

## Waterborne UV Curable Coatings for Industrial Market Segments

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### Abstract

Ultraviolet (UV) light cured waterborne polyurethane dispersions (PUDs) have demonstrated their versatility in many industrial market segments. Today there are ever-increasing customer requests for film properties specific to more than one market. There is no general solution: each customer has his/her own list of coating requirements. To meet customer expectations, the formulator needs a general approach for formulation development. In this paper we discuss a formulating strategy for using blends of UV curable PUDs and non-UV curable PUDs to attain desired film properties.

### Introduction

Ultraviolet (UV) light cured waterborne polyurethane dispersions (PUDs) have demonstrated their versatility in many industrial market segments<sup>1</sup>. However, the increasing demands of the market place challenge the formulator to develop timely coatings solutions; the emphasis is on timely: often the formulator is expected to use limited resources to formulate coatings for new applications from his existing product portfolio. We will examine a not-so-new approach and tool for the formulator to use. We will also include some test examples to illustrate the power of the tool—design of experiments (DOE).

Usually there is a groan at this point and those of you who feel the pressure of new product development will gasp and politely change the discussion to ways that you can avoid a horrendous number of experiments. I suggest that those of you who are wedded to OFAT (Stat-Ease, Inc. terminology for one factor at a time) need to consider that (a) principles of DOE are firmly established and (b) software advances have produced strong analytical tools to analyze the results that you've worked so hard to obtain. Several software manufacturers will be happy to teach you either in person or online.<sup>2</sup> I'll concentrate on a real life example that we recently encountered in the BMS laboratories in Pittsburgh.

Let me close this introductory section by stating that I am not a statistician. I am a paint formulator who has been privileged to work at several paint companies with first rate formulating chemists. You are not putting your technical training aside when you use DOE software; quite the contrary, you'll find that you can use your experience to develop more robust formulations than the ones you've been tweaking over the months and years.

### Relevance of DOE to Paint Formulation Development

We regularly examine our portfolio of waterborne products for new applications in new markets. We do the usual tests that you'd do for classifying PUDs according to their coatings properties—hardness, chemical resistance, flexibility, impact resistance, durability, to name a few. These performance properties are important and often are specified by the customer. A recent need to characterize some of our PUDs provided us with the opportunity to set up a DOE for such an evaluation.

We had done some preliminary work with several of our PUDs for general property characterizations. I've listed the ones below that we'll be discussing today (Table 1). The properties are listed in our technical literature. We had reason to ask if there were additional simple characterizations relevant for formulation development.

Table 1. Properties of WB PUDs

WB PUDs	Supply form (%)	Viscosity 23° [s – DIN 4]	pH value	Tg [°C]	%Elongation at Break
A*	39	< 80	8.2	28	13
B*	42	< 50	7.8	90	<5
C	40	≤ 70	6.5	-49	500
D	60	≤90	7.5	-49	700
E	40	≤ 70	8.0	-47	700

\*Waterborne UV curable PUDs

We did this set of experiments in two parts. We began with a four component design comprised of A, B, C, and D. We used a commercially available software package and confined our study to the interactions of A, B, C, D as a mixture of paint components in a mixture design.<sup>2</sup> After some internal discussion we settled on a design of a Simplex Centroid design augmented with axial points with 2 replicates for the whole design. This resulted in 38 formulations which we prepared according to internal formulation guidelines. We were interested in the interactions of the waterborne UV curable PUDs with waterborne PUDs which did not UV cure nor would further crosslink after application. We have included key application and cure data in the appendix. All PUDs are commercially available.

After we had completed our initial work, we substituted PUD D with another PUD E. We used the same experimental design for a second series with the same guide formulation and application/cure parameters.

In the analysis of the experimental results we used output from a Fischerscope 100HC Nanoindenter.<sup>3</sup> Although the Martens Hardness, HM (N/mm<sup>2</sup>), is an often cited result, we included hmax $\mu$  ( $\mu$ m), maximum indentation depth of the indenter at maximum test load and elastic modulus, EIT/(1-vs<sup>2</sup>) (GPA)<sup>4</sup>. Both of these latter terms are standard output from this instrument.<sup>3,4</sup>

We will focus on the general trends that we see from the indentation experiments. We found the option of "contour plots" provided within the DOE software to be helpful. Briefly, the concentrations of each PUD (A, B, C, D, E) are 100% of each component at the 3 vertices. The midpoint of each side of the triangle is equal to 0% for each component at the opposite vertex. We intentionally wanted to see the interaction of both waterborne UV-curable with the non-UV curing components; therefore, each contour plot contained one or both UV-curable resins.

