

Recent advances in photocuring and stabilization of water-borne coatings

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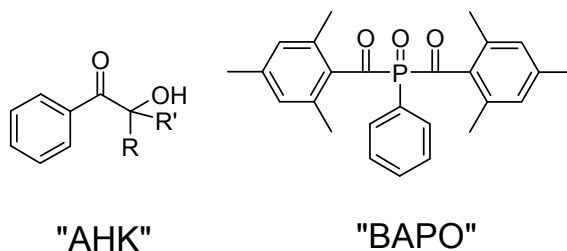
Abstract

Recent advancements in resin and additive technologies have permitted the engineering of highly durable (weather resistant) UV curable water-based coatings. These types of coatings are designed to be eco-friendly, have low or negligible VOC, and be able to rapidly crosslink and cure under UV light. The finished coatings exhibit high solvent resistance and low color. They effectively remain unchanged for many years.

These types of coatings are very attractive for decks, wood, plastics, glass or other common materials requiring and protection against UV light. The trick is to achieve the performance is the selection of the right resin along with an optimal photoinitiator and light stabilizer package. An arylphosphine oxide based photoinitiator package was developed to work with special UV blockers in water-based media, to achieve the desired UV cure speeds and also the UV blocking power in the final coating. It was found that the new nano-encapsulated technology (NEAT) based light stabilizers provided distinctly enhanced photo-stability of these water-based UV curable coatings.

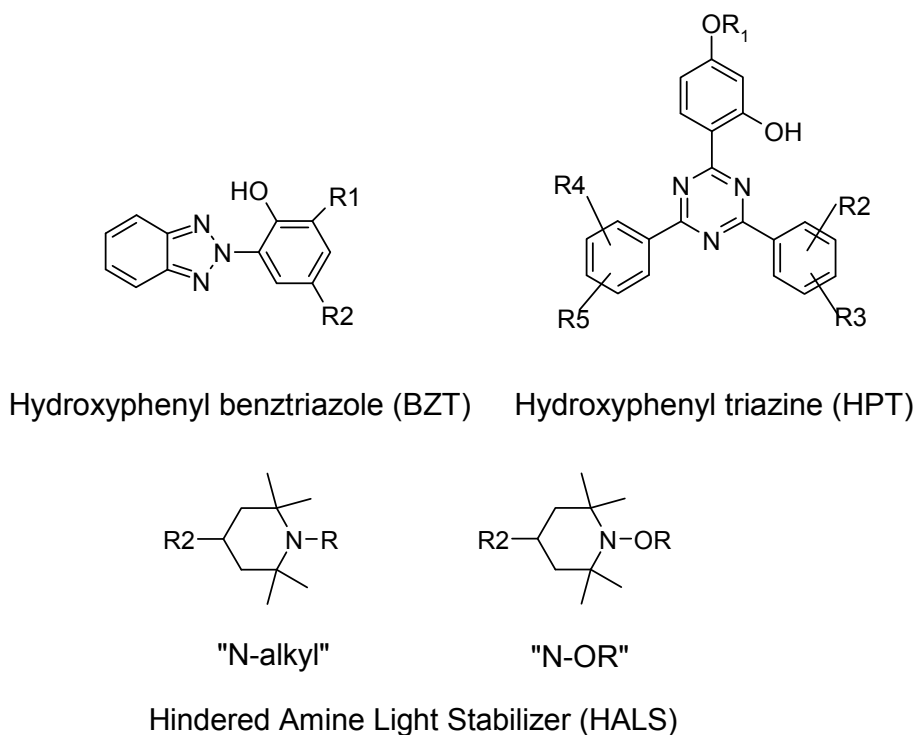
1. Introduction

In recent years the field of water-borne UV curable coatings has taken on greater significance as the coatings industry recognizes how it can help increase production efficiencies, lower VOC's, and deliver high end performance^{1,2}. In previous work we described how various water-borne urethane acrylate dispersions could be photocured and also photostabilized^{3,4}. We found a particularly effective strategy for photocuring was to use two or more photoinitiators. The individual photoinitiators target specific regions (surface and bottom) of the coating. Short wavelength absorbing photoinitiators were found to effectively cure the top coating surface. On the other hand, a long-wavelength absorbing and photobleachable photoinitiator can be effective for deep through-curing. Examples of the common photobleachable, long wavelength absorbing photoinitiators are mono-acylphosphine oxide (MAPO) and bis-acylphosphine oxide, BAPO.



