Novel Light Stabilizer Enhances the UV-Filtering Ability of Waterborne UV-Curable Coatings without Sacrifice on Curing Speed

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Abstract

Waterborne Ultra Violet (UV)-curable coatings have been developed to replace conventional UV-curable coatings to lower VOC content. Due to fast-drying and short processing time, UV-curable coatings are widely used in various industries. However, there are 2 major challenges: the first one is discoloration after long-term exposure to sunlight; the other is to keep the ability of UV filtering ability since waterborne UV-curable coatings are usually applied to the surface as a protection top coat.

The novel light stabilizer (NLS) is developed specifically for waterborne UV-curable coatings. Design of Experiment (DOE) was used in the study. Test data showed that the designed NLS would not interfere the curing speed of the tested clear waterborne UV-curable coating system. Moreover, the results confirmed that by increasing the concentration of NLS could enhance the UV filtering ability and weatherability of the tested clear top coat more effectively than by increasing the coating thickness: at 365nm wavelength, the effect factor of NLS is 62.5%, while DFT (dry film thickness) is 20.9%; at 380nm, the effect factor of NLS is 47.7%, while DFT is only 27.4%. Our test results confirmed the designed NLS could block the UV light without compromising the UV-curing speed, and is suitable for enhancing the weatherability and protection ability of the clear waterborne UV-curable coatings.

Keywords: UV curable coatings, waterborne UV curable coatings, UV degradation, light stabilizer, design of experiment, UV filtering

Introduction

UV curing is a photochemical process which offers higher production efficiency comparing with traditional drying methods, and are already widely used in many different industries such as packaging, printing inks, and various protective coatings for wood, plastics and metal etc [1]. Among all different UV-curable resins, waterborne UV-curable resin combines the advantages of both UV-curing system and the waterborne system, offering a perfect option for eco-friendly coating with low VOCs, non-toxic, and fast processing time.

However, there are still several challenges for waterborne UV curable coatings: such as the discoloration after long-term exposure to ultraviolet light, which will further lead to degradation of the coating layer; the second challenge is the instant yellowing during UV curing process which cause appearance problem and further quality issue. The last one is the protection requirement for near-visible light sensitive materials. To solve the above-mentioned challenges, usually UV absorbers (UVA) and hinder amine light stabilizers (HALS) are used.

UV absorbers will absorb UV energy to protect the polymer form degradation. However, in UV curing process, photo initiators are used and also need UV energy to initiate curing reaction. As the result, UV absorber and photo initiator would compete for UV energy, and therefore cause negative impacts to curing speed and the production efficiency.

A novel light stabilizer(NLS) is rolled out to meet the challenges above [11-16]. The objectives of this article is to demonstrate our latest development on liquid NLS especially designed for waterborne UV-curable coating system, and to effectively enhance the weatherability without sacrifice on curing speed.

Experiment

Materials

- Waterborne UV curable polyurethane (Bayhydrol® UV 2282), Industrial Grade, Bayer
- Photo-Initiator (Irgacure® 500), Industrial Grade, BASF
- Novel Light Stabilizer (NLS), Industrial Grade, Everlight Chemical
- Waterborne UV Absorber, Waterborne HALS, Industrial Grade, Everlight Chemical

Equipment

- UV Curing Drying Equipment: C Sun / UV-201M
- High Energy UV Integrating Radiometer: EIT / Model: UVICURE Plus® PLUS-365;
- QUV Accelerated Weathering Tester: Q Panel / Model: QUV Basic
- Spectrophotometer: KONICA MINOLTA / Model: CM-3500d

Methods:

- Design of Experiment (DOE) was used to design test runs as well as to analyze the data.
- Waterborne UV curable coating preparation and UV curing process: waterborne UV curable coating formulation was shown in Table 1. Mix the blended waterborne UV curable coating with different types and doses of light stabilizers (shown in Table 2 and 3). Use the Film Coater to evenly apply the mixed blend onto a tinplate or glass plate with size at 10 cm×7 cm×0.1 cm, put the coated plate in 60℃ oven for 2 mins, then transfer into the UV Curing Drying Machine for curing process.
- Minimum Required Energy Test: Use the High Energy UV Integrating Radiometer to monitor the minimum energy required to complete the curing process on the tested sample.
- Accelerated weathering test: ASTM G154-1 (2006 version), Test standard: 340nm, 60℃, 8hrs / 50℃, 4hrs cool down)
- Testing method for blocking efficiency of wavelength at 365nm and 380nm: Use the Spectrophotometer to monitor the blocking status of 365nm or 380nm during the accelerated weathering test.
- Software and analysis: JMP version 5.0 (SAS Institute)

