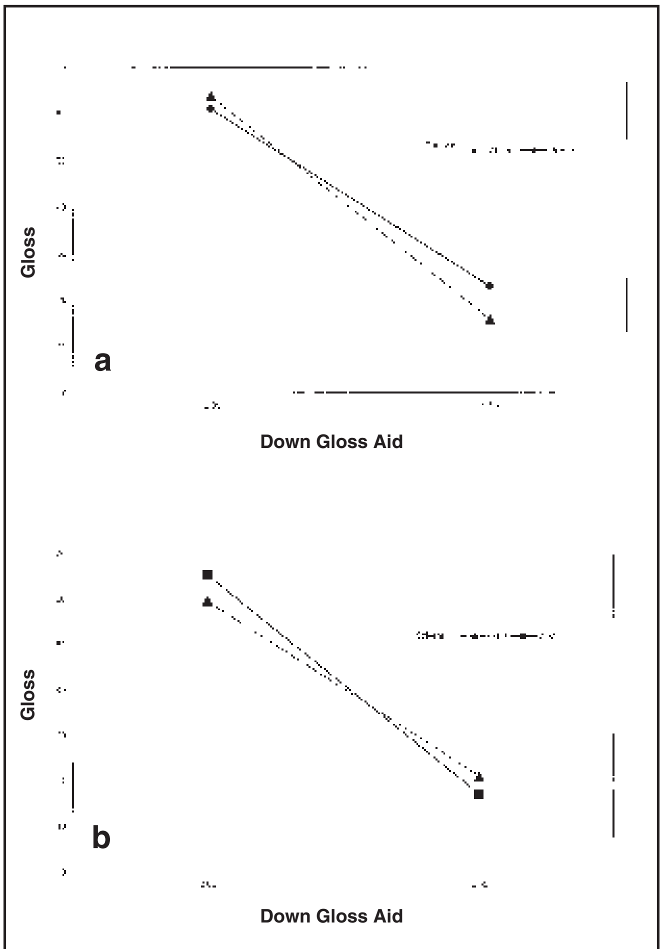

Figure 1a-b—Interactions affecting gloss (a) catalyst × down gloss aid; (b) solvent × down gloss aid

Formulation and Application

The formulation used in this study is formulated at NCO:OH ratio of 1:1 and a solid of 35%. The coating is applied by conventional gun at a WFT of 3 mil over an oak veneer panel as both sealer and topcoat. The drying process is 15 min flash at room temperature and 15 min bake at 140°F.

Evaluation

The evaluation carried out for the statistical experimental design was broken down into two categories:

• Continuous Responses: Gloss, DOI, pendulum hardness, and viscosity (detailed procedures are included in *Appendix* A).

• Categorical Reponses: Chemical resistance (detailed procedures are included in *Appendix* B).

Table 2—Summary of the Effects on Continuous Responses

Factor/Effects	Gloss 60°	Gloss 20°	DOI	Hardness (sec) 1 Hr	Hardness (sec) 4 Hr	Hardness (sec) 1 Day	Hardness (sec) 1 Week	Hardness (sec) 2 Weeks	Viscosity (cps)
Flow aid							—[b]		—[a]
Thickener			—[c]						—[d]
Defoamer		—[a]		—[a]					
Down gloss aid	—[d]	—[d]	—[d]			—[c]	—[c]	—[c]	
Solvent	—[a]			—[d]	—[d]	—[d]	—[d]	—[d]	
Catalyst	—[b]			—[c]	—[c]				
Flow Aid × thickener			—[b]						—[b]
Thickener × defoamer		—[c]							—[a]
Thickener × down gloss aid		—[b]							
Defoamer × catalyst			—[c]						
Down gloss aid × solvent	—[c]	—[c]							
Down gloss aid × catalyst	—[c]	—[c]							
Flow aid × solvent									—[c]
Thickener × solvent									—[c]
Flow aid × catalyst									—[c]

(a) Confidence level of 95%.
(b) Confidence level of 99%.
(c) Confidence level of 99.9%.
(d) Confidence level greater than 99.9%.