Scheme 1. Common photoinitiator type used for UV curing of light stabilized water-borne acrylate coatings (AHK = alpha hydroxyl ketone, BAPO = bisacyl phosphine oxide)

Photoinitiators that work well to cure the surface are aromatic alpha hydroxy ketones (AHK) and mixtures of benzophenone/AHK⁵. To ensure good through-curing arylphosphine oxide photoinitiators were employed⁶. Deep through cure was particularly critical for coatings that contained UV blocking materials (light stabilizers and/or pigments/fillers). Water dispersible benzotriazole (BZT) and polar hindered amine light stabilizers (HALS) were found to be useful in these early studies³. These light stabilizers are, however, are not necessarily the top performers for low wash-out and high photopermanence.



Scheme 2. Light stabilizers used in UV curable water-borne acrylate coatings

Since that time newer high performance water-borne UV curable resins have emerged⁷, and these in turn place more stringent requirements on the photoinitiator and light stabilizer packages. Further, the higher durability requirements often are not met with traditional light stabilizer packages.

Part of solving the light stabilizer problem was trying to get high performance and hydrophobic additives into the resin system. An ingenious way to overcome this barrier was recently introduced to the coatings industry^{8,9}. The solution was to use an encapsulation technology for the high performance additives. The so called Novel Encapsulated Additive Technology (NEAT) was found to provide a way easily incorporate the materials to aqueous paints without using co-solvents and without requiring high energy dispersion equipments.

The goal of this work is to explore the use of the NEAT additives for a UV curable water-borne resin, which yields a photostable coating. We found that stability, control over color and increased weatherability was achieved using the NEAT light stabilizers with liquid based photoinitiators.

2. Experimental Material and Methods

2.1. Materials

Ethylene glycol monobutylether (“EB”) was used as an additive cosolvent for selected photoinitiators and/or light stabilizers. EB was obtained from Acros Organics.

Photoinitiators were obtained from BASF Corporation and were used as received. The photoinitiators included the alpha hydroxyketones (AHK), mixtures of benzophenone and AHK, mono and bis acyl phosphine oxides. The AHK photoinitiators used were: Irgacure 2959 (I-2959), which is a solid, water soluble AHK, blended Irgacure 184 with EB (“I-184/EB”), and an experimental liquid AHK (LAHK). The Irgacure 500 (I-500) was a 1:1 liquid blend of benzophenone and I-184. The arylphosphine oxide photoinitiators included the monoacrylphosphine oxide (MAPO) and the bisacylphosphine oxide (BAPO). The BAPO examined was in three forms: dispersion, liquid mixture with either MAPO or AHK. The Irgacure 819DW is a water dispersion of BAPO. The liquid Irgacure 2022 (I-2022) is a blend of AHK/BAPO⁶. The Irgacure 2100 (I-2100) is a liquid blend of BAPO/MAPO⁶.

The light stabilizers consisted of UV absorbers (UVAs) and hindered amine light stabilizers (HALS). Tinuvin 1130 (UVA-BZT) and Tinuvin 292 (HALS-292) were obtained from BASF Corporation, and used as received. The Tinuvin 123-DW (HALS 123-DW) is a nonpolar HALS (Tinuvin 123), which uses the NEAT technology to render it 30% active in an aqueous solution. The Tinuvin 400-DW (UVA 400-DW), Tinuvin 477-DW (UVA 477-DW) are both hydroxyphenyl triazene UV absorbers. The UVA 400-DW and UVA 477-DW are both 20% active in an aqueous solution.

2.2. Polyurethane dispersion (PUD) formulation

The BASF Laromer 8949 was selected as the resin for the UV curable aliphatic polyurethane dispersion. The Laromer 8949 is 38-42% active. It is a water-borne radiation-curable aliphatic urethane dispersion with physical drying properties. This high performance resin is intended for the production of coatings for paper, wood, wood-based materials, plastic and printing inks⁷.

A low gloss fast curing formulation using the Laromer 8949 as the base resin is given in Table 1. This formulation, hereafter referred to as “PUD” is suitable as a coating for wood and/or for plastic.

Table 1. Polyurethane dispersion (PUD) UV curable formulation

Type/description	parts
Aliphatic urethane dispersion (Laromer LR 8949)	77.3
Thixotropic agent (Aerosil 200) ^a	0.6
Matting agent (Syloid C 809, Syloid C 906) ^b	2
Thickener (Optiflo H 400) ^c	0.3
Water	13.2
Anti-foam	0.8
DPM (Dipropylene glycol monomethyl ether)	2.1
Leveling agent	0.3

a) Evonik Corp.; b) Grace Davison Columbia, MD, c) Southern Clay Products, Louisville KY

Photoinitiators were added by simple mixing to the formulation to make the resin UV curable. The light stabilizers were also added by simple mixing, and they were used to determine their effect on photodurability, color and photoresponse.