Table 1 Compositions of waterborne UV model formulation

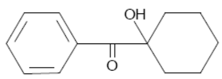
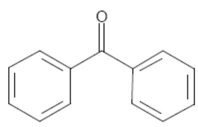
Materials	Characteristic	Structure
Bayhydrol® UV 2282	Polyurethane Dispersion (for water-based system)	---
Irgacure® 500	50% Acyloin + 50% Benzophenone	 + 

Table 2 Classification of light stabilizers

Ingredients	Characteristic
WUVA	UVA (for Water-based system)
NLS	Formulation of novel light stabilizers
WHALS	HALS (for Water-based system)

Results & Discussion

Screening Design

Screening design (Table 3) was used to identify factors that affect the curing speed of waterborne UV curable coatings. Mathematical model derived from data (Table 4&Table 5) indicates all factors –Waterborne UVA, HALS, NLS and film thickness – exhibit some degrees of influence to the curing speed.

Table 3 Details of Screening Design and Test Results(R^2=0.99, Radj^2=0.97, RMSE=0.008)

RUN	Pattern	UVA	NLS	HALS	DFT (μm)	The min. energy to reach curing need (J/cm2)
1	+ + - -	1%	1%	--	15	0.108
2	- - + -	--	--	1%	15	0.123
3	- + + -	--	1%	1%	15	0.123
4	+ - + -	1%	--	1%	15	0.197
5	- + - -	--	1%	--	15	0.071
6	- - - -	--	--	--	15	0.071
7	+ + + -	1%	1%	1%	15	0.197
8	+ - - +	1%	--	--	15	0.108
9	+ + - +	1%	1%	--	50	0.057
10	- - + +	--	--	1%	50	0.063
11	- + + +	--	1%	1%	50	0.063
12	+ - + +	1%	--	1%	50	0.065
13	- + - +	--	1%	--	50	0.051
14	- - - +	--	--	--	50	0.051
15	+ + + +	1%	1%	1%	50	0.065
16	+ - - +	1%	--	--	50	0.057

Table 4 Parameter estimates(R^2=0.99, Radj^2=0.97, RMSE=0.008)

Term	Estimate	Std. Error	t Ratio	Prob>|t|
Intercept	0.1179286	0.006255	18.85	<.0001
WUVA	0.02975	0.004584	6.49	0.0013
NLS	8.327e-17	0.004584	0.00	1.0000
(WUVA-0.5)*(NLS-0.5)	-8.67e-18	0.009168	-0.00	1.0000
WHALS	0.04025	0.004584	8.78	0.0003

(WUVA-0.5)*(WHALS-0.5)	0.0165	0.009168	1.80	0.1318
(NLS-0.5)*(WHALS-0.5)	1.735e-18	0.009168	0.00	1.0000
DFT	-0.001879	0.000131	-14.34	<.0001
(WUVA-0.5)*(DFT-32.5)	-0.001471	0.000262	-5.62	0.0025
(NLS-0.5)*(DFT-32.5)	-1.74e-17	0.000262	-0.00	1.0000
(WHALS-0.5)*(DFT-32.5)	-0.001729	0.000262	-6.60	0.0012

Table 5 Analysis of variance (ANOVA)