RESULTS AND DISCUSSION

A 16-trial, fractional factorial design of resolution IV[6] was employed to study the main effects and possible interactions of the additives. The design matrix is shown in *Table* 1. The trials were replicated three times to compensate for the relatively poor sensitivity of the ordinal responses representing chemical resistance.

A characteristic of the experimental design employed here is that the main effects are clear but two-factor interactions are confounded with one another. This approach is frequently used in screening studies to reduce the total number of trials. Following analysis of the first 16 experiments, additional trials were added to resolve ambiguities concerning two-factor interactions.

The statistical analyses of data have revealed several significant correlations between the additive levels and various performance parameters. Most interestingly, the analyses have also shown some correlation between the continuing response parameters and categorical response parameters. The results from statistical analyses are summarized in *Table* 2 for continuous responses and *Table* 3 for categorical responses.

Continuous Response

GLOSS: Without any surprise, the effect of down gloss aid dominates this response. In addition, the presence of catalyst and solvent are found to have significant effect on gloss. The increasing catalyst level was shown to increase 60° gloss and, to a lesser extent, 20° gloss. The presence of the solvent, on the other hand, decreases 60° gloss but had little effect on 20° gloss.

Two-factor interactions between down gloss aid and catalyst, and down gloss aid and solvent were also observed (*Figures* 1a-b). In both cases, the down gloss aid lowers the gloss, but the presence of catalyst moderates this effect while the presence of solvent enhances this effect. These effects, although statistically significant, are minor in comparison to main effects. Based on comparison of the results of statistical analysis, 20° gloss tends to be a more sensitive indicator on the effect of additives. The responses are also highly correlated.

Table 3—Summary of the Effects on Categorical Responses

Factor/Effects	Chemical Resistance: Lipstick	Acetone	Amyl Acetate	50% EtOH	Nail Polish Remover	Coffee
Defoamer		—[c]				
Down gloss aid		—[c]				
Solvent	—[a]					
Catalyst		—[c]				—[d]
Flow aid × solvent				—[a]		
Solvent × catalyst	—[c]	—[a]				

(a) Confidence level of 95%.
(b) Confidence level of 99%.
(c) Confidence level of 99.9%.
(d) Confidence level greater than 99.9%.

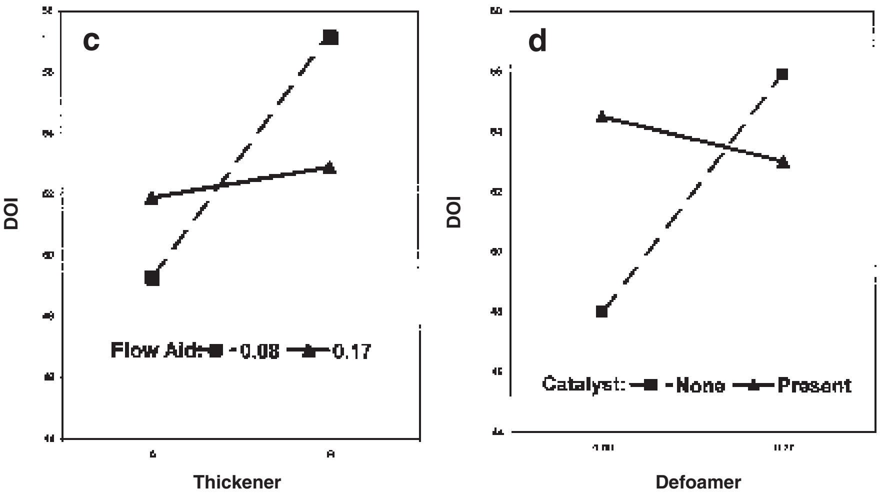

Figure 1c-d—Interactions affecting DOI (c) flow aid x thickener; and (d) catalyst x defoamer.

