

Weather Stabilization and Pigmentation of UV-Curable Powder Coatings

Ljubomir Misev and Oliver Schmid—Ciba Specialty Chemicals Inc.*

Saskia Udding-Louwrier, E. Sjoerd de Jong, and Richard Bayards—DSM Resins bv†

INTRODUCTION

Binders for UV-curable powder coatings and high performance photoinitiators developed and commercialized in recent years now open up new application and market opportunities. UV-curable powders address the need for application of solvent-free formulations on shaped substrates by spraying, but also satisfy requirements for safer handling in terms of lower toxic hazards due to their polymeric structure. Their cure is triggered by exposure to high intensity UV light after film formation at melting temperature. Thus, in contrast to thermosetting powders, where complete cure is achieved by baking at temperatures much above their melting point, UV-curable powders can be used on heat sensitive substrates, such as MDF, solid wood, plastics, and even paper. The neat separation of the heat induced melting from the light induced curing process, improving flow and film formation, and energy savings are further merits of the UV-curable systems.

Solid UV-curable formulations impose special requirements on photoinitiators. They must be easily dispersible in the powder resins by conventional manufacturing techniques and exhibit sufficiently low volatility and high thermal stability to avoid heat induced losses during extrusion and film formation. The UV curing of pigmented powders requires, in addition, the use of long wavelength active and photobleachable photoinitiators. Such products, originally developed for pigmented liquid UV-curable coatings, have shown excellent properties in corresponding UV powder systems.

The present work aims at extending the application scope of UV-curable powders. Their weathering resistance has been studied under accelerated and outdoor conditions. The second part of our study addresses the increasing market interest for white and colored coatings. We present curing results for a selection of organic and inorganic pigments.

UV-CURABLE POWDER COATING

The binder system used in this study is a blend of an unsaturated polyester, which contains maleic or fumaric

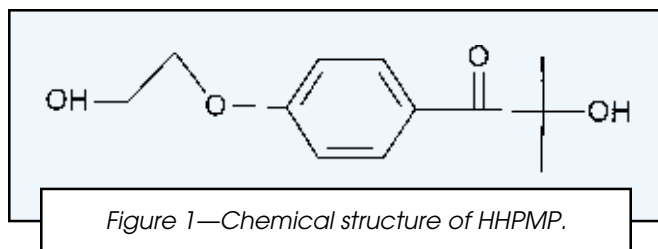
A UV-curable powder coating based on an unsaturated polyester binder and a vinyl ether crosslinker has been tested for weathering resistance. Accelerated and outdoor weathering demonstrate the combined protective action of a UV absorber and a hindered amine light stabilizer (HALS). Successful coatings cure of various colors and shades from organic and inorganic pigments is also reported in this study. Curing performance mainly depends on pigment absorption and particle size. A combination of a bis-acylphosphineoxide and an α -hydroxy-acetophenone photoinitiator overcomes limitations imposed by filtering of UV radiation by the pigments and provides balanced cure.

unsaturations, and a vinyl ether polyurethane crosslinker. The UV-curing mechanism of this binder is a free radical initiated 1:1 copolymerization of the electron-rich vinyl ether group with the electron-poor maleate or fumarate groups.

The UV-curable powder coating may be produced by the conventional powder coating manufacturing process, as the glass transition temperature of this solid binder system is sufficiently high. Photoinitiators, pigments, and additives are added to the binder and a homogeneous mixture is obtained via melt extrusion at 70°C. Flow agent is added to avoid surface defects. After cooling, grinding, and sieving, a fine powder is obtained. As polymerization of the binder will only be initiated by exposure to UV light, the powder is chemically stable

*Ciba Specialty Chemicals Inc., 4002 Basel, Switzerland.

†DSM Resins bv, P.O. Box 615, 8000 AP Zwolle, The Netherlands.



