Photolatent Effect ADDITIVES for Coatings

by J. Benkhoff, K. Dietliker, K. Powell, T. Jung, K. Studer, and E.V. Sitzmann
Ciba Specialty Chemicals Inc.*

UV light curing is one of the most economical and environmentally compatible curing technologies known. It has successfully enabled numerous industrial applications over recent decades. However, there still remain challenges that prevent penetration into broader areas of interest. For example, there are intrinsic limitations associated with radical photopolymerization, e.g., oxygen inhibition, insufficient curing of shadow areas, poor curing of thick or highly pigmented coatings, lack of adhesion on certain substrates, etc.

Recent developments using photolatent additives have specifically targeted these deficiencies and thus support the expansion of the scope of UV curing technology in industrial applications. In addition, novel photo-induced effects have been developed, which open up new application areas that have been unexploited to date.

INTRODUCTION

Photolatent additives play a crucial role in the coatings industry.[1,2] These are thermally stable or latent materials that become reactive after they absorb a photon. Photolatent initiators and catalysts are well known examples of these types of additives.[3,4] Photoinitiators are required for photo-induced polymerization, which can be used to cure coatings. The thermally stable photoinitiators serve as triggers and turn an otherwise dormant or latent system into an active one once they are activated by light.

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*Coating Effects Segment, CH 4002 Basel, Switzerland.

Using light as a trigger is an important way to gain better control in the way coatings are made and, in certain cases, how they can be used. Light also can be used to generate other effects as well. For example, photolatent colorants are colorless and once activated by light they chemically change to produce new colors. Photolatent fragrances, as the name suggests, are additives that generate pleasant aromas or fragrances once they are photoactivated.

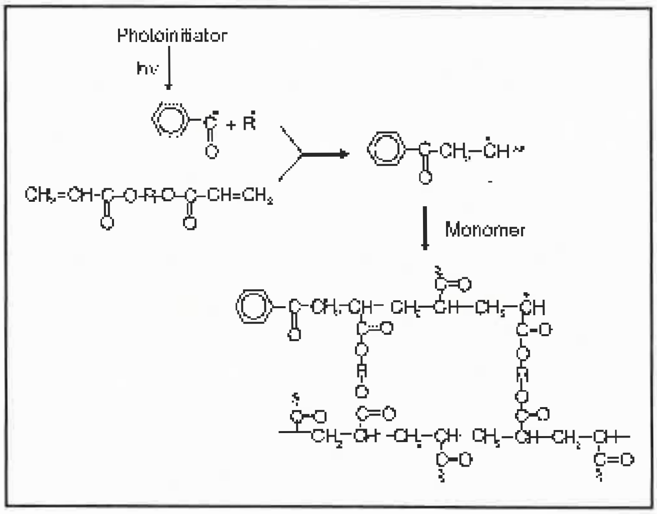
The purpose of this article is to better understand what these photolatant additives are and where they can be used. Another aim of this work is to examine how these photolatent additives can bring value by addressing shortcomings in traditional coating systems. Lastly, it is interesting to see how new technical developments, such as plasma UV-curing or LED arrays, can be used with photolatent catalysts to further advance the way coatings can be made more efficiently.

NEW FREE RADICAL PHOTOINITIATORS

Photoinitiators have traditionally been used to initiate the polymerization of vinyl groups (acrylates, methacrylates, and other unsaturated groups).[3,4] More than 90% of light-cured coatings used commercially are produced by free-radical initiation (*Table* 1). Other photoinitiators, such as photoacid generators, can be used for carbocationic polymerization. A new and emerging class of photoinitiators is photolatent amines, which can potentially be used in many base-catalyzed coating systems.

The dominant mode of action of the photoinitiator commonly used commercially is to initiate free-radical polymerization. The free-radical photoinitiators used generally undergo Type I photocleavage (bond homolysis) or Type II (hydrogen abstraction) to produce energetic free radicals. The radicals are short-lived chemical intermediates and are very reactive. These free radicals add to double bonds and cause polymerization and crosslinking to occur, as shown in *Figure* 1.

Figure 1—Free radical photocuring of an acrylate monomer, using a Type I photoinitiator.