2.3. Formulation stability testing

The formulations were prepared containing various additives and stored at 23°C. The samples were examined for any change in appearance over time, such as the development of phase separation, thickening and/or gelation.

2.4. Photocuring and characterization

Samples were applied using a Bird bar onto white aluminum panels, dried at room temperature for 5 to 10 minutes, then placed in a convection oven at ~53 °C for 10 minutes. The dried specimens were subsequently photo-cured in air at ambient temperature with Fusion UV 600 watt gallium doped “V” lamp followed by an iron doped (“D”) lamp at various energy levels. The typical line speed was 20 feet per minute. A single pass under the lamps corresponded to a UVA energy of 3.8 J/cm².

A radiometer UV Power Map from EIT Inc. was used to measure UV-light on the conveyer belt. The diode detector is sensitive to the following regions: UVV (395-445 nm), UVA (320-390 nm), UVB (280-320nm), UVC (250-260 nm).

2.5. Xenon Accelerated Weathering

The Xenon WOM measurements were performed with an Atlas weatherometer, following the SAE J1960 test protocol. To this end the xenon arc burner was equipped with a quartz inner filter and a “Type S” borosilicate outer filter. A Cam #180 also was installed. The light cycle used had an irradiance of 0.55 W/m² @ 340 nm, with black panel temperature at 70°C, wet bulb depression at 12°C and conditioning water at 45°C; dark cycle used: black panel temperature at 38°C, conditioning water at 40°C.

The CAM#180 installed provided 120 minutes of light and 60 minutes of dark in the following cycle: 40 minutes of light followed by 20 minutes of light and front specimen spray, followed by 60 minutes of light, followed by 60 minutes of dark with back rack spray and repeating. The coated samples specimens were visually inspected after exposure and characterized for changes in color and/or solvent resistance.

2.6. FTIR double bond conversion

A Nicolet Avatar 370 DTGS spectrophotometer (ThermoElectron Corp.) was used to obtain the FTIR/ATR spectra. The spectrophotometer was equipped with a diamond crystal and a smart orbit accessory. Data acquisition used a resolution 4 cm⁻¹ and data spacing of 1.929 cm⁻¹, and each spectrum was an average of 32 scans, taken from 4000 cm⁻¹ to 400 cm⁻¹ and referenced against an air background.

The reported percent double bond conversion (%conv) was determined from ATR-FTIR spectra. The double bond conversion is expressed as %conv = 100*(“Initial”-“Final”)/“Initial”, where “Initial” &

“Final” observables are integral ratios of (Acrylate Absorbance Integral at 815 cm^{-1}) / (Carbonyl Absorbance Integral at 1704 cm^{-1}). ATR-FTIR spectra were done on top and bottom sides of the coating.

2.7. MEK solvent resistance of the photocured coatings

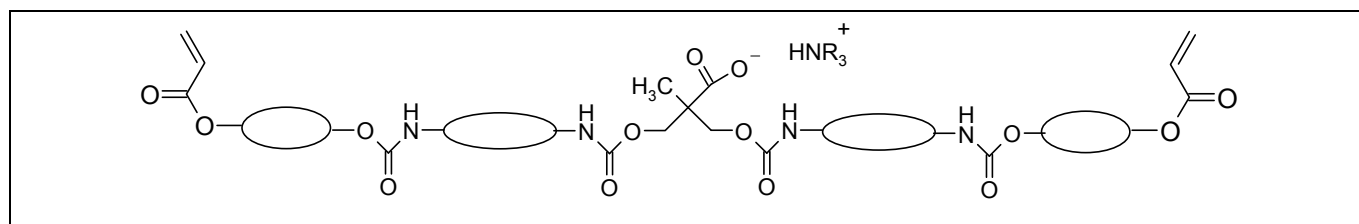
The solvent resistance is a well known measure of cure. The use of methyl ethyl ketone (MEK) as the solvent is often used in the industry. The method is to perform double rub on the coating surface with a cloth soaked with MEK solvent ¹⁰.

2.8. Coloristics

Colorimetric measurements were performed with a Minolta Spectrometer CM 3600d. The color values were specifically quantified by determining the CIE L*a*b* system, following ASTM E 308 methods ¹¹. A higher positive number for the b* value indicates a stronger yellow color.

3. Results and Discussion

The PUD formulation used the high performing Laromer LR 8949, which is a water-borne radiation-curable aliphatic polyurethane dispersion for coatings for wood, wood-based materials, paper, plastic and printing inks. A generic structure of the resin is shown in Scheme 3.



The substructures  represent oligomeric backbones.