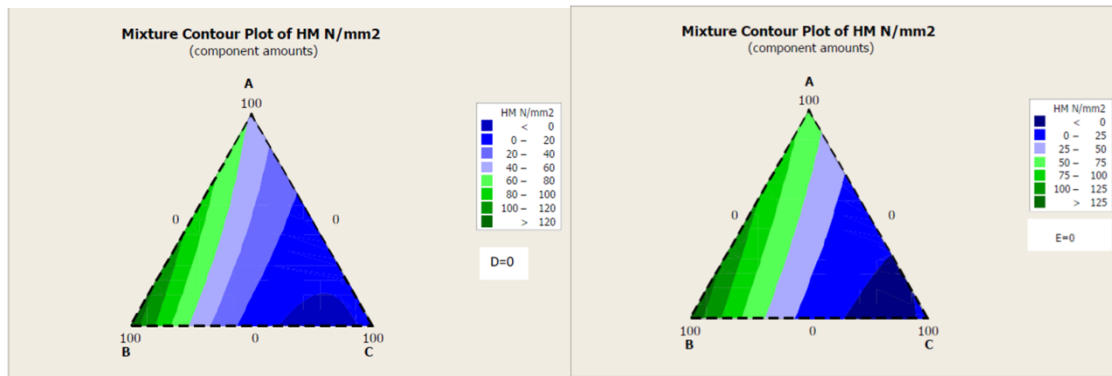
## Martens Hardness HM

Initially, we consider the case of formulation ABC in which either D or E is held constant at zero (Figure 1). The contour plot for ABC with D=0 differs slightly from ABC with E=0, due to the model generated from setting D=0 versus E=0 produced by the software based on the input mixtures.

The ranges of HM are color coded and range from 0 to  $>125$  N/mm<sup>2</sup>. The contour plots were constructed based on the model heretofore described. Note that within the dark green region, the model predicts that one can obtain a Martens Hardness ranging from 80 to 100 H/mm<sup>2</sup>; moreover, when E is substituted for D in the same guide formulations, the model predicts the same Martens Hardness range in the same region of the model. This is an expected result and also confirms the high predictability of the DOE model for both cases.<sup>4</sup>

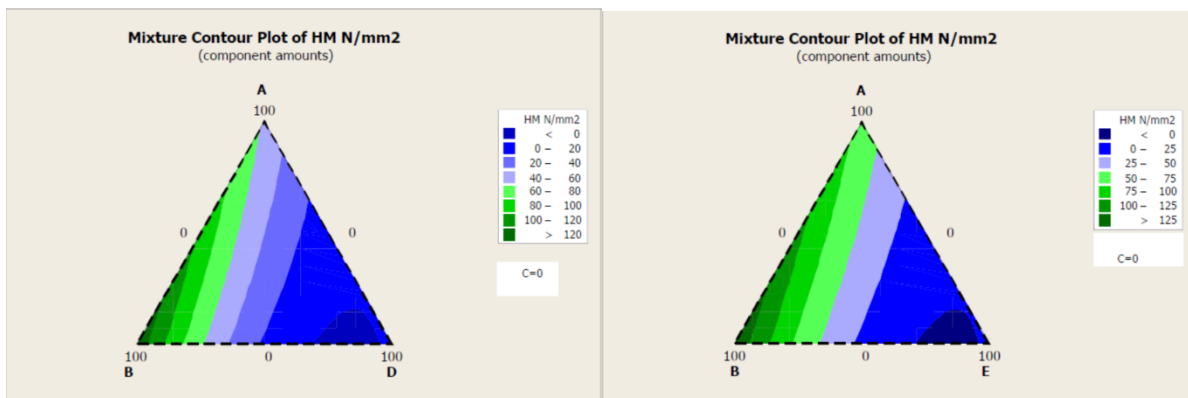
Henceforth, we'll refer to contour plots ABC with C=0 or D=0 for comparisons.

