Photoinitiators for UV Curing

Ciba

Formulators' Guide for Coatings

Additives

Value beyond chemistry

An increasing number of companies now rely on Ultra Violet (UV) cured coatings to achieve environmental compliance and improve customer satisfaction. UV curing is one of the most rapidly growing technologies within the coatings, graphic arts, adhesives and related industries. On wood, plastic, paper and other coatings, UV curing systems have been used to dramatically increase line speeds and develop coatings with superior environmental resistance and better gloss. Laminating, pressure sensitive and structural adhesives utilizing UV curing exhibit superior chemical resistance and physical properties and benefit from UV curing technology's inherent efficiencies.

Today, UV curing technology has grown and expanded far beyond the original wood filler application containing Ciba® IRGACURE® 651 photoinitiator. UV topcoats are now employed in prefinished wood flooring, kitchen cabinets, and some three dimensional furniture applications, all enabled by the development of the fast curing alpha hydroxyketone family of photoinitiators. Growth of UV curable coatings is due to a number of factors — low VOCs, significant increases in productivity yielding higher throughput of parts in a given time frame and excellent abrasion and stain resistance properties from the cured coatings. With the introduction of Irgacure 819, UV curing can now successfully deliver complete through cure of heavily pigmented wood coatings including whites.

The list of UV cured coatings applications seems limited only by the imagination. That's why more and more formulators and end users are calling UV curing the best solution under the sun.

Photoinitiators for Coatings

The selection of the correct photoinitiator or photoinitiator combination is critical to achieve the desired speed and balance of cure film properties.

Generally for coatings, products of the alpha Hydroxyketone family (Irgacure 184, Irgacure 2959 and Ciba® DAROCUR® 1173) are preferred when curing unpigmented/clear coatings and for delivering SURFACE CURING in highly pigmented systems as part of a photoinitiator package. For THROUGH CURING of thicker sections and for highly pigmented systems, a Bis Acyl Phosphine Oxide (BAPO) type of photoinitiator such as Irgacure 819 is suggested.

BAPO type photoinitiators are especially designed to be activated by longer wavelength UV light in the near visible region above 430 nm. Light of this wavelength penetrates deeper into the lower layers of the coating, thus enabling the through curing desired. Shorter wavelength light, around 230 nm, is of higher photon energy but is less penetrating than that of longer wavelengths. Light of this shorter wavelength is particularly useful for surface curing. Moreover, BAPO type photoinitiators also allow UV absorbers to be formulated into the coating for improved outdoor weatherability. In addition to excellent through cure properties, BAPO photoinitiators PHOTOBLEACH after UV exposure to give a clean white appearance in contrast to the off-white color associated with other long wavelength absorption photoinitiators.

Selection of the best individual photoinitiator or combination is dependent on a number of variables including chemistry of the resin system (UPES, epoxy acrylate, urethane acrylate), selection of monomers (monofunctional, multifunctional acrylate monomers), UV lamp type and orientation, cure speed required, coating property requirements, substrate and many others.

Ciba Photoinitiators for UV Curing

Key Product Features

Irgacure® 149	Blend containing 95% Darocur 1173 with 5% first generation BAPO. Delivers a through cure boosted Darocur 1173.
Irgacure® 184	Best for non-yellowing applications; low odor.
Irgacure® 369	Strong broad absorption characteristics make it most useful for curing thick pigmented formulations.
Irgacure® 500	Liquid blend of Irgacure 184 and benzophenone gives good balance of surface cure and through cure.
Irgacure® 651	General purpose initiator; useful for curing unsaturated polyester resins.
Irgacure® 784	Visible light initiator responds to all UV and visible light sources including visible lasers.
Irgacure® 819	Latest generation BAPO provides the most cost-effective curing of white and thick clear coatings. Also allows the formulation of light stable UV curable coatings.
Irgacure® 907	Strong absorption characteristics make it useful for curing pigmented inks and coatings; excellent surface cure initiator.
Irgacure® 1700	Efficient initiator for curing inks or coatings containing TiO_2.
Irgacure® 1800	Blend of first generation BAPO with Irgacure 184.
Irgacure® 1850	Higher concentration (50%) of first generation BAPO, blended with Irgacure 184.
Irgacure® 2959	Very low odor and low volatility photoinitiator; also has terminal hydroxyl group which may be reacted into polymer backbone. No benzaldehyde generation after cleavage.
Darocur® 1173	Liquid non-yellowing photoinitiator. Good solvency properties makes it ideal for making photoinitiator blends.
Darocur® 4265	Excellent for curing white inks and coatings.