Scheme 3. General structure of the water-dispersible urethane acrylate

Coatings based on the PUD formulation were tack-free after physical drying (evaporation of the water) and therefore are well-suited for three-dimensional substrates. After curing with UV light the cured films show excellent resistance to water and chemicals (such as MEK), and are also very scratch and block-resistant.

The methodology used to optimize the formulation with respect to selecting the photoinitiator and light stabilizer packages was to divide the screening work into three parts: 1) formulation stability, 2) photocure response, and 3) accelerated weathering.

3.1. Effect of additives on solution stability

As a first step in selecting the additives, it is necessary to determine their effect on stability of the water-borne formulation. Since this is a UV curable PUD formulation, we need to assess the stability of the

individual photoinitiators (which are needed for curing), the light stabilizers (which are needed for photostabilization after curing and/or color management) as well as the combination of both them together.

As given in Table 2 it was found that the photoinitiators commonly used for water-borne coating [ref] systems showed excellent stability characteristics. For example, good stability (> 140 days) was observed for the dispersed BAPO (I-819DW), for I-500 as well as for the liquid AHK's (LAHK and I-184/EB).

Table 2. Effect of various photoinitiators on the shelf life stability of PUD

Photoinitiator (in PUD formulation)	Days of stability
no photoinitiator	>96
I-819DW (1%)	>142
I-819DW (0.5%)	>142
I-819DW (1%) + I-500 (1%)	>142
I-819DW (0.5%) + I-500 (1%)	>142
I-819DW (0.3%) + I-500 (1%)	>142
I-819DW (1%) + I-525 (1%)	>142
I-819DW (0.5%) + I-525 (1%)	>142
I-819DW (0.3%) + I-525 (1%)	>142
I-819DW (0.5%)+I-184/EB (1%)	>142
I-2022 (1%)	>98
LAHK (0.6%)	>98
I-184/EB (1.2%)	>98
I-184/EB (2%)	>65
LAHK (1.33%)	>148
I-184/EB (2%)	>148

It was found the solution stability with the PUD was more greatly affected by use of the light stabilizers. As given in Table 3, the combination UVA-BZT/HALS-292 proved unusable, because the shelf life stability was less than 1 day. In an effort to see if a small amount of co-solvent could overcome some of the stability issue, we co mixed EB with the UVA-BZT/HALS-292. This resulted in an improved shelf life, but the stability still remained too low to be useful. In contrast, the NEAT products were especially good, and the shelf-life was up to greater than 90 days.

Table 3. Effect of light stabilizers on the shelf life stability of PUD

Light stabilizer in PUD formulation	Days of stability
UVA-BZT/HALS-292, 2:1 (3%)	1
UVA-BZT/HALS-292, 2:1 (3%) - resin only without matting agents	2
UVA-BZT/HALS-292, 2:1 (3%) + EB (3%)	> 63
control - no PI, no LS	> 96
T400-DW (2%)+T123-DW(1%)	> 125
T477-DW (2%)+T123-DW(1%)	> 96

Following the early work [ref], we initially examined the use of I-819 DW in combination with the light stabilizers of the NEAT (T-DW) type. The results in Table 4 showed without exception low stability (<30 days) resulted for all formulations containing I-819 DW. The stability was as low as only 10-15 days for formulations with higher I-819 DW content. The results indicate that for this particular PUD formulation the I-819 DW is not a good option.

Table 4. Effect of combining photoinitiators with light stabilizers on the shelf life stability of PUD

LS Package			PI package							Time to failure, days
T400DW	T123DW	T477DW	I 819 DW	I 2022	I 2100	I-2959	LAHK	I-500	I-184/EB	
2	1		1					1		10
2	1		0.5					1		21
2	1		0.3					1		29
2	1		0.3				1			21
2	1		0.3			1				29
	1	2	1					1		10
	1	2	1				1			15
	1	2	0.5				1			21
	1	2	0.5						1	21
	1	2	0.3				1			21
2	1				0.2		0.6			>136
2	1				0.2			0.6		>136
2	1				0.2				1.2	>136
2	1			1						>136
	1	2			0.2		0.6			>136
	1	2			0.2			0.6		>132
	1	2			0.2				1.2	>132
	1	2		1						>132

Prompted by these results we investigated a variety of photoinitiator packages involving I-2022 or combinations of I-2100 with LAHK or I-500 or I-184/EB. Since the UV absorbers will block UV light below 375 nm (see Figure we will still need the BAPO or MAPO photoinitiators to ensure good through cure. The stability results for these formulations without I-819 DW presented also in Table 4 are very good, all formulations displaying stability in excess of 132 days that is of practical interest for the industry.