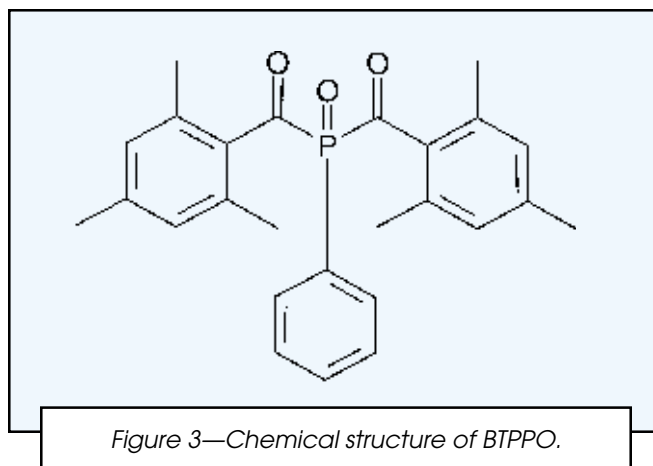
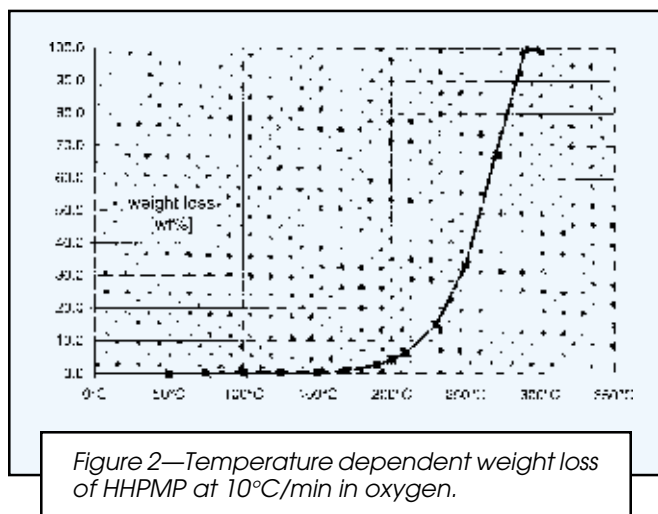
during storage. Physically, the powder is stable at 35°C for four weeks.

The powder is applied onto a substrate with conventional spray application and melted at 100–160°C with IR radiation or in a convection oven. Upon melting, the powder particles coalesce and form a continuous liquid film which is subsequently cured with UV radiation. Both mercury vapor arc UV lamps and microwave powered UV lamps were found suitable for curing of such films.

PHOTOINITIATORS

Previous studies¹ have narrowed the number of photoinitiators usable in UV-curable powders. The best overall results were obtained with α -hydroxy-acetophenones and bis-acyl-phosphineoxides (BAPO).

Solid α -hydroxy-acetophenones provide excellent cure in clear coatings. From the commonly used compounds, (1-hydroxycyclohexyl)phenyl-methanone and 2-hydroxy-1-[4-(2-hydroxyethoxy)-phenyl]-2-methyl-1-propanone (HHPMP), the latter is the preferred choice because of its very low volatility at common extrusion and film formation temperatures of UV-curable powders. Its chemical structure (see Figure 1) contains a polar hydroxyethoxy substituent in the *para* position of the benzoyl group to which the low volatility (see Figure 2) can be attributed. HHPMP is successfully used in UV-curing processes involving a heating step, for instance with waterborne coatings, which may require flash-off temperatures of 100°C.² Virtually no photoinitiator loss has been detected under the processing conditions of UV-curable powder coatings.



Low-molecular weight by-products of the photochemical cleavage reaction are mainly responsible for the odor formed by α -hydroxy-acetophenones after irradiation. Benzoyl radicals which are not consumed by initiating a chain reaction may form the gaseous and easily perceptible benzaldehyde by hydrogen abstraction. However, the aldehyde formed from HHPMP under such conditions is a solid with a melting point of 38–41°C and does not contribute to odor generation. The lack of yellowing, a property common to all commercial α -hydroxy-acetophenones, qualifies HHPMP equally for use in clear and pigmented coating systems.

The more recently introduced BAPO photoinitiators have proven indispensable for a thorough UV cure of powder coatings containing light absorbing components. They absorb light at the borderline between the visible and the near UV spectral range and form radical species which are transparent to this radiation. These two key properties enable them to cure very opaque white and colored coatings, without contributing to yellowing or color change, and also clear coatings in the presence of UV absorbers used as light stabilizers. Among the commercially available products, bis(2,4,6-trimethylbenzoyl)-phenyl-phosphineoxide (BTPPO) was found to give best overall performance in both liquid and solid pigmented coatings. This product (see Figure 3) is representative of the aromatic BAPO photoinitiators. Like other BAPO compounds it forms four radical species per molecule in a stepwise photolysis.³ The expected increase in curing efficiency compared with mono-acyl-phosphineoxide analogues, e.g., 2,4,6-trimethylbenzoyl-diphenyl-phosphineoxide, which can provide only two radicals, has been found in various radiation curing studies.⁴ BTPPO has been identified as the most versatile and efficient BAPO photoinitiator. Aside from the applications presented in this article, it has demonstrated an impressive performance in UV curing of corresponding liquid coatings and composites.⁵ The temperature dependence of its weight loss is shown in Figure 4.