For additional information about individual products or specific applications, please contact your local Technical Representative.

Applications

Wood Coatings

Wood coatings, specifically unsaturated polyester wood fillers, represent one of the first commercially successful uses of UV curing technology. In wood fillers, the photopolymer compounded with silica, talc, and other inert components are applied by a roll coater to fill voids in a particle board substrate. Sandability of the filled substrate then becomes an important physical characteristic.

Top coats can be formulated from unsaturated polyester (UPES)/styrene or acrylate oligomers depending on the cure performance required. Often the slower UPES resins are diluted with acrylate monomers to boost cure speed and crosslink density. Both pigmented and clear coatings are applied to the full range of wood substrates for furniture applications. Waterborne UV curable formulations are also of growing interest to wood coating formulators. In these systems, the resin can either be dilutable with water or processed as a dispersion.

Wood Coatings	Film Thickness	Photoinitiator	Conc.
Clear wood topcoat	0.5 - 4 mils (15 to 100 microns)	Irgacure 184 Darocur 1173 Irgacure 2959* Irgacure 500**	2-4.% 2-4% 2-4% 2-5%
For through cure enhancement also use		Irgacure 819	0.5-2%
Wood fillers (unsaturated polyesters & acrylates)	0.5 - 2 mils (15 to 50 microns)	Irgacure 651 Darocur 4265 Irgacure 819***	2-3% 2-3% 0.5-1%
Pigmented wood	0.5 - 2 mils (15 to 50 microns)	Irgacure 819 Darocur 4265	2-3% 2-3%

* Especially for waterborne formulations
** Together with an amine co-synergist
*** In combination with Irgacure 651 or an alpha Hydroxyketone, Darocur 1173

Clear Coatings

Clear coatings encompass an impressively wide range of applications including coatings onto metal, wood, glass and plastic. Coating thickness can range from < 25 microns for coatings onto fiber optics through < 50 microns for can coatings and up to 50 to 100 microns (2 to 4 mils) for coatings onto floor tiles. Alpha hydroxyketone photoinitiators such as Irgacure 184 have found broad acceptance in clear coatings onto a wide range of substrates. To improve through curing and boost cure speed, Irgacure 819 is suggested.

To improve weatherability of UV cured clear coatings, hindered amine light stabilizers (HALS) and Ultraviolet Absorbers (UVAs) have proven useful. They act synergistically and do not interfere with the UV cure process when using BAPO type photoinitiators such as Irgacure 819. Gloss retention can usually be improved and cracking and yellowing minimized by the use of an appropriate HALS. UVAs help protect the physical integrity of the coating and to screen any potentially harmful UV radiation from the sun from reaching the substrate once the coating is in service.

Clear Coatings	Film Thickness	Photoinitiator	Conc.
Clear coatings on plastic, metal, wood	< 1 mil to > 4 mils (< 25 microns to > 100 microns)	Irgacure 184	2-4%
		Irgacure 2959	2-4%
		Darocur 1173	2-4%
		Irgacure 500*	2-4%
		Irgacure 819**	0.5-1%

*Together with an amine synergist
**Particularly recommended for thicker coatings as a cure speed booster when used in combination with 1-2% of the above photoinitiators

Pigmented coatings

Early photoinitiators were superb at curing thinner pigmented formulations such as offset printing inks but were not very effective in the through curing of pigmented systems. Developments in the last decade, coupled with continuing research, have yielded photoinitiators that can successfully be used in the pigmented coatings industries.

Curing of thicker pigmented coatings advanced significantly in the mid-to-late 1990s with the introduction of the BAPO (bis acyl phosphine oxide) class of initiators. With the 1997 worldwide commercialization of Irgacure 819, it became possible to cure the entire range of pigmented coatings from white to black, and the entire color spectrum in between. The combination of Irgacure 819 with Irgacure 184 at ratios from 1:2 to 1:1 have proven most successful, delivering an excellent balance between surface and through curing without the need to use specially adapted lamp arrangements.