Figure 1. ABC Contour Plots of HM with D= 0 and E=0



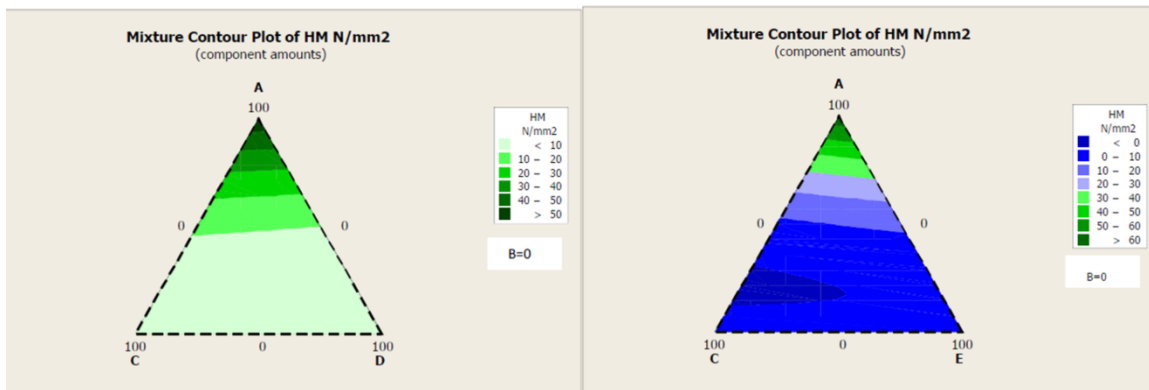
If we now consider the case of formulations ABD and ABE in which C=0 (Figure 2), we see qualitatively the same trends as for the ABC formulation. These HM results indicate little or no change when PUDs C, D, E are interchanged as the 3<sup>rd</sup> component in AB formulations.

Figure 2. ABD and ABE Contour Plot of HM with C=0



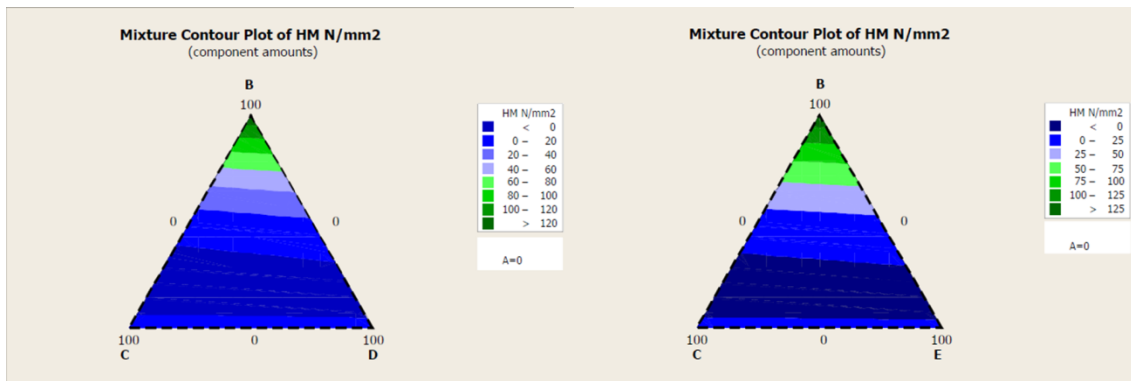
If we then consider the case in which one of the UV-curable waterborne resins, B, is set to zero, we see a dramatic shift for ACD formulations: it is not possible to reach Martens Hardness values greater than 50 N/mm<sup>2</sup>; substituting E for D produces even softer films within the design space of ACE formulations of (Figure 3).

Figure 3. ACD and ACE Contour Plots of HM with B=0



If we now substitute UV curable PUD B for A, we have the results in Figure 4.

Figure 4. BCD and BCE Contour Plots of HM with A=0



At this point we have accumulated considerable knowledge about the interactions of waterborne UV-curable resins A and B with non-UV curable resins C, D and E; moreover, the change from AB mixtures to ones containing only A or B produce either lower ranges of HM values or more narrow ranges of formulations for maximum HM values.

We conclude at this point that removal of either A or B from the formulation will make it more challenging to create formulations with high levels of hardness.

These contour plots are based on a very high correlation of the data with the model<sup>5</sup>. Consequently, **one can predict with a high degree of probability the Martens Hardness results of mixtures within the design space that were not part of the original test series**. Moreover, formulations ABC, ABD, and ABE are more robust than ACD, ACE, BCD, and BCE: one has a wider formulating window with ABC, ABD, and ABE to attain desired hardness than with ACD, ACE, BCD, and BCE.