DOI: Besides the main effect caused by down gloss aid, the different brands of thickeners had strong correlation with DOI. Both thickeners A and B are hydrophobically modified ethoxylated urethane (HEUR) associative thickeners. However, thickener B offers a much higher DOI than thickener A. There are two-factor interactions between flow aid and thickener, and between defoamer and catalyst. These interactions are shown in *Figures* 1c-d. Note that the presence or absence of a catalyst completely reverses the effect of the defoamer on DOI.

Hardness: The hardness data were interpreted using repeated measures analysis, a multivariate statistical analysis procedure. Statistically significant effects were observed for polar solvent, catalyst, and down gloss aid. These effects are presented graphically as profile plots in *Figures* 2 through 4.

The effect of polar solvent is presented in *Figure* 2. Clearly, the presence of the solvent has significantly lowered the hardness (average 20 sec) consistently over the entire time interval. The effect of down gloss aid, presented in *Figure* 3, is more complex. The down gloss aid tends to reduce the pendulum hardness, but the effect is not apparent until after one day. This might be due to the fact that at that point of time during curing process, most down gloss aid molecules have migrated to the surface of the film. This orientation phenomenon, in combination with a certain degree of shrinkage, could result in an increasingly uneven film surface profile microscopically. This roughness of the surface contributes to the down gloss effect but also could damper the oscillation of the pendulum swing and result in lower pendulum hardness results. This effect, thus, might not represent a true hardness change of the film. The catalyst, on the other hand, definitely affects the hardness profile over time, as presented in *Figure* 4, but the effect is only profound in the early curing stages. Initially, material with the catalyst is approximately 20 sec harder than the coating without catalyst. The difference, however, rapidly diminishes after four hours, and the final hardness of the coating is not affected by the presence of the catalyst.

Viscosity: Viscosity was the most complicated of the continuous responses studied, with three main effects and five two-factor interactions being identified as statistically significant. The main effect of thickener was the strongest observed response, with thickener B producing substantially lower viscosity than A. This result cannot be interpreted correctly, however, without simultaneously considering the factors that interact with the thickener. A very strong interaction was observed between the thickener and solvent (*Figure* 5a). In the absence of solvent, thickener A produces higher viscosity than B, but the results are reversed in the presence of solvent. This interaction is crucial to the understanding of the true behavior of the thickener on viscosity, and

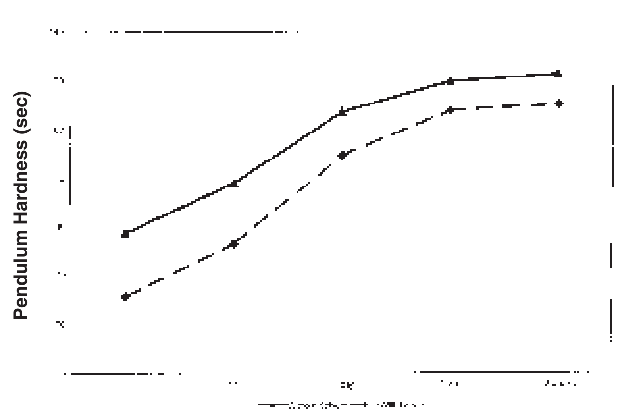

Figure 2—Effect of polar solvent on hardness.

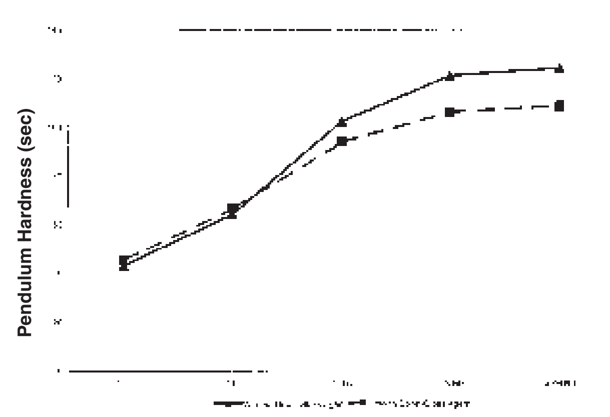

Figure 3—Effect of down gloss aid on hardness.