Pigment selection also plays a pivotal role in the overall curing characteristics of pigmented systems. In general the larger the pigment particle size, the greater the surface area and, therefore, the better the curing.

Functions Influencing Cure Behavior

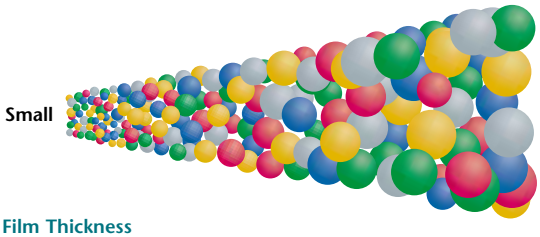
Poor → Medium → Good

Color

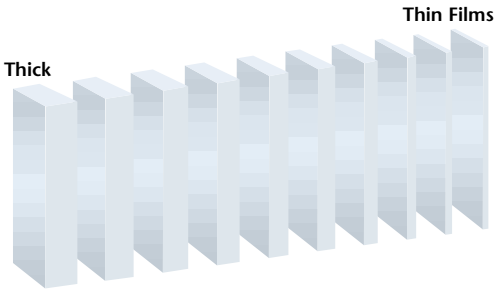
Red Yellow Green Blue Pigments

Pigment Concentration

Particle Size



Film Thickness



Resin

UPES < Polyesteracrylate < Epoxyacrylate

Thick Section Curing

Thick section curing also covers a large number of industries and end use applications including sealants, adhesives, glass reinforced composites, gel coats and now UV curable powder coatings. In order to achieve the required through curing performance for thicker coatings, it is important to formulate with a photoinitiator able to capitalize on the longer-wavelength, more penetrating part of the UV spectrum in the region above 400 nm. To obtain a balance of surface cure **and** through cure, a photoinitiator which can harness light of shorter wavelengths is required. BAPO type photoinitiators (Irgacure 819) are best suited to deliver through cure especially in pigmented systems and in composite and gel coat formulations. Photoinitiators of the alpha Hydroxyketone class (Irgacure 184) are especially useful as partners to ensure the correct level of surface cure. Irgacure 369, a photoinitiator of the alpha Aminoketone class, is also an effective product for achieving curing of intermediate thick section coatings. Because of its inherent yellow coloration, Irgacure 369 is best suited to dark colors and formulations without white pigments and fillers.

Thick Sections	Film Thickness	Photoinitiator	Conc.
Variable	>5 mils (>125 microns)	Irgacure 819 Darocur 4265 Irgacure 184 Irgacure 369	0.5-2% 1-2% 1-3% 2-5%

UV Curable Composites and Gel Coats

The curing of unsaturated polyester (UPES)/styrene resins is conventionally initiated by free radicals generated from peroxides. However, this conventional peroxide initiation has several limitations including styrene emissions, handling of the peroxides, limited shelf life of the peroxide-containing formulation, large ovens, high energy costs and cure speeds. These problems can be overcome by the use of photocuring which involves the generation of radicals by light from a BAPO photoinitiator such as Irgacure 819.

Current tests indicate that glass reinforced composites and gel coats cure significantly quicker using photocuring compared to conventional redox systems, while delivering reduced styrene emissions and providing excellent mechanical properties.

The UV curing of composites and gel coats is achieved by using a diffuse light source which has most of its emission in the long wavelength UV/visible light range. These diffuse lamps have the additional benefit of operating from a regular electricity supply. Photocuring also means that one can achieve cure on demand: By exposing the formulation to the diffuse UV source, the crosslinking reaction is initiated. Yet, removing the light stops the cure and allows further working of the composite or gel coat if required, yielding wide processing flexibility to the composite fabricator.

It is the BAPO photoinitiator, Irgacure 819, which enables the curing of composites by UV to become a reality. Irgacure 819 enables one-component, storage-stable composite or gel coat formulations, which are fast reacting, reduce styrene emissions and eliminate the handling and storage of peroxides.