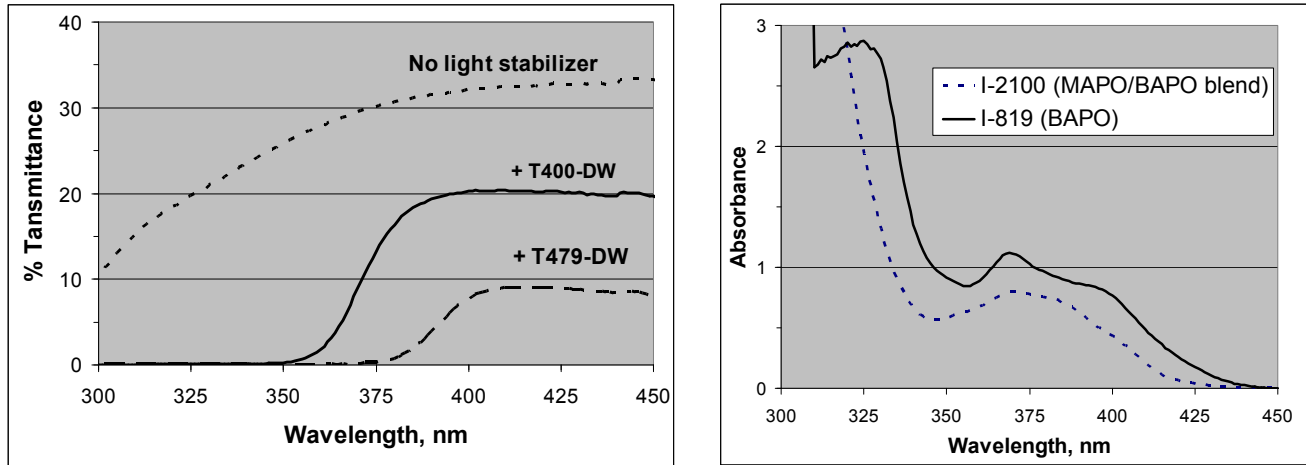


Figure 1. Transmission spectra of UV cured PUD coating (2.2 mil dry thickness) containing various UV absorbers and BAPO (I-819) and BAPO/MAPO blend (I-2100) photoinitiators.

In summary, traditional additives caused stability issues with the resin system. UVA-BZT and HALS-292 were unusable; the I-819DW by itself was acceptable but when combined with a light stabilizer caused major stability problems. Thus, the use of NEAT (T-DW) based light stabilizers was critical for the formulation stability where the liquid photoinitiators combined with the T-DW light stabilizers gave the best overall stability.

Having found the preferred photoinitiator/light stabilizer combinations, the next questions are how these additives affect the UV curing profile and long term weathering.

3.2. Effect of additives on photocure response

The UV cure profile can be assessed by a number of ways, such as spectroscopically and/or through physical testing such as tensile analysis or solvent resistance. In this study we examined the double bond conversion and solvent resistance.

FTIR analysis was used to determine the degree of conversion (low of the acrylate double bond). The results of how the UV exposure affects the conversion are shown graphically in Figures 2 and 3. From the FTIR analysis it was found that at the surface the double bond conversion was at best 60%. In contrast, excellent double bond conversion (90%) was seen for the bottom side of the coating.

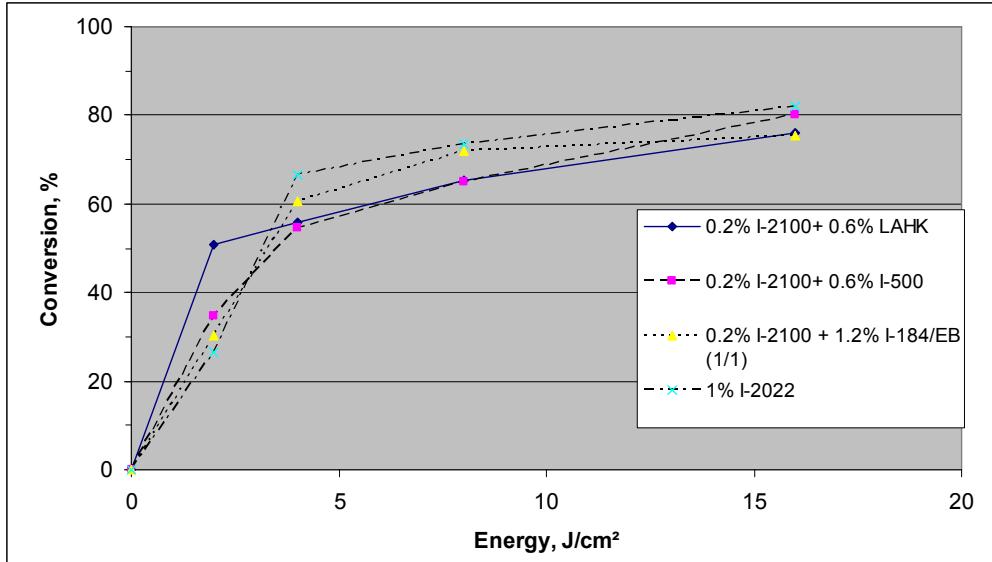


Figure 2. Conversion vs. energy. Top side of cured PUD. Light stabilizer package in the formulations was: 2% T 400 DW + 1% T 123 DW. Film thickness: 10 mil wet (2.2 mil dry).