There are two other outputs from the nanoindenter that we'll consider in the same fashion:  $h_{max\mu}$ , maximum penetration beneath specimen's surface in mm (nm) at maximum test load and  $EIT/(1-\nu_s^2)$ , elastic modulus, an object or substance's tendency to be deformed elastically (i.e., non-permanently) when a force is applied to it.<sup>4</sup>

### Maximum Penetration at Maximum Test Load $h_{max\mu}$

If we compare the  $h_{max\mu}$  plots (Figures 5, 6 and 7), we see the same trend: ABC, ABD, and ABE provide a wider range of formulations for desired  $h_{max\mu}$  values than ACD, ACE, BCD, and BCE. This trend is opposite to that of HM because  $h_{max\mu}$  is a measure of the depth of penetration;  $h_{max\mu}$  decreases as the formulations are enriched in A or B and increases as formulations are enriched in C, D, or E. The higher glass transition temperatures of A and B compared to C, D, and E may explain this trend.

Figure 5. ABC Contour Plots of  $h_{max\mu}$  with D= 0 and E=0

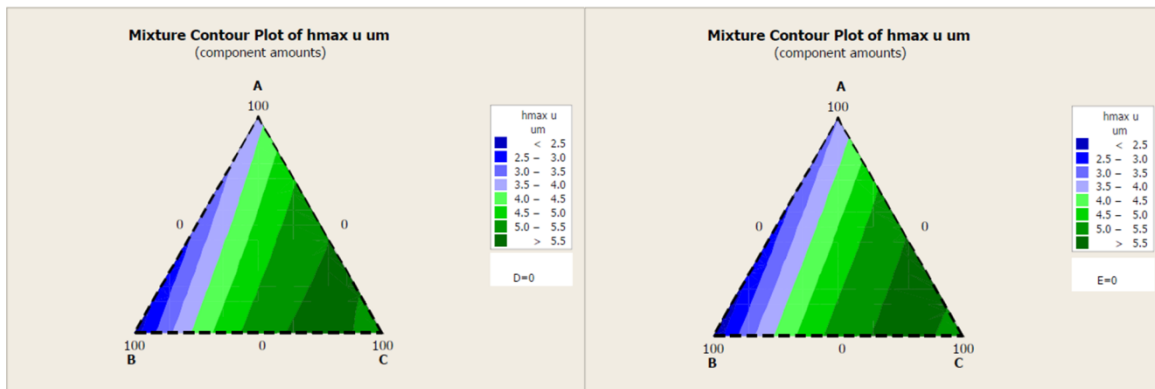