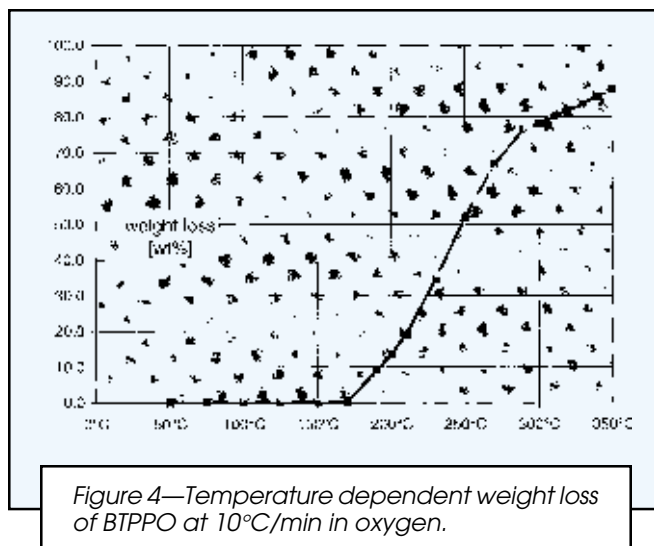
LIGHT STABILIZERS

Coatings in outdoor use are exposed to detrimental processes caused mainly by the UV portion of solar radia-

tion, gaseous pollutants, and acidic rain water. Depending on the intended end use, service life of up to five or even 10 years may be required. Such high performance coatings must be protected by stabilizing agents in order to withstand a harsh environment during such long periods. Combinations of UV absorbers and Hindered Amine Light Stabilizers (HALS) have proved very effective in providing the required protection to conventional coatings. They have found widespread use in automotive topcoats which are subject to strict lifetime specifications. When used in clearcoats, UV absorbers protect the underlying layers against color change and photochemical degradation leading to delamination, while HALS retain gloss and flexibility by scavenging harmful species, such as peroxy radicals, arising from polymer degradation.

The concept of light stabilization appears to contradict the criteria for a radically UV-curable system. The UV absorber may compete with the photoinitiator for the available light and reduce the amount of initiating radicals formed, while the activated HALS compound, a radical in nature, may scavenge photoinitiator and growing chain radicals. It has been shown, however, that the filtering effect of the UV absorber can be partly overcome by a careful selection of UV absorber and photoinitiator.⁶

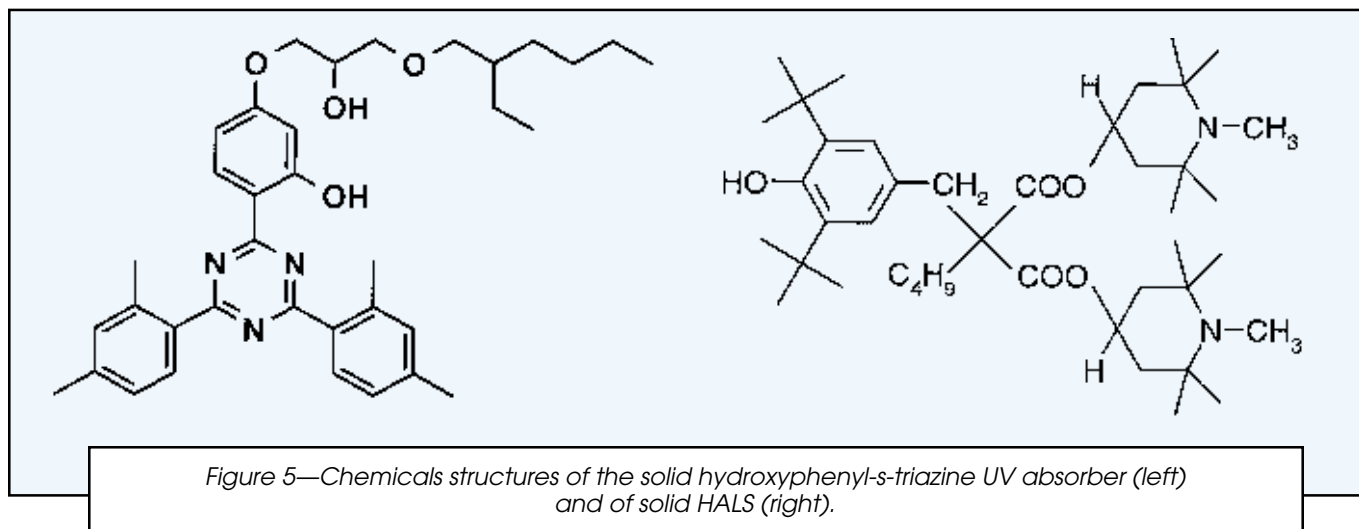
UV-cured urethane acrylate clearcoats can be as resistant to accelerated and outdoor weathering as thermally cured 2p-PUR systems, considered as the state-of-the-art for automotive topcoats, if suitable UV absorber/HALS combinations are used. They withstood 10,000 hr accelerated exposure and five years outdoor weathering without any cracks or loss of adhesion and maintained a rather high gloss level.⁶ An FTIR analysis of the chemical changes occurring during QUV exposure of a UV-cured aliphatic urethane acrylate clearcoat has revealed moderate urethane decrease and carbonyl increase, at 1521 and 1766 cm^{-1} , respectively, during the first 50 hr.⁷ These changes are attributed to reactions induced by the photolysis of the initiator remaining in the UV-cured coating on the basis of an earlier study showing that the photoinitiator disappears completely after 50 hr of QUV exposure.⁸ No change in the UV absorber concentration ow-



ing to UV curing exposure has been detected while the techniques available were not sensitive enough for an analogous detection of the HALS compound.