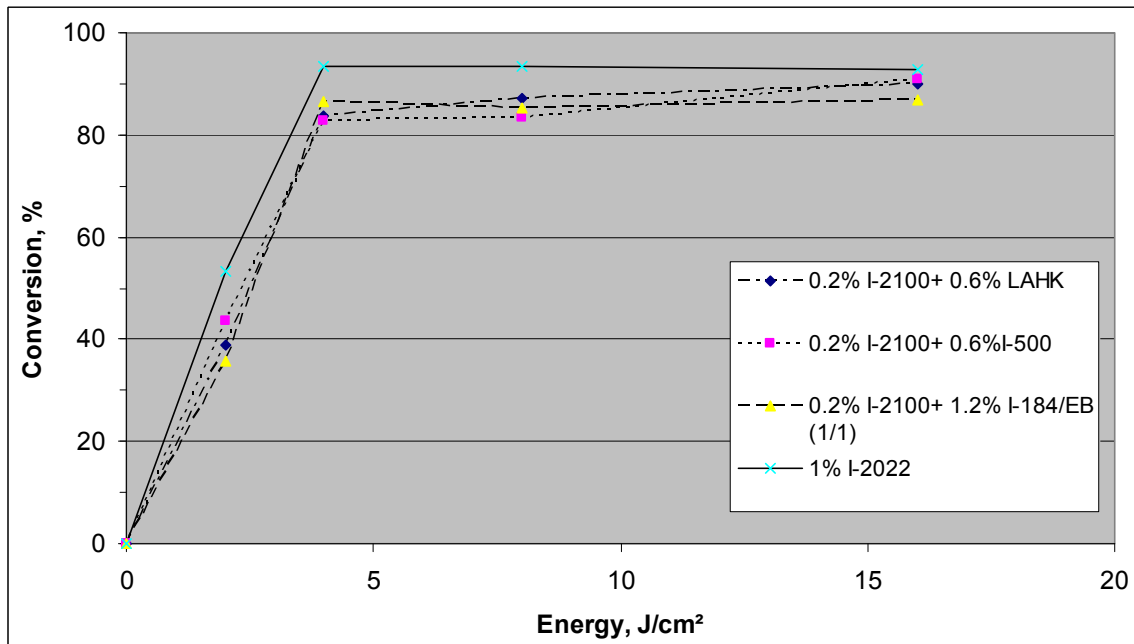


Figure 3. Conversion vs. Energy. Bottom side of cured PUD. Light stabilizer package in the formulations was: 2% T 400 DW + 1% T 123 DW. Film thickness: 10 mil wet (2.2 mil dry).

As shown in Figure 4X, the exposure to UV lamps caused, in some cases, an increase in color. Without light stabilizers the coating becomes increasingly more yellow ($\Delta b^* > 0$) with increasing UV lamp exposure. Adding in the LS reduces the effect. Thus, without a LS package, the b^* increases on all samples. With the LS the color is more stable. Using the T-477 DW as the light stabilizer, we see that the coatings have a much higher initial b^* (which is expected since the T 477 is a super red shifted). The best results were seen with the use of T-400-DW/T-123-DW.