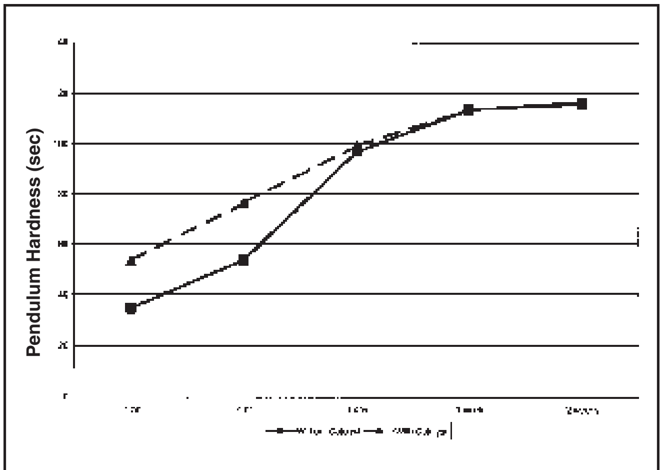

Figure 4—Effect of catalyst on hardness.

demonstrates the value of statistically guided experimentation as opposed to one-factor studies. This interaction could not have been discovered using a one-factor approach. In addition, the presence of a defoamer is found to lower the viscosity of the system. Two very strong and one moderate interactions were observed between the flow aid and solvent, flow aid and catalyst, and flow aid and thickener (*Figures* 5b-d). Note that most of the factors involved in these relatively important interactions were observed as main effects, once again confirming the application of statistical experimental design to these studies. In each case, the effect of the flow aid on viscosity depends on the level of the other factor.

Categorical Response

COFFEE: Strong correlation was observed between coffee resistance and the level of catalyst. The presence of the catalyst has detrimental effect on the coffee resistance.

ACETONE: Three main effects were observed for this response factor. The presence of the defoamer and the absence of the catalyst definitely correlated to poor acetone resistance while the use of down gloss aid improved the acetone resistance. One two-factor interaction between solvent and catalyst is found to affect the acetone resistance (*Figure* 6a).

LIPSTICK: The presence of solvent is found to detrimentally affect the resistance to lipstick. A strong interaction between solvent and catalyst is also found (*Figure* 6b).

100% ETHANOL: No main effect was found for ethanol resistance. However, a two-factor interaction between flow aid and solvent is found to affect ethanol resistance (*Figure* 6c).