A suitable UV absorber should exhibit a steep transmission cut-off at a wavelength just long enough to provide UV protection in the relevant range. This requirement is best met by the newly developed class of hydroxyphenyl-s-triazines⁹ from which a solid product (see Figure 5) with a melting point at around 78°C was used in the present study. BAPO photoinitiators, such as BTPPO, overcome the filtering effect of the hydroxyphenyl-s-triazines and cure a UV protected coating without a significant reactivity loss. The absorbance spectra of a hydroxyphenyl-s-triazine UV absorber (Figure 5) and a 3:1 blend of the photoinitiators HHPMP and BTPPO in the relevant spectral range are shown in Figure 6 for the concentration ratio used in the formulations in Table 1.

HALS compounds are transformed into active nitroxyl radicals ($>\text{NO}\bullet$) by a photooxidation process requiring several hours to establish a significant concentration level.¹⁰ With radiation curing processes terminating after only a few seconds of exposure to intense UV light,



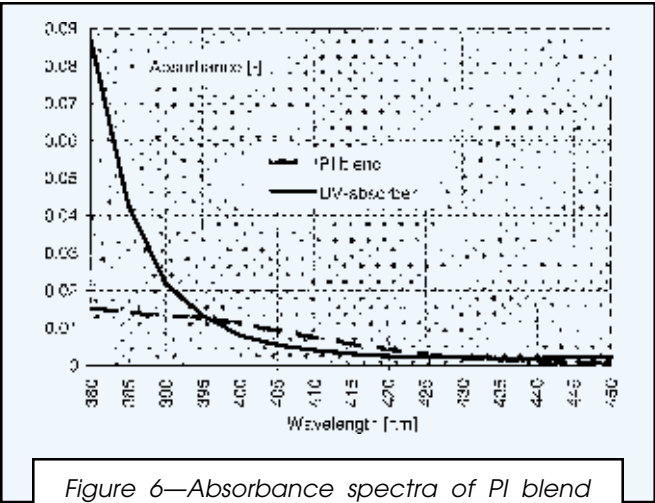


Figure 6—Absorbance spectra of PI blend (HHPMP and BTPPO at 3:1) and solid hydroxyphenyl-s-triazine UV absorber in CHCl₃ at 0.05 and 0.1 g/l, respectively (1 cm cell).

noticeable inhibitive interaction between nitrosyl radicals and those governing the polymerization process is unlikely to occur and has not been found experimentally. For this study, a solid HALS compound containing a phenolic antioxidant group as an additional functional moiety has been chosen (see Figure 5). This product has demonstrated excellent properties in thermosetting powder coatings.

WEATHERING STUDIES

Three UV powder formulations (see Table 1) have been prepared for the weathering tests. The powders were sprayed electrostatically by a tribo gun on coil-coated aluminum test panels at a weight resulting in a coating thickness of around 55 μm after melting and curing. The coatings were melted in a convection oven at an air temperature of 130°C and, while still liquid, exposed under two 80 W/cm medium pressure mercury lamps at a conveyor belt speed of 3 m/min. After cooling to room temperature, the degree of cure was evaluated by specific tests.

Table 1—Composition of UV Powder Formulations

Formulation No.	1	2	3
Solid unsaturated polyester ^a	830	830	830
Solid vinyl ether crosslinker ^b	170	170	170
Degassing agent ^c	5	5	5
Flow agent (silicon free) ^d	10	10	10
Photoinitiator HHPMP ^e	7.5	7.5	7.5
Photoinitiator BTPPO ^f	2.5	2.5	2.5
Solid HALS ^g		10	10
Solid hydroxyphenyl-s-triazine UV-absorber			20

(a) Uralac[®] ZA 3125-P, DSM bv
(b) Uralac[®] ZW 3307-P, DSM bv
(c) Worlee[®] Add 900, E.H. Worlee & Co. bv
(d) Resiflow[®] PV5, E.H. Worlee & Co. bv
(e) Irgacure[®] 2959, Ciba Specialty Chemicals Inc.
(f) Irgacure[®] 819, Ciba Specialty Chemicals Inc.
(g) Tinuvin[®] 144, Ciba Specialty Chemicals Inc.

Accelerated weathering resistance of the UV-cured powder coatings has been tested under QUV-A exposure and in a Xenon-Weatherometer (WOM) using the following standard cycles:¹¹

- QUV-A: Fluorescent lamps UVA-340; 8 hr UV, 70°C; 4 hr condensation, 50°C.
Xenon-WOM: 0.35 W/m² at 340 nm; interior and exterior filter: boron silicate; 102 min UV dry, 57-63°C, 18 min UV rain, 37-43°C.