Figure 6. ABD and ABE Contour Plot of  $h_{max\mu}$  with C=0

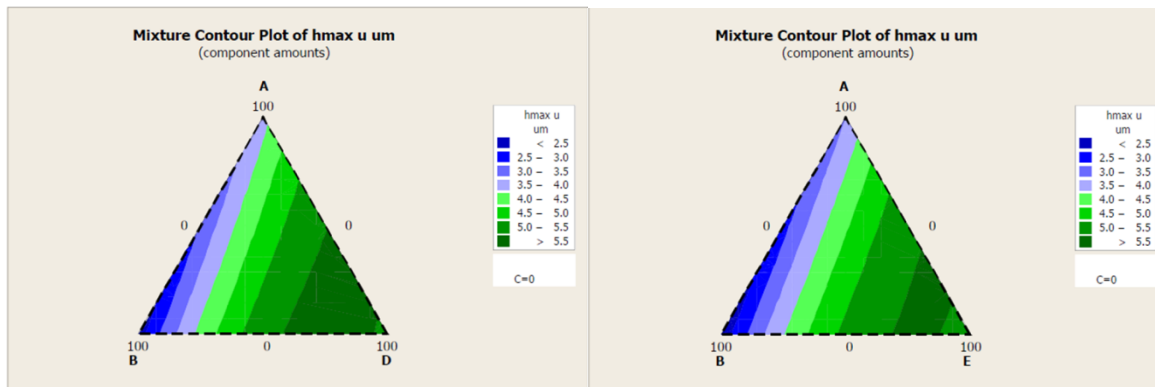
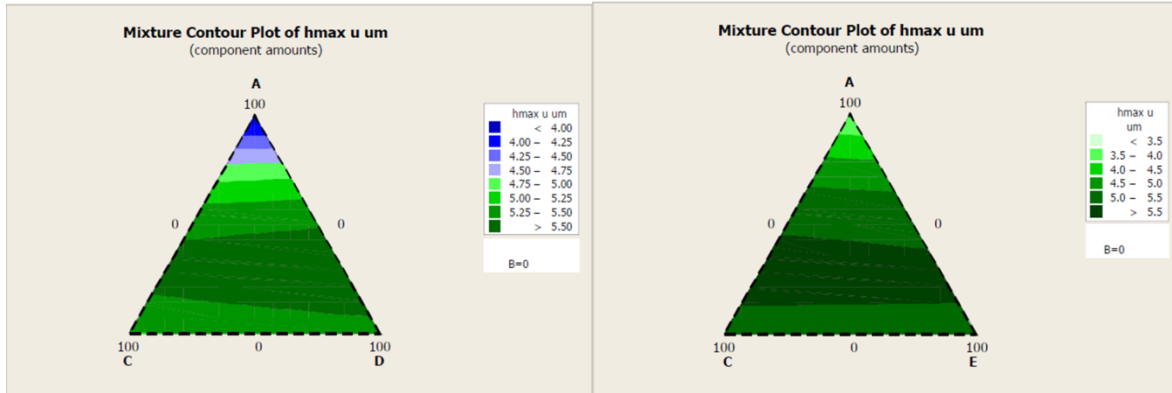
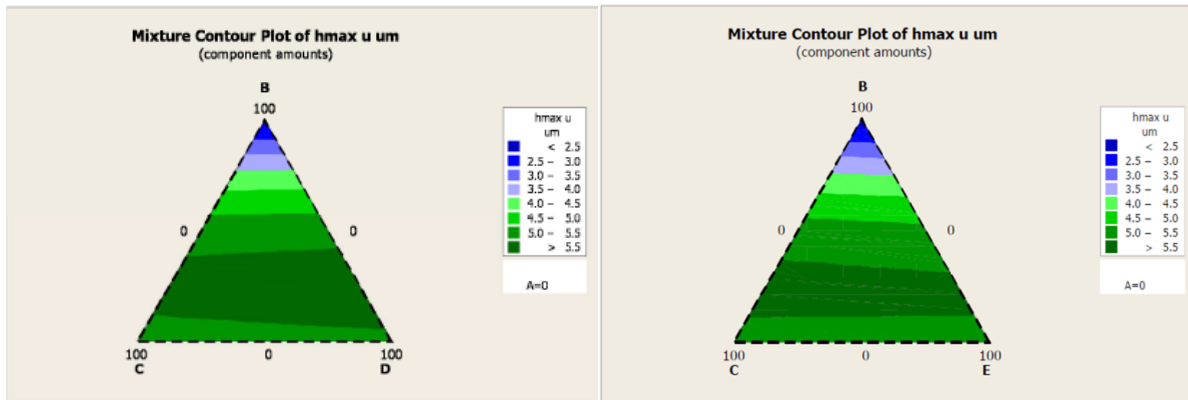


Figure 7. ACD and ACE Contour Plots of  $h_{\max} \mu$  with  $B=0$ Figure 8. ACD and ACE  $h_{\max} \mu$  Contour Plots with  $A=0$ 

### Elastic Modulus $EIT/(1-\nu_s^2)$

Lastly we consider  $EIT/(1-\nu_s^2)$ , elastic modulus. Contour plots ABC, ABD, and ABE have the same general appearance as the HM plots of ABC, ABE, and ABE (Figures 9 and 10 and Figures 1 and 2). Likewise, contour plots ACD, ACE, BCD and BCE have the same general appearance as HM contour plots of ACD, ACE, BCD, and BCE (Figures 11 and 12 and Figures 3 and 4). These data show elastic modulus to be trending the same as HM in this series. This is intuitively obvious if one recalls that elastic modulus increases with increasing stiffness of the film due, in part, to the higher glass transition temperatures of UV-curable PUDs A and B.<sup>6</sup>