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	10	0.03389750	0.003390	40.3302
Error	5	0.00042025	0.000084	Prob > F
C. Total	15	0.03431775		0.0004

$$\rho_{WUVA} = \frac{SS_{WUVA} - \varphi_{WUVA} \times MS_E}{SS_T} = \frac{0.003540 - 1 \times 0.000084}{0.03432} = 10.1\ \%$$

$$\rho_{WHALS} = \frac{SS_{WHALS} - \varphi_{WHALS} \times MS_E}{SS_T} = \frac{0.006480 - 1 \times 0.000084}{0.03432} = 18.6\%$$

$$\rho_{NLS} = \frac{SS_{NLS} - \varphi_{NLS} \times MS_E}{SS_T} = \frac{0 - 1 \times 0.000084}{0.03432} \cong 0\%$$

$$\begin{aligned}&\text{Curing Energy Y } (\text{J}/cm^2) = \\ &0.1179 + 0.02975 \times [\text{WUVA}] + 0.04025 \times [\text{WHALS}] + 0.0165 \times [\text{WUVA - 0.5}] \times [\text{WHALS - 0.5}] \\ &- 0.001879 \times [\text{DFT}] - 0.001471 \times [\text{WUVA - 0.5}][\text{DFT - 32.5}] \\ &- 0.001729[\text{WHALS} - 0.5][\text{DFT} - 32.5] \pm 2 \times 0.00042\end{aligned}$$

Figure 1 The effect of curing energy with waterborne UVA, HALS and NLS in waterborne UV curable model formulation

Effects of waterborne UV absorber

Photo-initiator absorbs UV energy to initiate curing processes. UV absorber (UVA) absorbs UV energy to prevent coatings from UV degradation. UV absorbers and photo-initiators are competing for UV energy and therefore cause negative impacts on curing speed. Our experiment results match the assumption above-mentioned. Model derived from data confirms waterborne UV absorber is a significant factor that cause curing speed to drop considerably. For UVA, the effect factor of curing energy is about 10.1% (see Figure 1).

Effects of waterborne HALS

Although HALS functionally don't absorb UV light; however, to our surprise, it exhibits the highest negative impact on curing speed among all the factors. One possible reason is the fact that HALS is an effective free radical scavenger which might interfere the free radical chain reaction initiated by photo-initiators, leading to premature termination of curing process and incomplete cured coating layer. As a result, for HLAS, the effect factor for curing energy is about 18.6% and it's higher than UVA (see Figure 1).

Effects of film thickness

Film thickness is the less significant factor in this study (see Figure 1). Its negative coefficient is in agreement with a known fact to the industry – in free radical polymerization mechanism, oxygen inhibition affects thinner film more than thicker film. Moreover, a positive coefficient, 0.1179, in the model indicates oxygen inhibition did occur to the coatings (see Figure 1).

Effects of novel light stabilizer (NLS)

NLS is developed specifically for waterborne UV curable coating system. Test data shows that NLS added in the waterborne UV curable clear coating would not interfere the curing speed. For NLS, the effect factor of curing energy is about 0% (see Figure 1).

Evaluation of optimized situation

Evaluation for optimized situation tests and results are shown in Table 6, it is used to identify the effect of NLS (novel light stabilizer) concentration and DFT (dry film thickness), factors that affect UV filtering ability at 365nm, 380nm wavelength and the yellowing status after weathering for 120hrs. Mathematical model derived from data indicates two factors –NLS and DFT – exhibit some degrees of influence to UV filtering and yellowing after weathering test.

Table 6 Evaluation of optimal results

(NLS)/%	DFT：Film thickness (μm)	365nm (T%)	380nm (T%)	ΔY：Delta Yellowness Index (After weathering test for 120 hrs.
0	10	82.5	89	6.5
0	30	71	81.3	7.6
0	50	68.4	79.2	8.4
0	140	52.3	62.1	12.4
1	10	68.7	80.5	3.1
1	30	39	62.5	4.5
1	50	33.5	57.4	5.4

1	140	2.89	19.2	6.7
3	10	50.2	74	1.8
3	30	12	37.1	2.5
3	50	7.86	33	3.2
3	140	1.67	18	3.7
5	10	24.6	55.1	0.8
5	30	6.7	31.6	1.3
5	50	0.7	11.5	1.9
5	140	0.09	6.88	2.2

Table 7 Analysis of variance (ANOVA) (R^2=0.92, $Radj^2$=0.88, RMSE=10.26)

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	11922.124	2384.42	22.6657
Error	10	1051.997	105.20	Prob > F
C. Total	15	12974.120		<.0001*