During exposure, 20° gloss and color change (ΔE) were determined at 200 hr intervals. The average values from measurements on two individually exposed panels were taken.

Under both accelerated exposure conditions weathering stability is significantly improved by the presence of a UV absorber and a HALS compound as shown in Figures 7-10. In the unstabilized coating, cracks occur after only 1800 hr exposure time, even though at a rather high gloss level. Addition of the solid HALS compound extends lifetime by 1200 hr under QUV-A and by 800 hr in Xenon-WOM. The solid hydroxyphenyl-s-triazine UV-absorber causes a further slow down of detrimental processes and prevents coating failure at a moderate gloss level for as long as 5200 hr under QUV-A conditions, while in Xenon-WOM the fully stabilized coating withstands 4800 hr exposure at a 20° gloss of 27%. The stabilization package also counteracts coating discoloration measured by the color change parameter ΔE. QUV-A caused a ΔE of 18 units in the unstabilized coating by the time of its failure and only of two units in the presence of UV absorber and HALS after an almost three times as long exposure time. The fully stabilized coating experiences a marginal color change of about 0.3 units until failure when exposed in Xenon-WOM which is generally known to cause less discoloration than QUV-A.

The UV-cured powder coatings have also been exposed to outdoor weathering in Florida (5° facing south, black box, unheated). Interim results are reported in this paper for 20° gloss (Figure 11) and color change (Figure 12). After 18 months the unstabilized and the partly stabilized coating (formulations 1 and 2) reached much

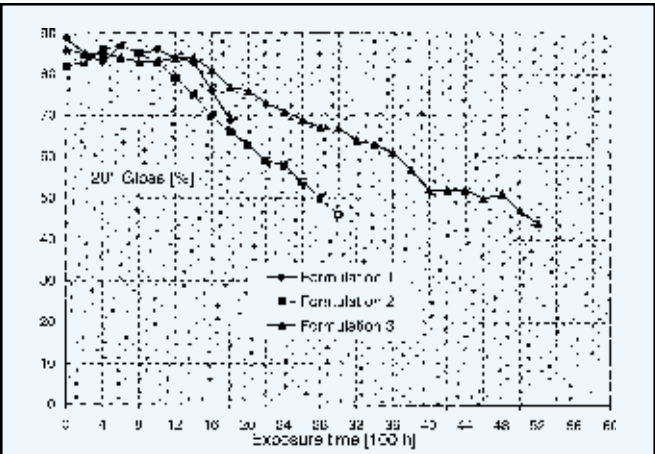
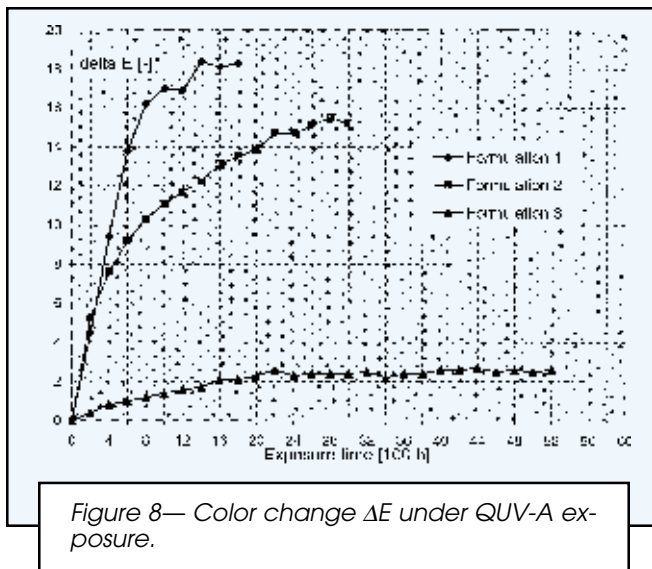


Figure 7—Gloss retention under QUV-A exposure. Significant cracking occurs at last readings.



lower 20° gloss levels without cracking than those exposed to artificial weathering. Otherwise, the Florida results confirm the superior joint stabilization effect of the UV absorber and the hindered amine light stabilizer previously found with accelerated weathering. In this study the question arises again whether outdoor performance can be predicted from accelerated weathering results. An unequivocal relationship between results from artificial and outdoor weathering tests could not be established. It is undisputed though that best agreement with outdoor conditions is generally achieved with xenon lamps whose radiation resembles that of sunlight when special filters are used.¹² The QUV-A exposure cycle, on the other hand, is considered to be closer to indoor conditions and therefore preferred by furniture manufacturers.

Higher weathering resistance is generally found with standard *thermosetting* clear powder coatings. For instance, the 20° gloss of a fully stabilized thermally cured powder coating based on carboxy-/epoxyfunctional acrylics dropped to 52%, from an initial value of 92%, after 4800 hr exposure in Xenon-WOM without cracking.¹² Florida outdoor exposure of the same coating caused a drop to 85% after 15 months. However, a meaningful performance comparison between thermally and UV-cured clear powder coatings must be based on the same or at least similar resin chemistry.