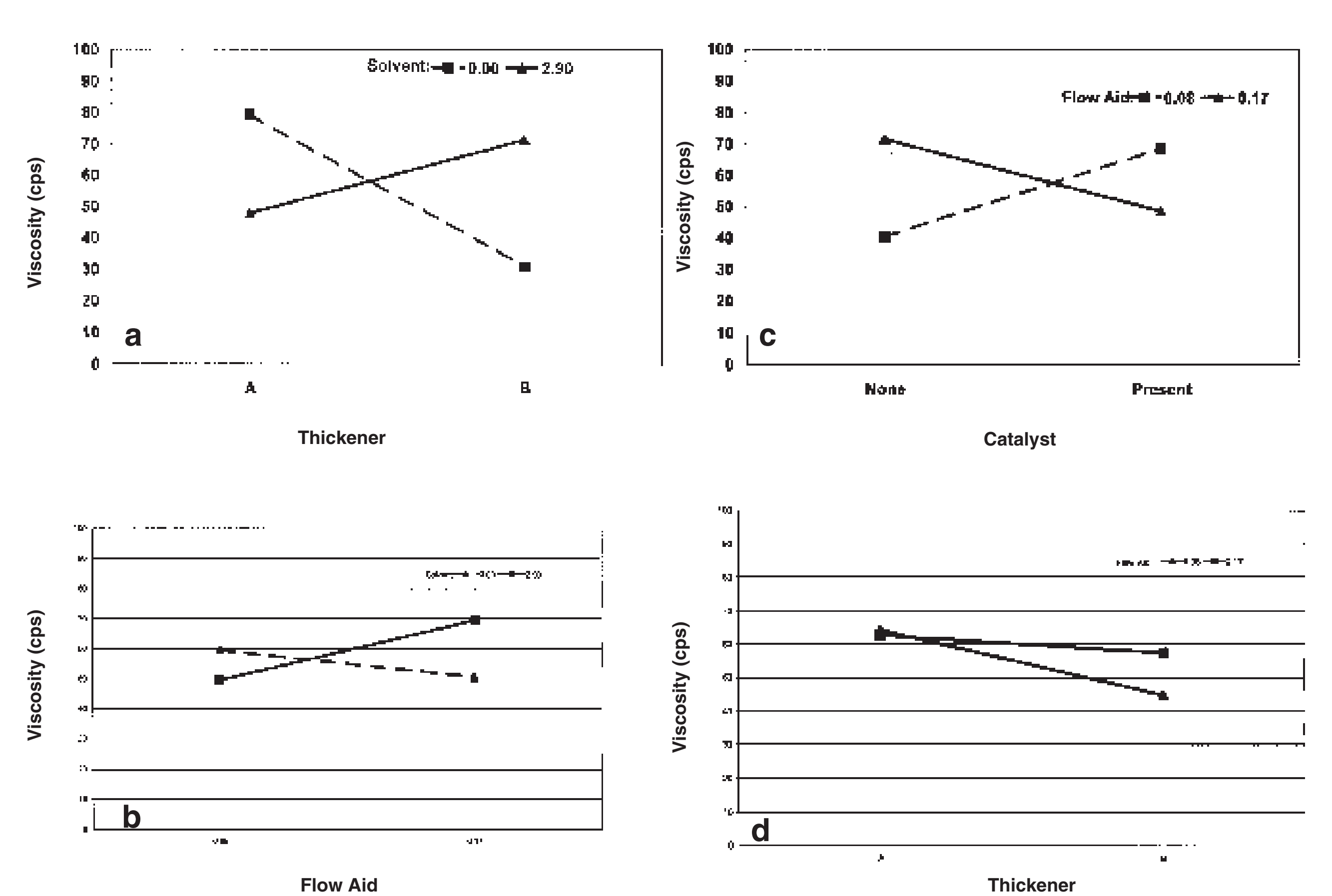

Figure 5—Interactions affecting viscosity (a) solvent x thickener; (b) solvent x flow aid; (c) catalyst x flow aid; and (d) thickener x flow aid.