Table 8 Parameter estimates

Term	Estimate	Std. Error	t Ratio	Prob>|t|
Intercept	65.628924	5.517302	11.90	<.0001*
NLS%	-12.68856	1.435575	-8.84	<.0001*
DFT	-0.477817	0.092393	-5.17	0.0004*
(NLS%-2.25)*(NLS%-2.25)	2.9716709	0.98726	3.01	0.0131*
(NLS%-2.25)*(DFT-57.5)	0.0302167	0.026875	1.12	0.2871

$$\rho_{NLS} = \frac{SS_{NLS} - \varphi_{NLS} \times MS_E}{SS_T} = \frac{8218 - 1 \times 105.2}{12974} = 62.5\ \%$$

$$\rho_{DFT} = \frac{SS_{DFT} - \varphi_{DFT} \times MS_E}{SS_T} = \frac{2813 - 1 \times 105.2}{12974} = 20.9\%$$

$$\mathrm{T}(365nm)\% =$$
$$65.63 - 12.69 \times [NLS] - 0.48 \times [DFT] + 2.97 \times [NLS\% - 2.25] \times (NLS\% - 2.25)$$
$$- 0.03 \times (NLS\% - 2.25) \times (DFT - 57.5) \pm 2 \times 10.26$$

Figure 2 Effects of NLS and film thickness at 365nm wavelength in waterborne UV curable model formulation

Effects of novel light stabilizer (NLS) and film thickness on 365nm UV filtering.

NLS is developed specifically for waterborne UV curable coatings. According to the results analyzed from Table 6-8 and Figure 2, the effect factor of NLS on 365nm UV filtering is 62.5%. For film thickness, the effect factor is only 20.9%. The result indicates that raise NLS concentration in waterborne clear coatings will have better 365nm UV filtering efficiency comparing with increasing film thickness (see Figure 2).

Table 9 Analysis of variance (ANOVA) (R2=0.91, Radj2=0.88, RMSE=9.98)

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	9452.817	3150.94	19.9193
Error	12	1898.223	158.19	Prob > F
C. Total	15	11351.040		<.0001*

Table 10 Parameter estimates

Term	Estimate	Std. Error	t Ratio	Prob>|t|
Intercept	86.278277	5.366302	16.08	<.0001*
NLS%	-10.38896	1.396286	-7.44	<.0001*
DFT	-0.510645	0.089864	-5.68	0.0002*
(NLS%-2.25)*(NLS%-2.25)	1.5204397	0.96024	1.58	0.1444
(NLS%-2.25)*(DFT-57.5)	-0.006172	0.026139	-0.24	0.8181
(DFT-57.5)*(DFT-57.5)	0.0043549	0.001699	2.56	0.0282*

$$\rho_{NLS} = \frac{SS_{NLS} - \varphi_{NLS} \times MS_E}{SS_T} = \frac{5509 - 1 \times 99}{11351} = 47.7\ \%$$

$$\rho_{DFT} = \frac{SS_{DFT} - \varphi_{DFT} \times MS_E}{SS_T} = \frac{3213 - 1 \times 99}{11351} = 27.4\%$$

$$\begin{aligned} &\mathrm{T(380nm)\%} = \\ &86.28 - 10.39 \times [\mathrm{NLS}] - 0.51 \times [DFT] + 1.52 \times [NLS\% - 2.25] \times (NLS\% - 2.25) \\ &- 0.006 \times (NLS\% - 2.25) \times (DFT - 57.5) + 0.004(DFT - 57.5) \times (DFT - 57.5) \pm 2 \times 9.98 \end{aligned}$$

Figure 3 Effects of NLS and film thickness at 380nm wavelength in waterborne UV curable model formulation

Effects of novel light stabilizer (NLS) and film thickness on 380nm UV filtering

The UV filtering at 380nm shows the same trend as at 365nm. For NLS, the effect factor on 380nm UV-filtering is 47.7%. For film thickness, the effect factor is only 27.4% (see Figure 3).

The effect factor of NLS concentration is stronger than film thickness. To improve UV filtering performance at 380nm, increasing NLS concentration is more effective than increasing film thickness.