Composites/Gel Coats	Film Thickness	Photoinitiator	Conc.
UV curable composites or gel coats	several mm	Irgacure 819	0.5%

UV Powder Coatings

Conventional powder coatings continue to grow rapidly, due largely to their zero VOC content, reduction in overspray and the ability for the coater to recycle overspray for second pass usage. Powder coatings have made significant strides in industrial markets in the past decade and are now starting to be used for high performance applications such as automotive top coats. Certain limitations, however, have prevented the usage of powders in some markets. These limitations include:

- Useful only on heat-tolerant substrates, eliminating their use on plastics or wood
- Very energy intensive — requiring long bake cycles at high temperatures
- Difficulty of achieving a "Class A" finish — because of crosslinking during the flow out processes
- Small processing window to achieve ideal flow — creating need for degassing agents which can contribute yellowing to the cured coating

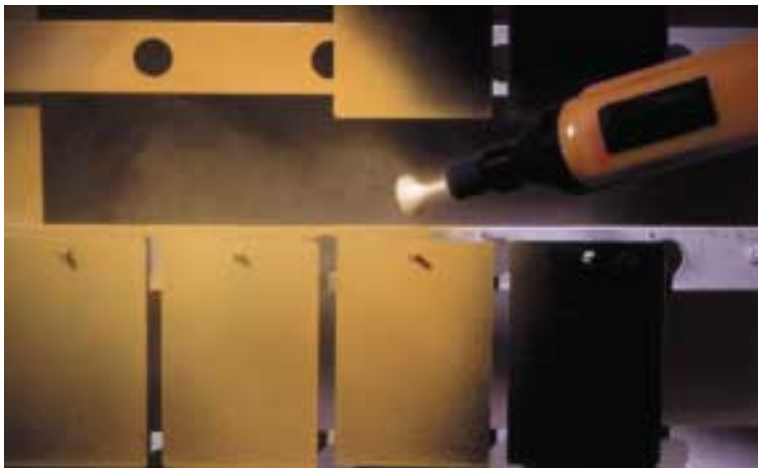
Combining the benefits of UV curing technology with those of powder coatings gives the coating formulator superior, UV curable powder coating systems which can:

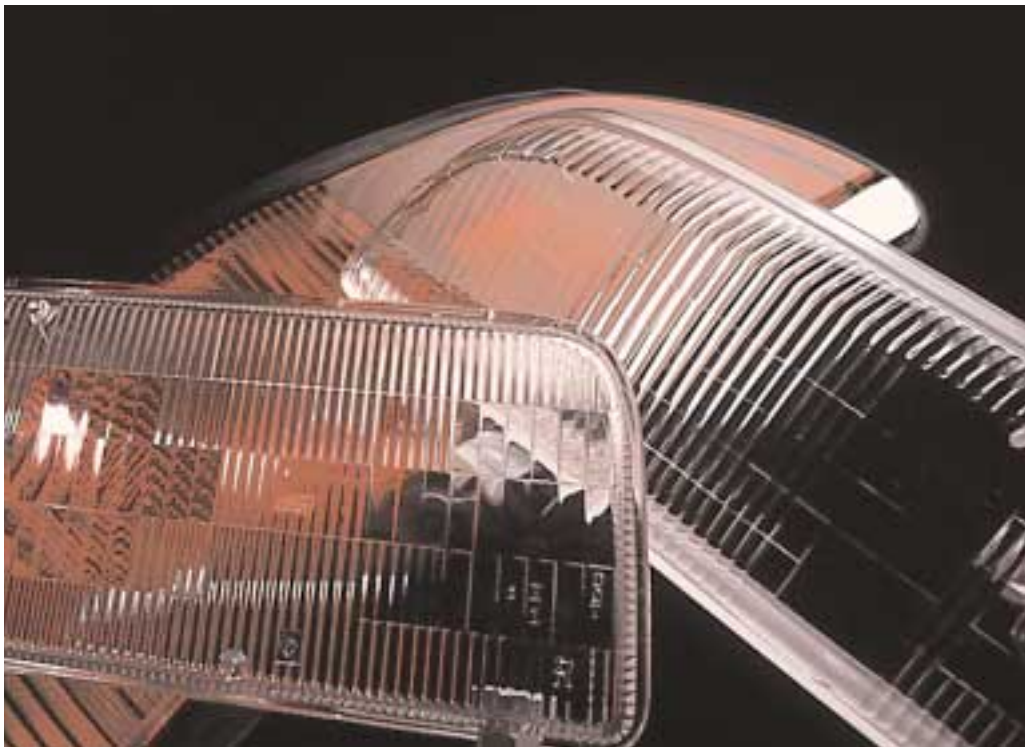
- Be applied to temperature sensitive substrates such as medium density fiber board (MDF)
- Give a "Class A" finish as the flow out and cure mechanism steps are separated, allowing ideal flow to be achieved BEFORE the crosslinking reaction is initiated
- Provide energy savings because of a relatively low temperature (~100°C) heat cycle for flow out