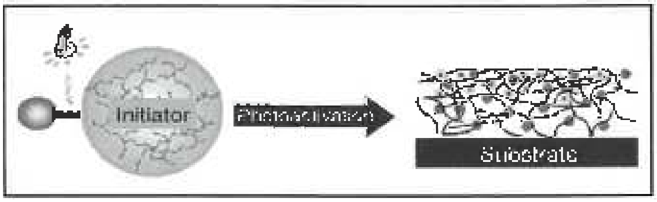
New photoinitiators in this class have been developed,[5,6] which offer advanced control over the UV-curing process and also can minimize certain unwanted effects. Some of the salient problems seen with traditional free-radical photocuring can be summarized as follows:

- Oxygen inhibition, especially at the coating's surface
- Odor, associated with volatility of photofragments (such as benzaldehyde formation) from the photoinitiator
- Unwanted color (i.e., yellowness) as a result of photocuring
- Requirement for direct line-of-sight to ensure completeness of cure, which is especially important for 3-D objects or articles that have complex shapes
- Inadequate through-cure, especially for pigmented or optically opaque coatings
- Poor adhesion, which occurs from inefficient curing and/or from shrinkage-induced stress buildup during photocuring

Table 1—Technology Platforms Used in UV Curing

	Radical Crosslinking	Cationic Crosslinking	Base-Catalyzed Crosslinking
Resins	Acrylates, Maleates, Styrene	Epoxides, Vinyl Ethers	Epoxy Polyol/Isocyanate Michael addition
Initiators	Aromatic Ketones	Diaryl Iodonium Salts Triaryl Sulfonium Salts Nonionic photoacid generators	Latent or blocked amines
Industries	Coatings Electronic Materials, Inks Adhesives	Electronic Materials, Inks, Adhesives	Coatings, Adhesives *Under Active Development*

Figure 2—Surface active photoinitiator.



Oxygen inhibition is a perennial problem for photocuring of many coatings. This leads to blocking (sticking) and low mar resistance. A new photoinitiator was developed to address this problem. This photoinitiator is surface active, as shown in *Figure* 2.

This developmental photoinitiator is liquid and nonvolatile and has an intrinsically low surface tension (26 dynes/cm at 21°C), which forces it to the surface. Used at additive levels, it can serve as a good leveling/slip agent. Used in photocurable coatings, it leads to good surface curing. Specifically, the photoinitiator can be photoactivated with UV-A light (it has a long wavelength absorption between 300–385 nm) and leads to low color coatings that show good slip properties. Because it is a photoinitiator, it grafts itself to the coating, rendering a permanent non-migratory slip property. The result is to generate low color coatings that have a surface that show good slip and high mar resistance.[7]

Another development is multifunctional photoinitiators that exhibit high photocure efficiencies. Two examples are shown in *Figure* 3.

The α-hydroxy ketone (AHK) is a preferred photoinitiator for inkjet inks or coatings that contain high levels of acrylate monomers. Low viscosity resins that have high monomer content (such as inkjet inks) generally are more susceptible to O_2 inhibition. Thus, this photoinitiator can help where air inhibition can be a problem. The dual functionality also renders it nonvolatile and allows it to serve as a crosslinker. In addition, this photoinitiator also can serve a rather unorthodox role as a low color photosensitizer for diaryliodonium salts.

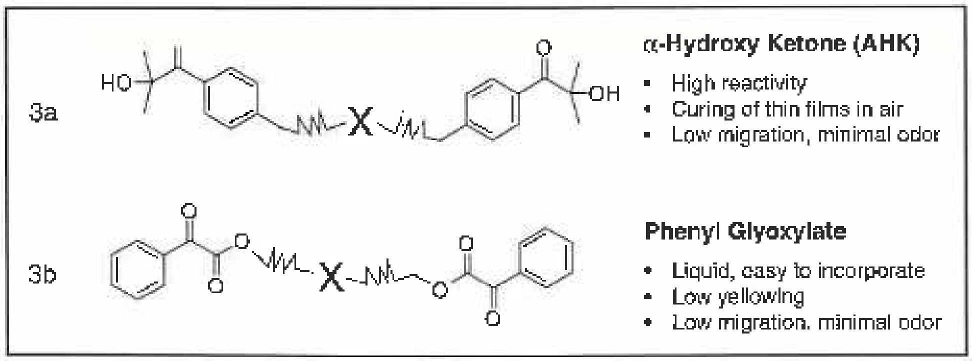
The multifunctional phenylglyoxylates (*Figure* 3B) is also an important new liquid photoinitiator. It can be used to reduce color in final cured coatings. A preferred practice is to use it with photobleachable long wavelength absorbing aryl phosphine oxide photoinitiators. This photoinitiator combination can be useful for obtaining good surface and bottom curing of thin and thick coatings. Typically, V+D lamps (which emit strongly between 300–450 nm) are used with this photoinitiator package for low color coatings over wood or plastic substrates.