Table 11 Analysis of variance (ANOVA) (R2=0.96, Radj2=0.94, RMSE=0.75)

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	142.84709	28.5694	51.0815
Error	10	5.59291	0.5593	Prob > F
C. Total	15	148.44000		<.0001*

Table 12 Parameter estimates

Term	Estimate	Std. Error	t Ratio	Prob>|t|
Intercept	5.2930763	0.402289	13.16	<.0001*
NLS%	-1.498163	0.104674	-14.31	<.0001*
DFT	0.0313252	0.006737	4.65	0.0009*
(NLS%-2.25)*(NLS%-2.25)	0.3394158	0.071985	4.72	0.0008*
(NLS%-2.25)*(DFT-57.5)	-0.006483	0.00196	-3.31	0.0079*
(DFT-57.5)*(DFT-57.5)	-0.000192	0.000127	-1.51	0.1619

$$\rho_{NLS} = \frac{SS_{NLS} - \varphi_{NLS} \times MS_E}{SS_T} = \frac{114.57 - 1 \times 0.559}{148.4} = 76.8\ \%$$

$$\rho_{DFT} = \frac{SS_{DFT} - \varphi_{DFT} \times MS_E}{SS_T} = \frac{12.09 - 1 \times 0.559}{148.4} = 7.7\%$$

$$\Delta Y = 5.29 - 1.5 \times [NLS] + 0.03 \times [DFT] + 0.34 \times [NLS\% - 2.25] \times (NLS\% - 2.25) - 0.006 \times (NLS\% - 2.25) \times (DFT - 57.5) - 0.0002(DFT - 57.5) \times (DFT - 57.5) \pm 2 \times 0.75$$

Figure 4 Effects of NLS and film thickness to yellowing reduction in waterborne UV curable model formulation

Effects of NLS and film thickness on yellowing

The effects of NLS and film thickness to reduce yellowing were evaluated in the experiment. For NLS, the effect factor of reducing yellowing is 76.8%; while for film thickness, the effect factor is only 7.7% (see Figure 4). The results show that comparing with film thickness, NLS concentration used in waterborne clear coats is the dominated factor for yellowing.

The Optimal Prediction Profiler

The optimal prediction profiler shows effects of NLS and DFT on UV filtering at 365nm, 380nm and yellowing difference after weathering for 120hrs. The results suggest the best condition of NLS concentration is 5% and film thickness is 140µm (as shown in Figure 5).