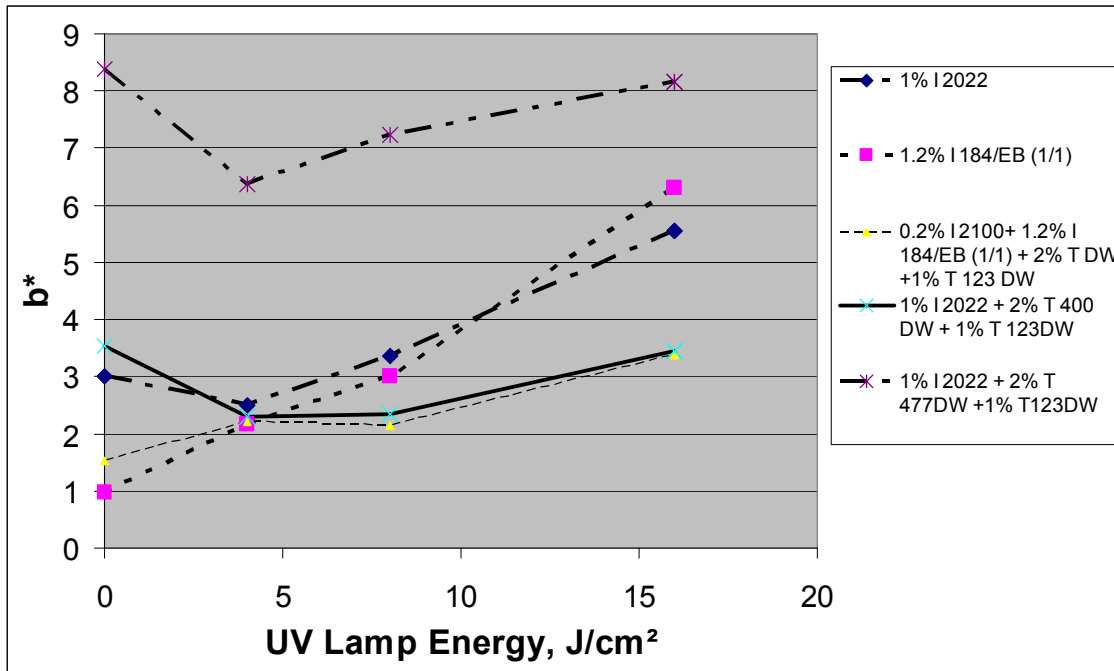


Figure 4. Effect of UV lamp exposure on color: b^* function as of energy (J/cm^2), for the PUD coating (2.2 mil dry)

The T-477-DW light stabilizer blocks light up to 400 nm. Indeed, it is the most red shift hydroxyphenyltriazene that is commercially available. Its ability to block light is exceedingly good. For thin coatings (< 1.5 mil) the long wavelength absorption does not cause a problem in giving the coating a yellow colored appearance. At a higher thickness, i.e., 2 mil, it can add color to the coating, which may be unacceptable. As shown in Figure 4, the coatings containing T-477-DW have a b^* of approximately 7 to 8. Thus, for color sensitive applications the preferred UV blocker would be T-400-DW.

A further advantage in using T-400DW in a UV curable system is that the arylphosphine oxide photoinitiators are easier to photo-excite, since the UV blocking is basically limited to < 375 nm and these photoinitiators absorb at longer wavelengths. This condition allows good through curing (see Figure 3).

Table 5. Effect of UV exposure on MEK solvent resistance

	Coating/Cure Conditions for PUD at 2.2 mil dry (10 mil wet)	MEK double rubs
1	Dry coating after water flash off, before UV lamp exposure	< 2
2	After UV exposure using $3.8 J/cm^2$ (1 pass, 20 fpm)	> 100
3	After 1200 hours Xe-WOM of th UV cured coatings	> 100

The question now is at what light exposure is the coating considered well cured? As summarized in Table 5, it was found that a single pass under the lamps at 20 fpm ($380 mJ/cm^2$) gave coatings with very high solvent resistance. From the MEK resistance test it was found that unexposed samples had poor solvent resistance (MEK double rubs < 2). After a single pass under the lamps all the coatings had a MEK double rub > 100, which indicated excellent cure.

Based on these results we used a single pass exposure to prepare samples for accelerated weathering. We used the light stabilizer package consisting of T-400-DW and T-123-DW.

3.3. Effect of additives on accelerated weathering

As given in Table 5, coatings maintained their solvent resistance properties even up to 1200 hours Xe WOM exposure. The question is whether their color also could be stabilized. As given in Figure 5, the light stabilizer package (which consisted of 2% T-400-DW and 1% T-123-DW) was critical in maintaining color. Indeed, as shown in the right side of Figure 5, with light stabilizers the Δb^* was within 0.5 units over 1000 hours Xe WOM. We also saw a general decrease in color when the light stabilizer package was used.

In contrast, the Δb^* shifted dramatically without light stabilizers (see left side of Figure 5). For example, during the first 500 hours of exposure the Δb^* increased (from 0.5 to 1.5 units). In subsequent exposure the Δb^* actually decreased (approximately 0.5 units). The lowest color without a light stabilizer package was with the photoinitiator I-184/EB (1:1).