UV-CURABLE WATERBORNE COATINGS

UV-curable waterborne coatings are becoming increasingly popular because they do not give off VOC-based solvents during curing. A number of photoinitiators are currently recommended,[8,9] such as the water-dispersed bis-acyl phosphine oxide (BAPO) and the AHK/BP eutectic blend. The eutectic blend is water dispersible into most common (meth)-acrylate functionalized polyurethane dispersions. It provides good surface cure and can be used in clear coatings. If the coating is pigmented and/or contains protective UV absorbers, then the water dispersed BAPO photoinitiator is also used. BAPO is an important photoinitiator that has proven itself in many demanding coatings, composites, and gel coat applications.

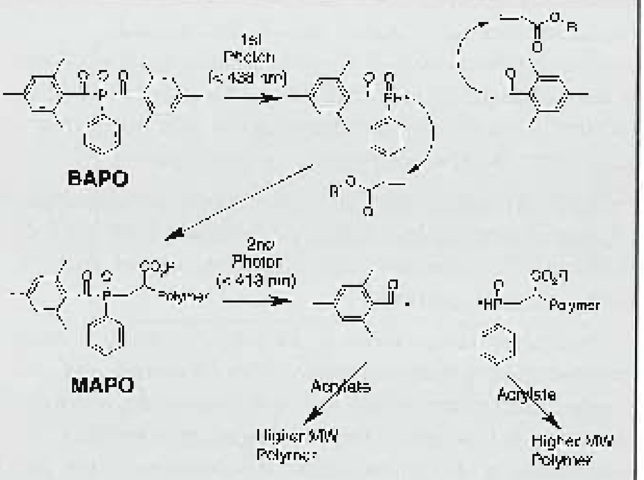
The main reasons for BAPO's success is that it can use two photons sequentially, producing two different radical pairs (see *Scheme* 1). It possesses a long wavelength absorption that photobleaches during curing. Thus, BAPO is desirable for long wavelength (up to 430 nm) photocuring. It is especially useful for LED array photocuring.

Figure 3—Multifunctional photoinitiators for increased photocure efficiencies.



LED VISIBLE LIGHT CURING

LED arrays were recently introduced for curing industrial coatings and adhesives. LED arrays as currently designed for these applications have an output at 400 ± 20 nm. These quasi-monochromatic light sources differ from standard mercury lamps, which have broadband spectral output. LED arrays are attractive be-



Scheme 1—BAPO as a two-photon photobleachable photoinitiator

cause they do not emit IR radiation (which may cause heating problems, as may be seen with Hg lamps) and they have a stable output. It was found[10] that when BAPO is used as the photoinitiator, up to 25 mil thick gel coats (containing 15 wt% TiO_2) are easily cured with the LED array, as shown in *Figure* 4.

This demonstration of deep through-curing of gel coats even with high filler shows the power of correctly matching the photoinitiator with the light source. The output of the LED array is "tuned" to the BAPO long wavelength absorption for efficient light coupling and photoactivation. The BAPO, in turn, photobleaches, permitting even deeper optical penetration into the gel coat. This combination results in surprisingly good through-cure, compared to when a mercury lamp is used.