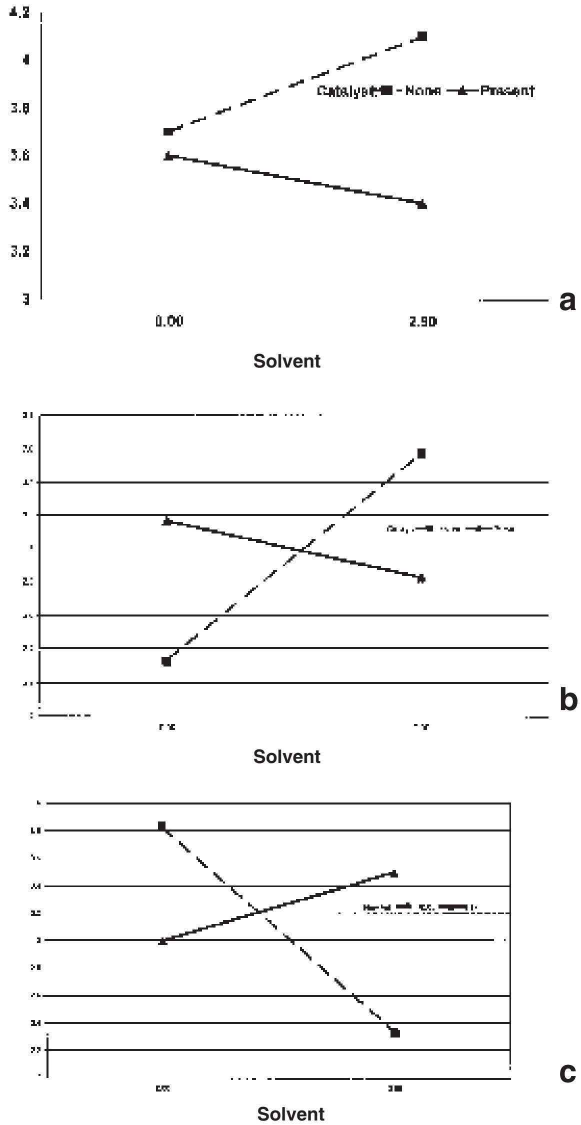

Figure 6—Interactions affecting chemical resistance (a) acetone; (b) lipstick, and (c) ethanol.

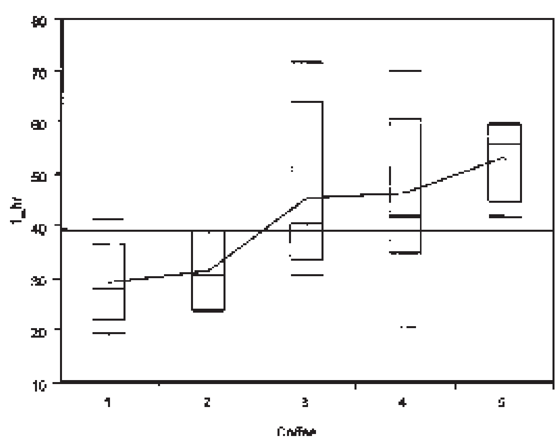

Figure 7—Correlation between 1-hr hardness (sec.) as a function of coffee resistance (1=best and 5=worst).

Neither main effects nor interactions were found that affect nail polish remover or amyl acetate resistance.

Correlation Between the Continuous and Categorical Parameters

Statistical analyses revealed that there are strong correlations between some of the continuous and categorical response factors.

Correlation Between Earlier Hardness and Chemical Resistance to Coffee, Acetone, and Ethanol

As shown in *Figure* 7, a very strong correlation was observed between one hour pendulum hardness read-

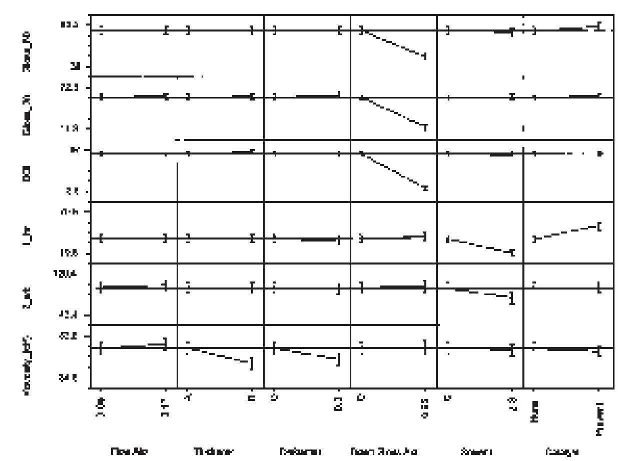

Figure 8—Main effects affecting continuous response factors.

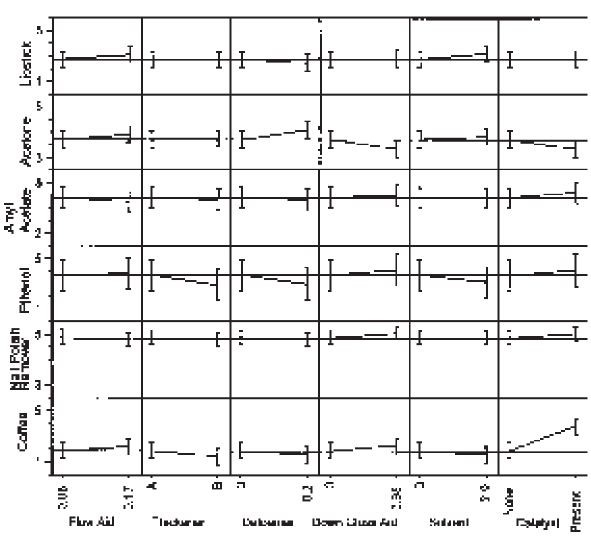

Figure 9—Main effects on categorical response factors.