PIGMENTED UV-CURABLE POWDER COATINGS

Successful UV curing of opaque white powder coatings has been reported in previous articles.^{13,15} Requirements of photoinitiators for such coatings, which exhibit a rather steep absorption edge, are rather obvious. In colored coatings, however, the penetration depth of UV light emitted by mercury lamps is controlled by a more complex absorption spectrum which makes photoinitiator through cure performance less predictable. Other factors governing light penetration and through cure in such systems are the pigment particle size and shape

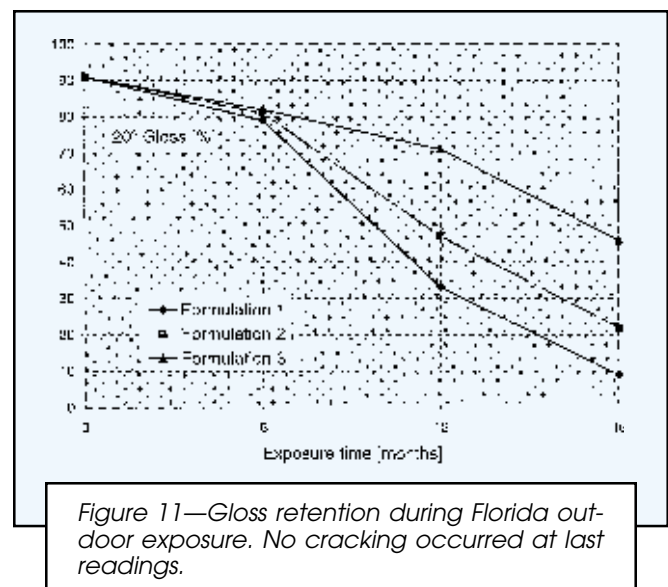
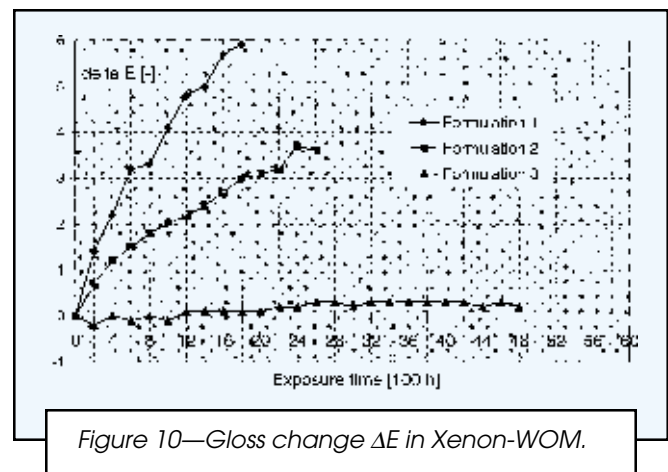
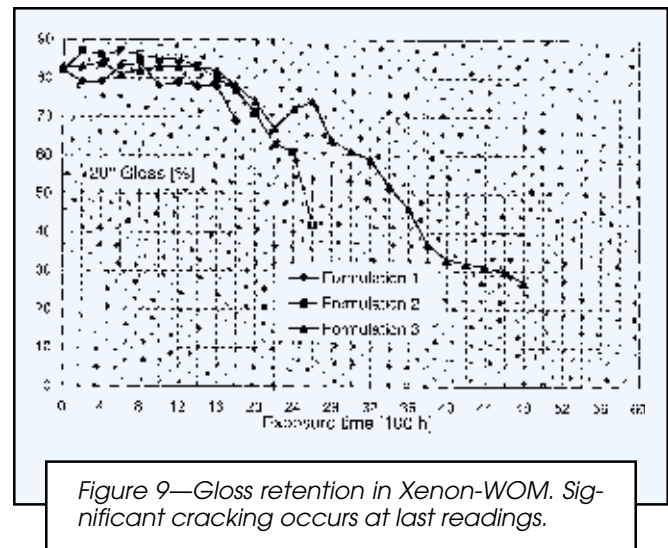


Table 2—Composition of Pigmented Formulations and Coating Properties after UV Cure

	Organic Pigments			Inorganic Pigments		
	Black	Red	Blue	White	Yellow	Caramel
Solid unsaturated polyester	822	797	765	623	747	747
Solid vinyl ether crosslinker	168	163	157	127	153	153
Degassing agent	5	5	5	5	5	5
Flow agent (silicon free)	10	10	10	10	10	10
Rutile titanium dioxide ^a			39	250		
Pigment Yellow 184 ^b					100	
Pigment Red 254; C.I. 56110 ^c		40				
Pigment Blue 15:3; C.I. 74160 ^d			39			
Carbon black ^e	10					
Pigment Yellow 119; C.I. 77496 ^f						100
Photoinitiator HHPMP	15	15	15	15	15	15
Photoinitiator BTPPO	15	15	15	15	15	15
Test Results						
Surface aspect (flow)	Excellent	Excellent	Excellent	Good	Good	Good
Gloss 20/60°	83/90	99/99	79/88	86/92	84/90	87/92
Hiding power	High	Medium	High	Medium	Poor	Poor
König hardness (s)	181	210	196	200	103	62
Through cure	Good	Good	Good	Good	Poor	Poor