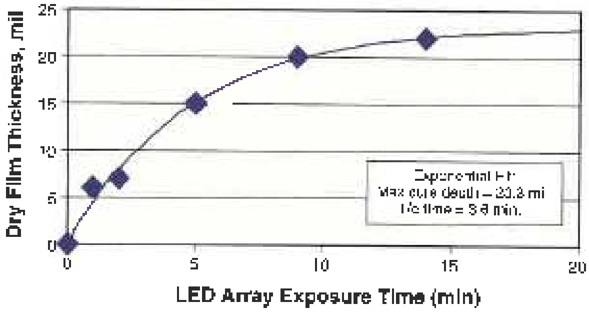
PLASMA UV-CURING FOR 3-D OBJECTS

When coating 3-D objects, one is often faced with the problem of getting uniform light exposure over all coated areas. The object can contain hidden areas, cavities, or small orifices that light cannot reach, which will mean these areas will be uncured or at best only partially cured.

An exciting new development that is capable of resolving this dilemma is to use UV light that is generated from plasma.[11,12] A gas (He/N_2 mixture) is used to surround the part, then, by switching on a microwave, UV light is generated from it. In essence, the part is placed inside the lamp (*Figure* 5).

In this way, UV light is generated for curing in regions that are normally inaccessible.

Figure 4—Photocure depth as a function of LED array exposure time in a white UPES gel coat (15 wt% TiO_2 + 0.3 pph BAPO).



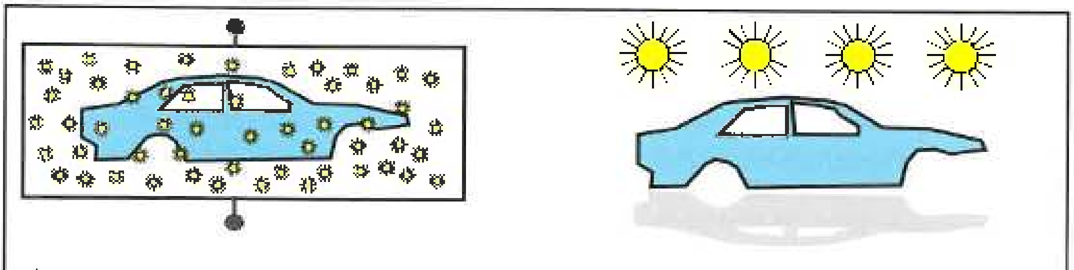
PHOTOLATENT ACID AND BASE CATALYSTS

To expand the capability of light curing, new photo latent acid and base catalysts were developed,[11–14] as shown in *Figure* 6. These novel photolatent additives generate a long-lived catalyst, which is distinctly different from the short-lived free-radical initiators.

The resins they cure also are different. In the case of photolatent base catalysts, they are used to photo-activate the curing of conventional coatings that cure *via* condensation reactions, such as for polyurethanes or epoxy based coatings as shown in *Figure* 7.

The photolatent base catalysts are a sharp departure from the more commonly used free-radical photoinitia-

Figure 5—Comparison between UV-plasma curing (Case A) and conventional UV curing (Case B).



(a) UV-curing of a car body using UV plasma curing process.

(b) UV-curing of a car body using a conventional UV system.

Figure 6—Photolatent acids and base catalysts.

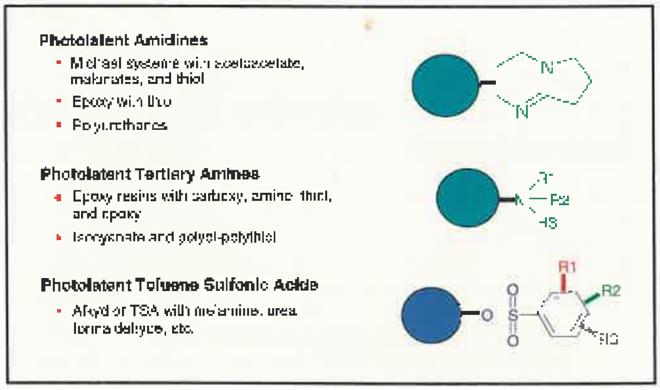


Figure 7—Conventional industrial coatings undergoing base catalyzed curing.