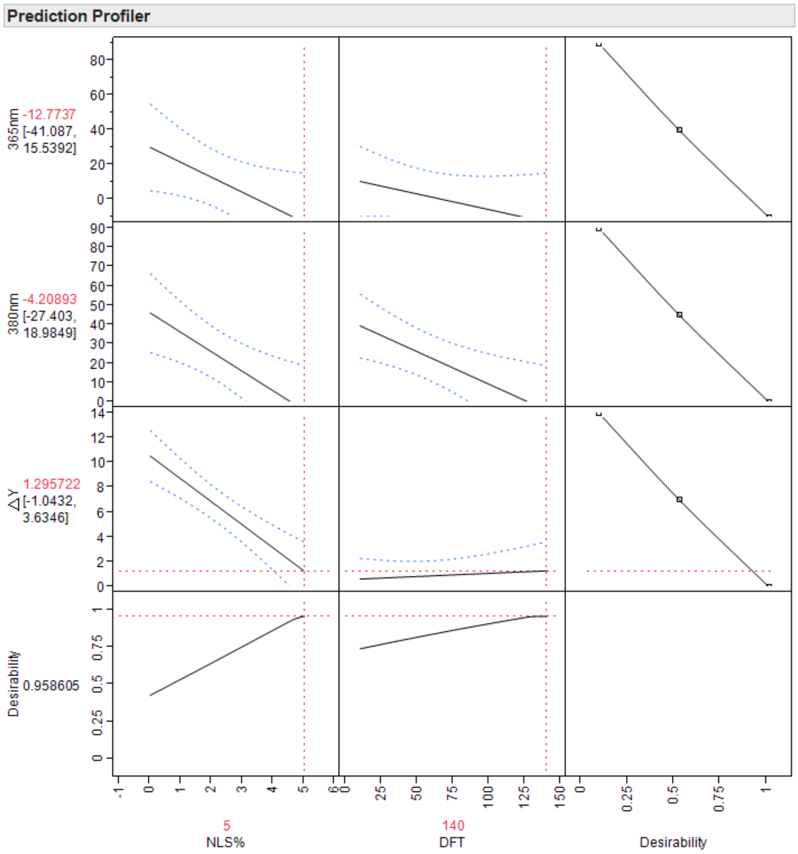


Figure 5 Effects of NLS and DFT at 365nm, 380nm and reduced yellowing after weathering for 120hrs (Optimal Prediction Profiler)

Response surface methodology (RSM)

Response surface methodology (RSM) is a collection of mathematical and statistical techniques for empirical model building. By careful design of experiments, the objective is to optimize a response (output variable are 365nm, 380nm and ΔY) influenced by several independent variables [input variables are NLS (%) and DFT (µm)]. The highlighted area from this model which is the optimal result in UV filtering at 365nm, 380nm and reduced yellowing (as shown in Figure 6-8).

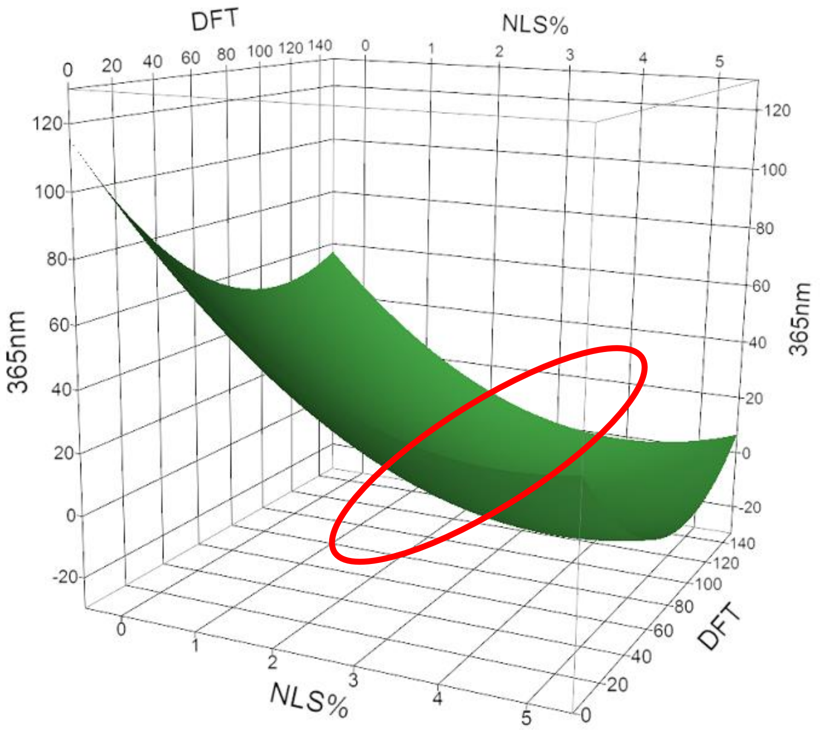


Figure 6 Response surface methodology (NLS vs. DFT vs. 365nm)