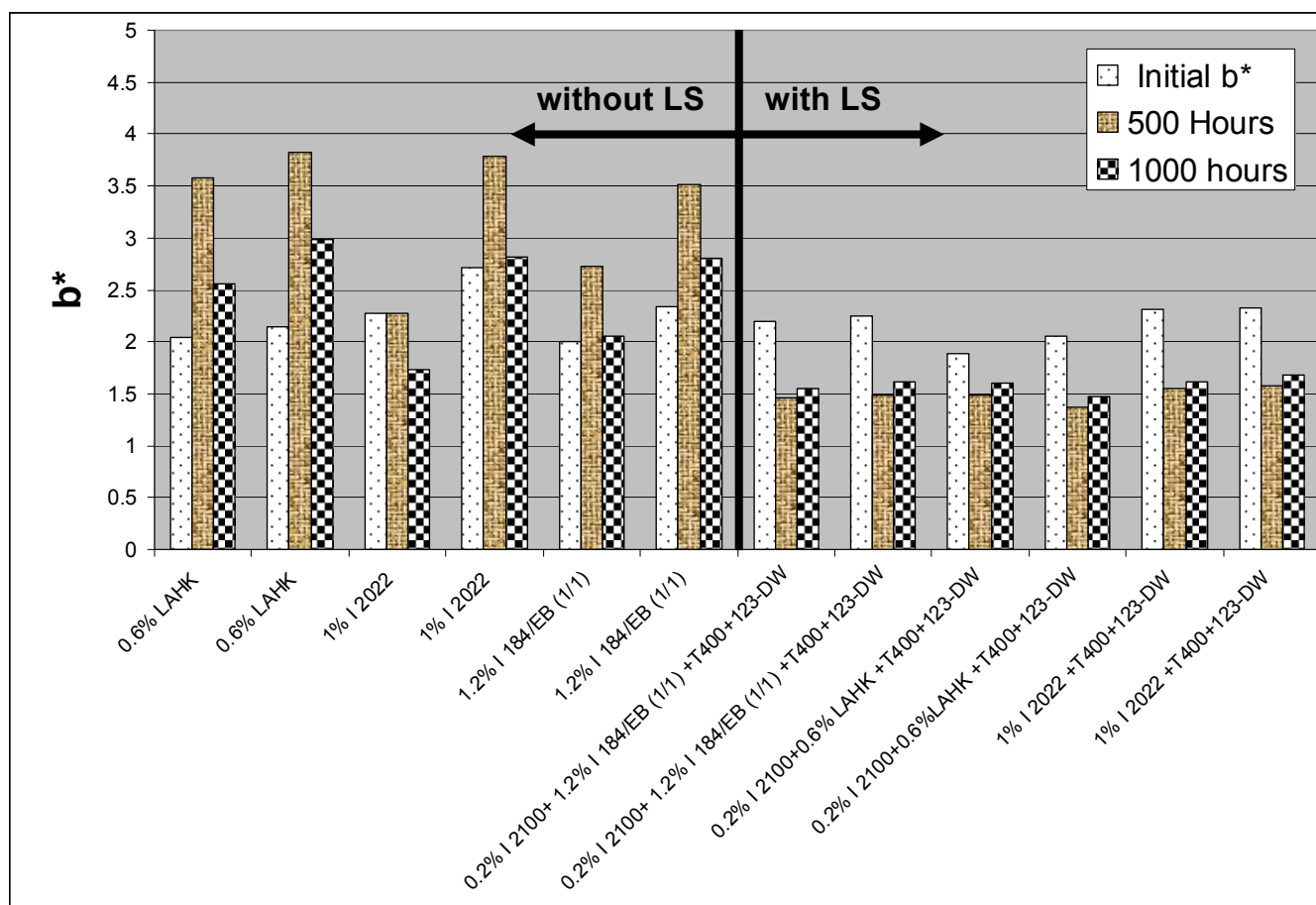


Figure 5. Effect on color (b*) after Xe WOM accelerated weathering for various photoinitiators and light stabilizer combination for 2.2 mil thick PUD coatings.

4. Conclusions

The fast UV curable water-based PUD resin exhibited very high solvent resistance and durability. It was found that the Novel Encapsulated Additive Technology (NEAT) was necessary for introducing high performance light stabilizers into the UV curable PUD formulation. The best overall performance was obtained using the NEAT light stabilizer products and liquid photoinitiators based on arylphosphine oxide. The optimal combination of light stabilizers (UV absorber 1% T-400-DW, and HALS 2% T-123-DW) with photoinitiators (0.2% I-2100 plus 1.2% I-184/EB) proved crucial for formulation stability and fast photospeed curing. They were also keys to maintain low color even under accelerated weathering conditions.

The outlook for the future in using this eco-friendly technology remains bright. We expect this formulation knowledge can be successfully applied to more even demanding applications, such as ultra-thin protective coatings for high end applications.

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