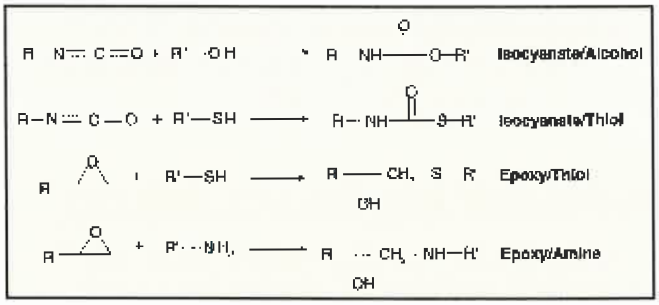
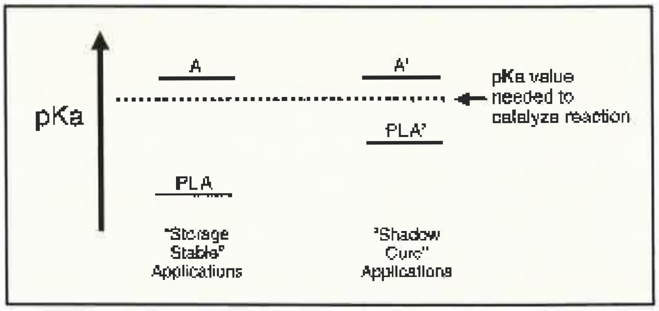


Figure 8—Optimizing pKa for photolatent amine (PLA) and free amine (A).



tors, which offer exciting possibilities to lower cost and increase productivity in those coating systems.

Leading the design development of these photolatent base catalysts is the effort to engineer them to match particular resins.[13] As described in *Figure* 8, this match is done by first understanding the pKa threshold value needed to drive the chemistry. Higher pKa values above this threshold generally lead to faster rates of catalysis. Similarly, when the pKa value is lower than the threshold, the reaction rate is diminished. Unlocking the power of the photolatent base catalysts is then reduced to tailoring the initial pKa of the photolatent form as well as adjusting the pKa jump that occurs when the free base amine is photogenerated.

Using this approach led to the recent development of photolatent amines and a photolatent DBN (1,5-diazabicyclo[4.3.0]non-5-ene). The photolatent amines liberate tertiary amines.

One photolatent form of the tertiary amine is an α-aminoketone (AAK) derivative. The AAK sterically shields the amine. When the AAK is photolyzed the shielding is lost and it yields a higher pKa tertiary amine that is also more active. It is because of the pKa's of the AAK and the resulting free-amine that makes this photolatent amine interesting. For example, with polyisocyanate/poly thiol-resin coatings, it permits fast curing (< 5 minutes) under direct UV-A light exposure as well as allowing for shadow curing.[14] At the appropriate concentration the AAK cures the resin in the dark (shadow areas) within four to six hours. The cure mechanism is not inhibited by oxygen, so good surface curing results. The overall cure kinetics are slower compared to typical free-radical curing of acrylates. This feature can, in principle, lead to better stress relaxation in the final polymer network. The photolatent catalyst is now being used in auto refinish coating applications, and permits faster, more efficient processing compared to conventional thermal curing.

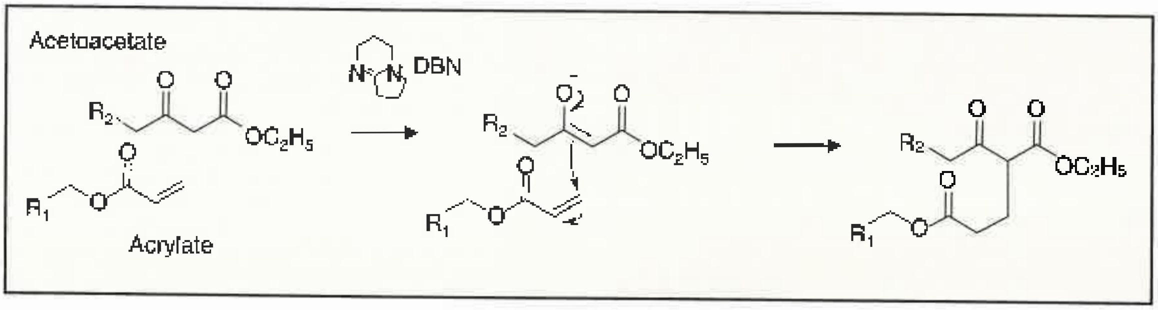
When the photolatent DBN is photoactivated, it undergoes a significant pKa jump (ΔpKa ~ 4). The DBN that is generated is a strong base and has a pKa = 13. Because of its high pKa value it can efficiently catalyze reactions such as Michael addition chemistry. The photolatent DBN has a pKa that is well below the threshold pKa to catalyze the Michael addition (*Figure* 9). Thus, storage stable or one-pack base catalyzed resins result.