Photoinitiator selection

Photoinitiator selection for powder coatings requires careful consideration — the photoinitiators should ideally be in the solid state and have a melting profile consistent with the characteristics of the powder coating formulation. Minimum volatility is a key parameter as powders are subjected to heat and shear forces during processing and application. In addition, the photoinitiator should not contribute to a lowering of the glass transition temperature (Tg) of the resin, which can lead to storage and handling issues. The products that ideally fit this demanding profile are Irgacure 2959 for clear systems and Irgacure 819 for pigmented formulations.

Powder Coatings	Film Thickness	Photoinitiator	Conc.
Clear systems	variable	Irgacure 2959	2-4%
Pigmented systems if required for extra surface cure		Irgacure 819 Irgacure 2959	0.5-2% 1-2%





Adhesives

UV-cured adhesives is a broad category encompassing adhesives and laminates for wood, paper, plastics, glass and metal. In addition, there are a large number of high value-added specialty applications for electronics, medical devices, solar films and automotive uses. In most of these applications, the adhesive film is relatively thick and requires longer exposure times in order to achieve acceptable through cure.

The photoinitiator selection must be carefully considered to meet the cure-performance needs of the application. Ciba's photoinitiator offerings cover a broad range of curing options. Alpha-Amino-ketone type initiators (Irgacure 369, Irgacure 907) and BAPO type (Irgacure 819) are normally the photoinitiators of choice since they have absorption characteristics that extend into the short visible region of the UV spectrum. The use of a film through which curing is activated can assist in achieving rapid cure due to an elimination of oxygen which can retard the rate of surface cure due to oxygen inhibition.

Photoinitiator concentrations of 1 - 4% are suggested and blends of Irgacure 819 together with shorter wavelength absorbing photoinitiators such as Irgacure 184 or Darocur 1173 can often achieve a balance of through and surface cure, as outlined previously. For low odor and for applications demanding low volatility such as hot melt adhesives, Irgacure 2959 is the product of choice. Irgacure 2959 has also recently received FDA approval for use in both hot melt and pressure sensitive adhesive formulations.

Adhesives	Film Thickness	Photoinitiator	Conc.
Pressure-sensitive adhesives	0.5 - 5 mils (10 - 125 microns)	Irgacure 184 Irgacure 2959*	1-4% 1-4%
Laminating adhesives	0.3 - 2 mils (5 - 50 microns)	Irgacure 184 Irgacure 2959* Irgacure 819	1-4% 1-4% 0.5-3%
Structural adhesives	Variable	Irgacure 369 Irgacure 819	1-4% 0.5-2%

* Irgacure 2959 is FDA regulated as a photoinitiator for adhesives and pressure sensitive adhesives complying with 21 CFR 175.105 and 21 CFR 175.125.

Formulation Guidelines

Incorporation Methods

When incorporating photoinitiators, it is generally recommended to dissolve the photoinitiator(s) in a monomer and then add the solution to the resin to ensure complete dissolution. A solid dispersion of photoinitiator in the formulation instead of a fully solubilized material will reduce the effective deployment of the photoinitiator and can lead to poor cure performance. Liquid photoinitiators can be added to either the monomer or the formulated coating as they are easier to dissolve.

Test Several Initiators

Because of differences in resin chemistry, lamp configuration, and the desired end properties, it is impossible to make universally definitive statements as to which initiator will be most useful under any given condition. We suggest that two or three different initiators be tested for initial screening. This is particularly important when starting a new formulation or curing under a new set of conditions. Ciba's broad range of photoinitiators allows an excellent choice for most applications. Please refer to our brochure *Photoinitiators for UV Curing: Key Products Selection Guide* for guidance on the choice of photoinitiator for your specific application.