ing and coffee resistance. The relationship is essentially discriminate, with hardness readings less than 30 sec associated with excellent coffee resistance, and hardness readings over 30 sec associated with poor resistance. Similar correlation is also present between one-hour hardness reading and acetone and ethanol resistance. Four-hour hardness readings are correlated to these resistance properties as well. Since a pendulum hardness reading can be determined much earlier on during the curing process and is much easier to measure, this correlation might provide a way to screen and evaluate a coating system's chemical resistance using a pendulum hardness reading as an indicator.

CONCLUSION

This study has demonstrated that the usage of various additives will have profound impacts on various coating performances beyond their known functions and purposes. *Figures* 8 and 9 summarize all the major effects we have established in this investigation. These impacts can be both positive and negative. More importantly, these impacts can also be the results of interactions between two different additives. With the understanding of these complex relationships, formulators could balance the choice of additives and develop formulations that offer optimal performances with minimal detrimental effects from additives. Statistical experimental design has proven to be an extremely valuable tool in studying the complex relationships between formulation parameters and coating film performances. In addition, interesting correlations were discovered between early hardness of the coating and coffee resistance, which potentially could lead to earlier and easier ways to measure chemical resistance properties of coating systems.

ACKNOWLEDGMENTS

The authors of this paper would like to thank Pam Rozman, Mary Crisic, and Kevan Hudson for their assistance in lab work. Special thanks to Mr. M.J. Dvorchak, Drs. T. Potter and D. Wicks for discussion and support.

References

(1) Jacobs, P.B. and Yu, P.C., *Proc. 20th Waterborne, High-Solids, and Powder Coatings Symp.*, New Orleans, LA, 1992.
(2) Renk, C.A. and Swartz, A.J., *Proc. 23rd Waterborne, High-Solids, and Powder Coatings Symp.*, New Orleans, LA, 1995.
(3) "Two-Component Waterborne Polyurethane Coatings," a technical brochure by Bayer Corporation and Rohm & Haas Company.
(4) Dvorchak, M., "Using High Performance Two-Component Waterborne Polyurethane Wood Coatings," JOURNAL OF COATINGS TECHNOLOGY, *69*, No. 866, 47 (1997).
(5) Feng, S., Dvorchak, M., Hudson, K.E., Renk, C., Morgan, T., Bender, H., Todd, D., Stanislawczyk, V., Papenfuss J., and Shuste, F., *Proc. 25th Waterborne, High-Solids, and Powder Coatings Symp.*, New Orleans, LA, 1998.
(6) Box, G.E.P., Hunter, W.G., and Hunter, J.S., *Statistics for Experimenters*, John Wiley & Sons, Inc., 1978.

Appendix A: Basic Test Procedures

Pendulum Hardness: Films (WFT=3 mil) were drawn down on a clean glass plate. Koenig Pendulum Hardness was measured at a given time period after hard dry time.

Viscosity: Formulated paint viscosities were measured at ambient temperature immediately after mixing using a Brookfield Viscometer.

Gloss and DOI: Films were formed by spray out on to a black glass panel using a conventional spray gun (atomizing pressure: 35 psi). After a 24-hour aging period, gloss was measured on a BYK Chemie Gloss Unit and DOI on a Dorigon II DOI meter.

Appendix B: Chemical Resistance Test Procedures for Office Furniture

Wood Panel Preparation: Presanded and stained wood panels were coated with a sealer and a topcoat (WFT = 3 mil) with light sanding (320 grit stearated paper) carried out between. Panels were flashed 15 min at the ambient temperature then baked 15 min at 140°F. Tests were conducted on the finished panels 14 days after the finish. Reagents (1 mL on a cotton ball if liquid) were placed on panel surfaces and covered with a watch glass for 16 hr before evaluation. Visual readings were carried out, with 0 being no effect and 6 being the worst effect. A reading of 2.5 is the minimal requirement for pass.