Some of the current applications where photolatent base catalysts were found to be important are summarized in *Table* 2.[15] It is expected that more photolatent amines will be developed in the future, which build on this new technology platform.

PHOTOLATENT COLORANTS

Photochromic materials are materials that undergo a reversible color change after exposure to light. A familiar example is materials used in eyeglasses that darken when in the sunlight, but then reverse to clear in the dark. What is of interest is to use light selectively to create a permanent color. One approach is to photochemically generate a new thermally stable chromophore

Figure 9—Michael addition of an acetoacetate/acrylate coating system.



(such as to produce red, green, or blue colors).[1,17] This type of an effect could be useful in branding, security, or identification applications.

PHOTOLATENT FRAGRANCES

Fragrances are important to the coatings industry. Unfortunately, they are fugitive, by virtue of their volatility. One way to overcome this problem is to photogenerate the fragrant aroma in-situ. The fragrance-on-demand concept was recently reduced to practice.[18]

The novel photolatent precursor is able to release fragrances of natural or synthetic source. It is thus possible to create scents from floral fruity sweet, fresh citrus and minty, to spicy herbal, or even wine-like or woody aromas.

The key benefit of a fragrant product is to provide a pleasant aesthetic perception. It also can serve as a signal, to give a unique branding of the product. Photolatent fragrances are not restricted to simply scenting a coated surface; they can also be conveniently used to conceal undesirable odors of newly manufactured products.

Table 2—Examples of Where Photolatent Base Catalysts Can Be Used

Resin Type	Typical Photolatent Base	Comments
Carboxy/Epoxy	AAK	Used in hybrid systems Photoresists Generally requires thermal post-cure step
R-NCO/R'SH	Modified AAK	Automotive refinish Shadow cure Low color
R-NCO/R'OH	PL-DBN	Adhesives and coatings
Epoxy/Thiol	PL-DBN	Metal car coatings
Michael Addition	PL-DBN	Broad utility (adhesives, coatings, inks)

Figure 10—Example of a photolatent colorant and how it can be used for photo imaging.

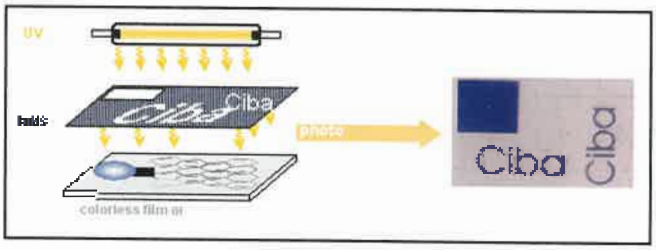


Figure 11—Photolatent fragrance which generates aroma under action of light.

- Thermally stable and durable coatings providing long lasting pleasant aroma
- Instantaneous scenting, which is long term and able to be reactivated
- Triggered by UVB, UVA, and daylight

Some of the odors emitted by new products, even if in low concentrations, have a negative image. Using photolatent fragrance additives in such systems can thus give a pleasant fragrance, which can add value. In this case, irradiation is the last step before packaging or if sufficient light transparency is given, the fragrance release can be triggered at any point via UVA light exposure through the packaging material.

Some of the fragrances are known to have a repellent effect on insects, e.g., citronellal, which is often used in candles or insect repellent lotions. The photolatent products could be used in paint for garden furniture or veranda boards, giving the double benefit of a pleasant scent and repelling insects.

SUMMARY

Photolatent additives offer useful benefits to the coatings industry. Work in developing this technology is ongoing. Recent developments have yielded important results that were aimed at improving or managing the limitations of light curing. These efforts help to expand horizons into new areas—such as the discovery of novel photo-induced effects that go beyond simple photocuring (color-on-demand and fragrance-on-demand, for example). The future thus holds great promise for even more innovation as these new effects become further developed and are exploited for specific applications.

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