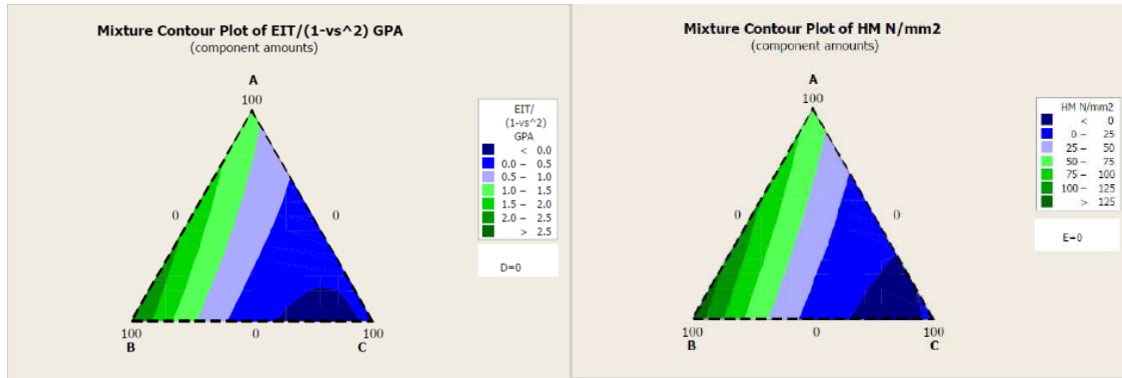
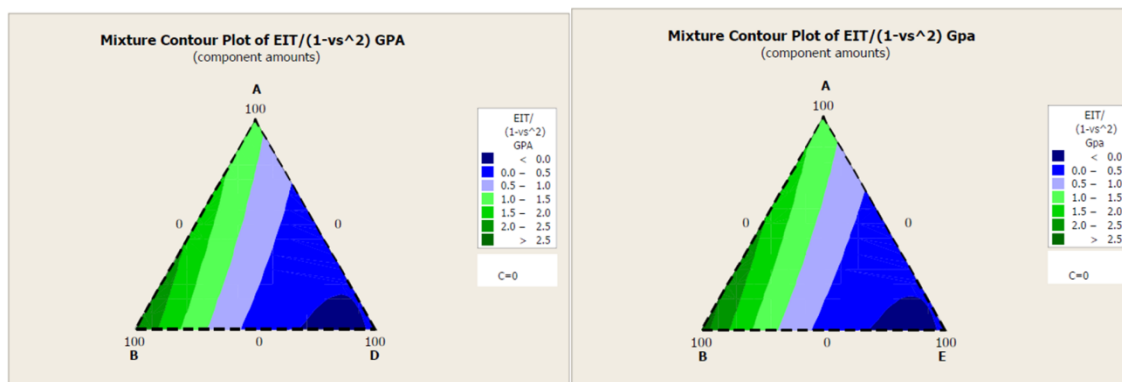
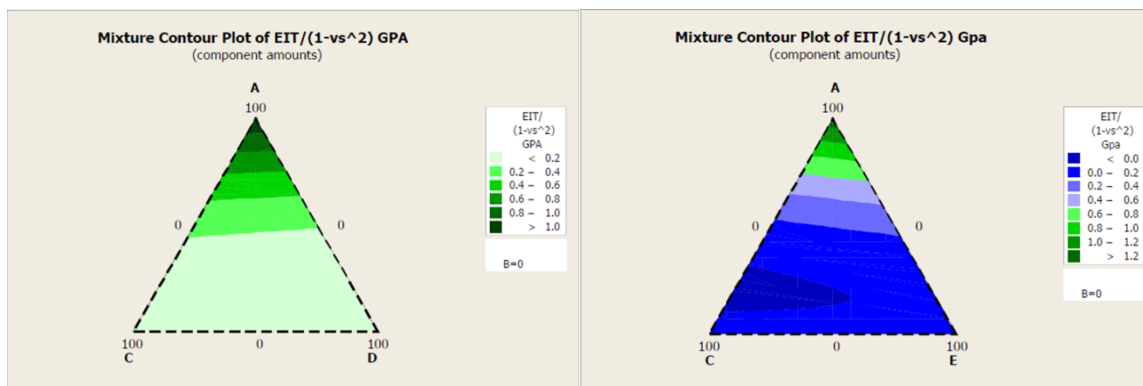
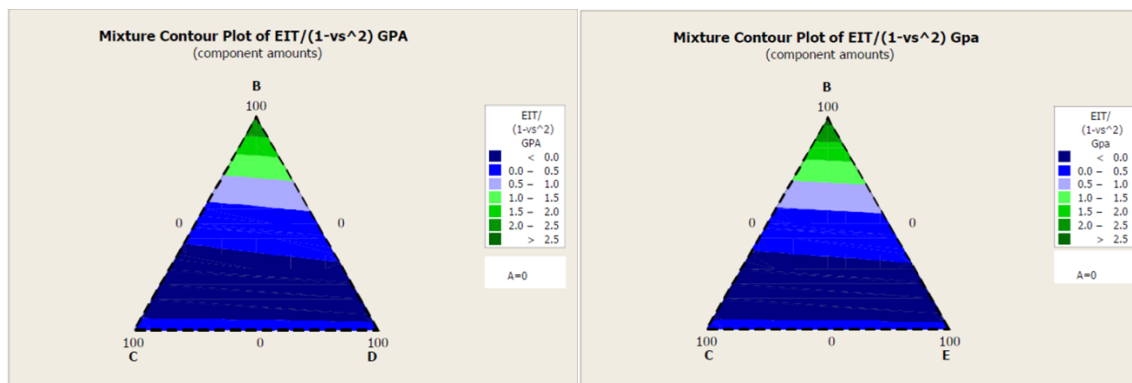
Figure 9. ABC Contour Plots of  $EIT/(1-v_s^2)$  with  $D=0$  and  $E=0$ Figure 10. ABD and ABE Contour Plots of  $EIT/(1-v_s^2)$  with  $C=0$ Figure 11. ACD and ACE Contour Plots of  $EIT/(1-v_s^2)$  with  $B=0$ 