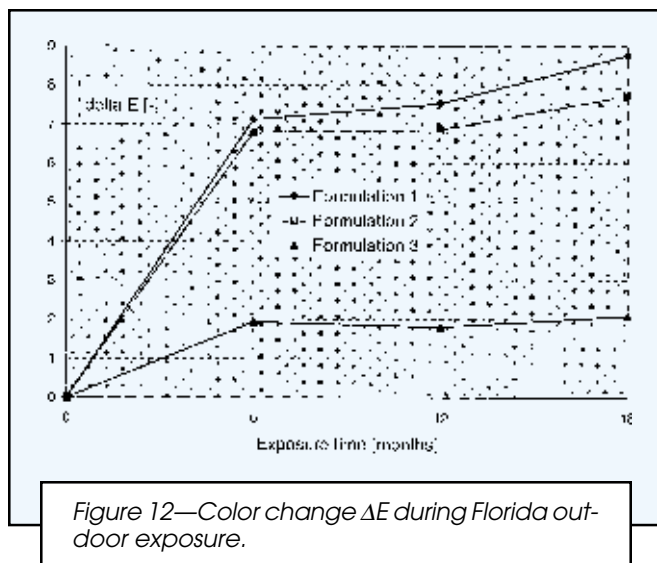
Inorganic Pigments						
	Red	Red	Red	Yellow	Yellow	Yellow
Solid unsaturated polyester	747	747	747	747	747	747
Solid vinyl ether crosslinker	153	153	153	153	153	153
Degassing agent	5	5	5	5	5	5
Flow agent (silicon free)	10	10	10	10	10	10
Pigment Red 101; C.I. 77491	0.1 µm sphere ^g 0.2 µm sphere ^h 0.7 µm sphere ⁱ	100	100			
Pigment Yellow 42; C.I. 77492	0.1 x 0.4 µm acicular ^j 0.2 x 0.3 µm prismatic ^k 0.2 x 0.8 µm acicular ^l			100	100	100
Photoinitiator HHPMP	15	15	15	15	15	15
Photoinitiator BTPPO	15	15	15	15	15	15
Test Results						
Surface aspect (flow)	Wrinkles	Good	Good	Wrinkles	Good	Good
Gloss 20/60°		84/91	80/90		85/93	83/90
Hiding power	No	High	High	No	Poor	Poor
König hardness (s)	Through	133	200	Through	98	50
Through cure	Cure	Poor	Good	Cure	Poor	Poor

(a)	R-TC2, Tioxide Ltd.	(g)	Iron oxide, Bayferrox [®] 105 M, Bayer AG.
(b)	Bismuth vanadate, Irgacolor [®] 3GLM, Ciba Specialty Chemicals Inc.	(h)	Iron oxide, Bayferrox [®] 130 BM, Bayer AG.
(c)	Diketo-pyrrolo-pyrrole, Irgazin [®] DPP Red 80, Ciba Specialty Chemicals Inc.	(i)	Iron oxide, Bayferrox [®] 180 M, Bayer AG.
(d)	Cu-phthalocyanine (B), Microlen [®] Blue 4GNP, Ciba Specialty Chemicals Inc.	(j)	Iron oxide, Bayferrox [®] 3910, Bayer AG.
(e)	Special Black [®] 250, Degussa AG.	(k)	Iron oxide, Bayferrox [®] 415, Bayer AG.
(f)	Iron oxide, Bayferrox [®] 3950, Bayer AG.	(l)	Iron oxide, Bayferrox [®] 930, Bayer AG.

which also determine the hiding power of the coating at a given pigment volume concentration. In liquid UV-curable coatings it has been found that both UV penetration depth and hiding power increase with pigment particle size.¹⁴