Optimize Concentration

When selecting a photoinitiator, it is important to work towards optimizing the concentration of the chosen products. This is especially significant when using Irgacure 819 to obtain maximum benefit from its photobleaching characteristics. Too much photoinitiator can prove just as problematic as not enough because of the "filter effect" caused by high levels of surface crosslinking which does not allow the UV light to effectively penetrate the coating to the lower layers required for through curing. It is recommended that you conduct a ladder study for each formulation to achieve the optimum concentration of photoinitiator. Usually 2 - 3 % of photoinitiator is a reasonable starting point. Blends comprising highly effective surface curing photoinitiators such as Irgacure 184 together with the through curing photoinitiators Irgacure 819 or Irgacure 369 often deliver the optimum in cure performance, especially for thick and pigmented formulations.

Curing in the Presence of Light Stabilizers

UV curable coatings and inks for exterior applications usually require the use of light stabilizers to prevent degradation due to damaging UV radiation from sunlight. Ciba has developed two different types of light stabilizers — Ultraviolet Absorbers (UVAs) and Hindered Amine Light Stabilizers (HALS).

HALS do not absorb UV light but are chemical stabilizers and operate via a number of different mechanisms, including the scavenging of free radicals

and the deactivation of hydrogen peroxides. HALS have little or no impact on the cure properties of photopolymers.

Ultraviolet absorbers (UVAs), as their name suggests, operate by a physical process whereby they absorb the incident ultraviolet light and are able to convert this into heat energy which can be dissipated through the polymer matrix in a non-damaging way. UVAs however, can compete with photoinitiators for the available light and therefore have an impact on the cure speed of most formulations. With the advent of BAPO type photoinitiators, this issue is now overcome. The special design of Irgacure 819 allows it to absorb light in the near visible portion of the UV spectrum and, as such, creates a curing window which does not compete with the UVA. This window allows the formulator to cure thick and pigmented coatings containing UVAs. As with most coating formulations, a combination of HALS and UVA usually offers superior UV protection because the two products complement each other in their mode of operation.

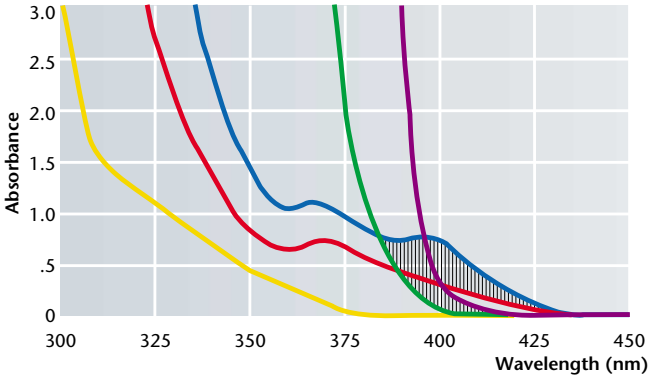
Overcoming Surface Cure Problems

Surface cure problems generally indicate that the formulation is not able to overcome the oxygen inhibition which is inherent in the UV curing of acrylates. Higher photoinitiator concentrations are generally recommended to solve this problem. The formulator may also want to concentrate on initiators with proven good surface cure properties, such as Irgacure 907, Irgacure 184 or Irgacure 500.

Overcoming Through Cure Problems

Through cure problems may show up as surface wrinkling or may be manifested through poor performance properties such as adhesion. The use of Irgacure 819 or Irgacure 369 will boost the through curing performance of most UV formulations. A loading of 0.5 - 1% for Irgacure 819 or 1 - 5% for Irgacure 369 is normally sufficient. Care must be taken not to add too high a concentration of photoinitiator, otherwise the filter effect may play a role, preventing the incident UV light from penetrating to the bottom layers of the formulation.

Your local Ciba technical representative is also available to discuss your specific requirements.



Absorption Spectra of Photoinitiators and UVAs

- **0.25 g/L Irgacure 184**
- **0.15 g/L Irgacure 184/819 (3:1)**
- **0.25 g/L Irgacure 184/819 (3:1)**
- **0.1 g/L Tinuvin 400**
- **0.1 g/L Tinuvin 384**

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