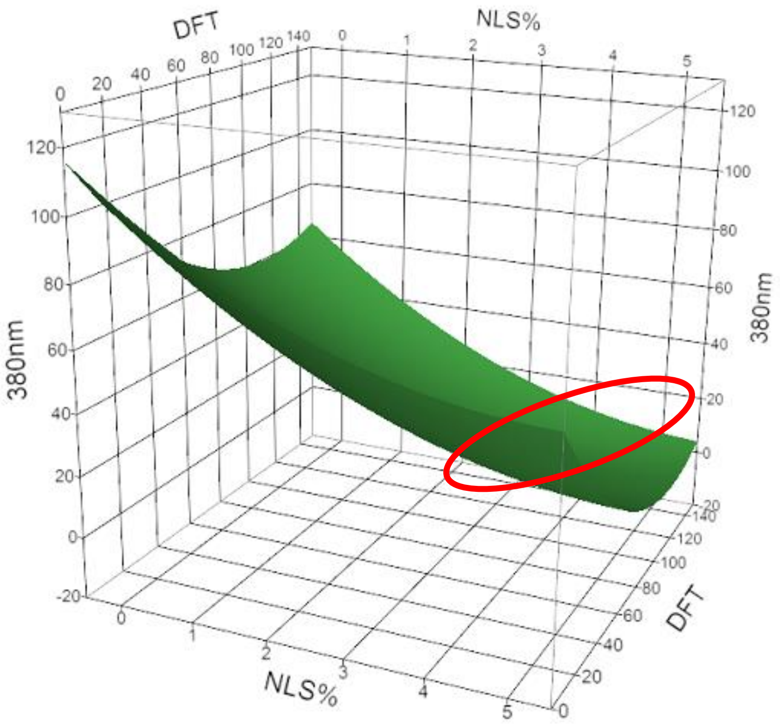


Figure 7 Response surface methodology (NLS vs. DFT vs. 380nm)

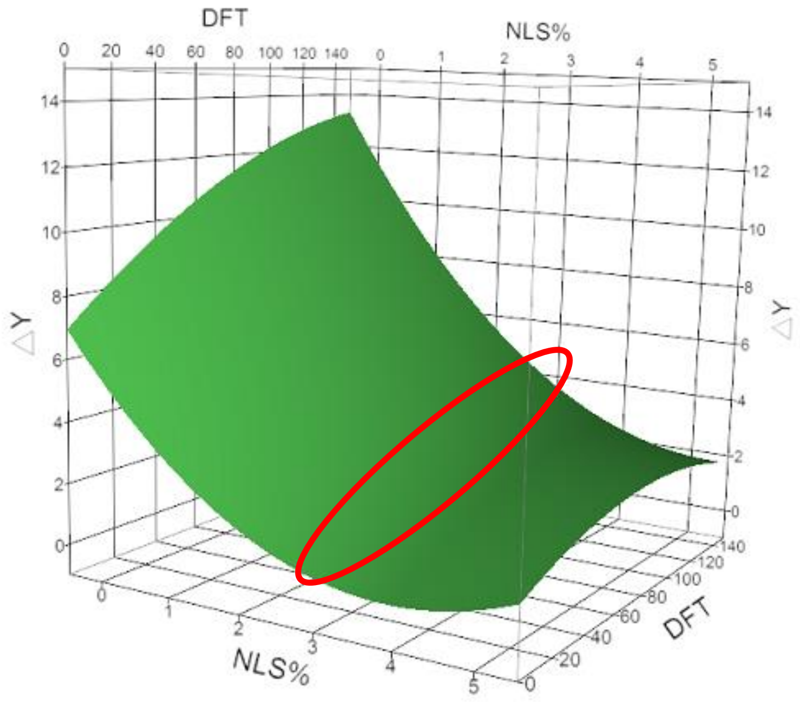


Figure 8 Response surface methodology (NLS vs. DFT vs. ΔY)

Conclusion

Eco-Friendly coatings are one of the most important development trends in coating industry. In this article we demonstrated the benefits of using the Novel Light Stabilizer (NLS) in waterborne UV-curable coating system.

The test result shows that the designed NLS would not interfere the curing speed of the tested waterborne UV-curable clear coating, and therefore won't have any negative impact on curing process. Moreover, the result confirms that by increasing the NLS concentration in the clear coat would have better efficiency on enhancing the UV filtering ability, comparing with increasing film thickness. At 365nm wavelength, the effect factor of NLS is 62.5%, while DFT (dry film thickness) is 20.9%; at 380nm, the effect factor of NLS is 47.7%, while DFT is only 27.4%. For NLS, the effect factor of reducing yellowing is 76.8%. For film thickness, the effect factor is only 7.7%.

Our test results proof the designed NLS could block the UV light without compromising the curing speed, and is the perfect solution for enhancing weatherability of waterborne UV-curable coatings. Coating manufactures may still need to run the experiments to confirm the compatibility. Also, a tailor-made UV absorber and light stabilizer package could be offered to fulfill your special needs.

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