Figure 12. BCD and BCE Contour Plots of  $EIT/(1-\nu_s^2)$  with  $A=0$ 

## Conclusions

1. Blends of waterborne UV-curable PUDs and waterborne non-UV-curable PUDs provide additional formulating aids to meet customer coating requirements.
2. DOE is a powerful tool for the formulator to assess interaction of binder components in paint formulations.
3. Analysis of DOE results can provide insights into how film properties vary within a design space, thereby allowing one to predict film properties for formulations not actually tested.
4. DOE requires both a sound design and analysis of results to enhance the skill of the formulator.

## References

1. "UV Curable Resins Market by Application (Coatings, Inks, Adhesives, & Others), End-User Industry (Graphic Arts, Industrial Coatings, Electronics, & Others) & Geography - Trends & Forecasts to 2018", <http://www.marketsandmarkets.com/Market-Reports/uv-curable-resins-market-1324.html>.
2. The author used Minitab® 16 for the design and analysis of the results reported herein.
3. Fischerscope® H100C Microhardness Measurement System with WIN-HCU® Software; Measurement of the Martens Hardness According to DIN 14577. Fischer Technology, Inc., 750 Marshall helps Road, Windsor, CT 06095 USA.
4. Anthony C. Fischer-Cripps. Nanoindentation, Third Edition, Springer, , pp. 14-15, 184-189



5. Regression Analysis from Minitab 16 (Mixture Design, Analysis of Mixture Design Results, Regression)

PUD Blends	Responses	S*	**PRESS	***R-Sq	****R-Sq(pred)	*****R-Sq(adj)
A B C D	HM (N/mm <sup>2</sup> )	8.16151	3092.62	96.18	93.67	94.96
A B C D	hmax $\mu$ ( $\mu$ m)	0.24721	2.72385	94.83	91.77	93.17
A B C D	EIT/(1-vs <sup>2</sup> ) (GPA)	0.16023	1.18333	96.12	93.61	94.87
A B C E	HM (N/mm <sup>2</sup> )	6.70973	2068.57	97.64	96.45	97.14
A B C E	hmax $\mu$ ( $\mu$ m)	0.22892	2.18201	95.97	94.01	94.68
A B C E	EIT/(1-vs <sup>2</sup> ) (GPA)	0.13473	0.86749	97.62	95.93	96.85

\*Standard error; \*\*Predicted Sum of Squares; \*\*\*R-Sq=R<sup>2</sup>; \*\*\*\*R<sup>2</sup><sub>pred</sub>; \*\*\*\*\*R<sup>2</sup><sub>adj</sub>

6. F. N. Jones et al., "Methods for Studying the Mechanical and Tribological Properties of Hard and Soft Coatings with a Nano-Indenter," JCT Research, Vol. 1, No.2, April 2004, pp. 117-125; [www.coatingstech.org](http://www.coatingstech.org)

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