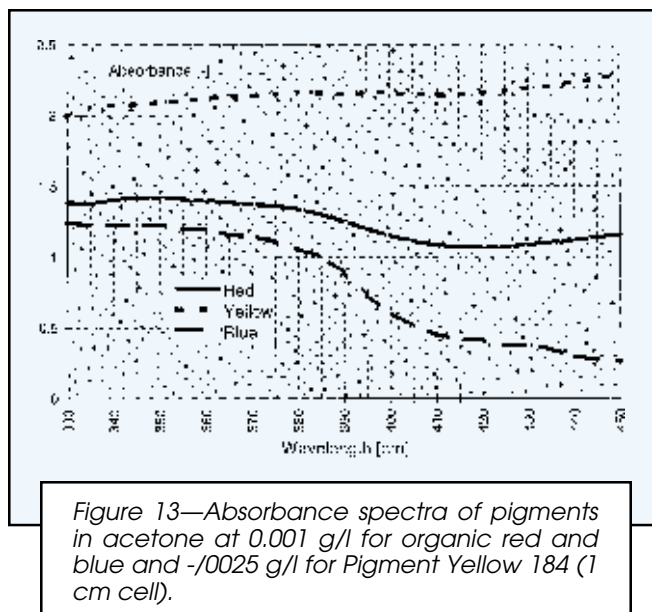
Twelve powder formulations (see Table 2) have been prepared for this study. Aside from carbon black and rutile titanium dioxide, two organic and eight inorganic pigments of various colors and shades were used. The

powders were sprayed electrostatically by a tribo-gun on aluminum test panels at a weight resulting in a coating thickness of around 40 µm after melting and curing. The coatings were melted in a convection oven at an air temperature of 160°C and, while still liquid, exposed under two 80 W/cm medium pressure mercury lamps at a conveyor belt speed of 5 m/min. Under such conditions the coating reaches a peak temperature of 120–130°C for up to 90 sec. Coating temperature drops by 20–



30°C during transfer into the UV curing unit where it increases again by 10-20°C due to infrared emission from the mercury lamps and crosslinking reaction exotherm.¹⁵ Without any UV exposure, the powder coating can cure thermally only if it is kept above 150°C for around 10 min. For qualitative assessment of through-cure, the irradiated coatings were carefully removed from the substrate after swelling with methyl ethyl ketone and inspected for colored liquid residue at the bottom. Koenig pendulum hardness was used as a quantitative method for through-cure evaluation. The powders were also applied and cured on white/black contrast panels for visual assessment of hiding power.

The coating containing 25% rutile titanium dioxide cures well under these conditions. Previous work has demonstrated, however, that the photoinitiator system used in this study enables the UV cure of thicker coatings at pigment levels of up to 33%. Excellent performance was also found with the coating containing carbon black. This pigment provides a high hiding power even at the very low concentration level of one percent. The curing of the black coating may, to some extent, benefit from coating temperature increase caused by enhanced heat (IR) absorption during exposure. The coatings containing organic red and blue pigments cure comparably well at considerable hiding power, while all coatings loaded with inorganic yellow pigments exhibit poor or no through cure at low hiding. This deficiency results mainly from the low transparency of yellow pigments in the 300-450 nm range which is relevant for photoinduced initiator radical formation. For illustration, the absorbance spectra of organic red and blue pigments and of the bismuth vanadate Pigment Yellow 184 are compared in Figure 13 at relative concentrations roughly corresponding to their content in the respective powder coatings. With the iron oxide Pigment Red 101 a considerable increase in through-cure performance is found with increasing pigment particle size. This is an indication that reflection properties of pigment particles can be as important as their absorption characteristics in determining the penetration depth of UV light in such coatings.



Wrinkle formation, as observed with a yellow and a red iron oxide pigmented coating, is a well known phenomenon from very opaque liquid UV-curable coatings. It results from an unbalanced crosslinking process characterized by premature skin formation or surface cure on top of a poorly cured coating body.

CONCLUSIONS

A powder coating photocurable by 1:1 radical copolymerization of maleate/fumarate with vinyl ether functional groups has been made weather resistant by addition of a hydroxyphenyl-s-triazine UV absorber and a hindered amine type radical scavenger.

On the basis of accelerated weathering results, time to failure in terms of cracking or delamination could be extended by a factor of around 2.5 compared with the unstabilized coating. Lifetimes of up to 5200 hr have been achieved under QUV-A exposure conditions even though at significant gloss reduction. The tested stabilization package has also proved very efficient in preventing coating discoloration. No unequivocal relationship between results from artificial weathering and Florida outdoor exposure could be established. The filtering effect of UV absorbers which usually affects the curing speed of a radiation curable coating can be efficiently overcome by use of bis-acyl-phosphineoxides as photoinitiators.

Addition of organic and inorganic pigments of various colors and shades affects the UV curing performance of the powder coating. Photoinitiator type, pigment absorption, and particle size require careful consideration in formulating an opaque coating. A combination of a bis-acyl-phosphineoxide and a low volatility α -hydroxy-acetophenone provides balanced cure and good hardness under mercury vapor lamps with rutile titanium dioxide, carbon black, blue Cu-phthalocyanine (β), red diketo-pyrrolo-pyrrole, and red iron oxide pigments. Through-cure performance increases with the

diameter of red iron oxide pigment spheres. The coatings containing yellow pigments based on bismuth vanadate and iron oxide exhibit low reactivity at poor hiding. The UV curing of these systems is strongly impeded by the high absorption of the yellow pigment in the spectral activity range of the bis-acyl-phosphineoxide photoinitiator.

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