Novel effects beyond radiation curing

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Introduction

Radiation curing is one of the most economic and environmentally compatible coating technologies known. It has successfully enabled numerous industrial applications over recent decades. There still remain, however, challenges that prevent penetration into broader areas of interest, such as:

- Flexible and robust processing, e.g., sufficient post curing in poorly and non-exposed areas on three dimensional objects
- Adhesion on “difficult” substrates (such as plastics, metals etc.)
- High reactivity of photoinitiators in combination with low volatility, odor and migration
- Oxygen inhibition of radically curing processes and economically feasible options for inerting on an industrial scale (to optimize surface effects, such as scratch and mar resistance)
- Environmental, health and safety concerns with regard to coating systems and workers protection from UV exposure, etc.
- Low or negligible yellowing of UV curable coating systems
- Colored coatings with good hiding power and through cure
- Flexibility in using alternative resin technology for radiation curing to realize novel effects and overcome existing deficiencies associated with radical polymerization processes of acrylate chemistry

Recent developments at Ciba Specialty Chemicals specifically target these deficiencies, which thus open up new turfs or new areas that have heretofore been inaccessible using current state of the art radcure methods.

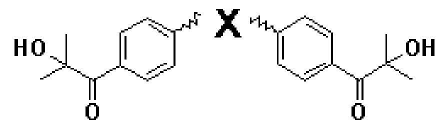
In addition, novel photo-induced effects - triggered by UV or visible light - beyond curing such as the controlled scenting or coloration of inks and coatings have been investigated recently. Those systems are colorless (pre-chromic) and thermally stable and open up new opportunities for radiation technology that have heretofore been unexploited.

Novel Photoinitiator solutions for Industrial Coatings

Our most recent innovations in photoinitiator chemistry have addressed abovementioned challenges aiming for maximized curing performance, process efficiency and environmental compatibility. For example, a liquid, water dispersible form of a bisacylphosphine oxide (BAPO) photoinitiator has been developed recently to address the global trend towards environmentally more friendly waterborne UV systems and the need of state-of-the-art performance of BAPO chemistry, which includes good reactivity, through cure and adhesion for pigmented and highly filled coatings, gel coats and composites[1].

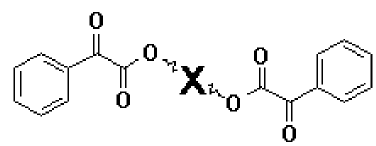
A high molecular weight dimeric alpha-hydroxy ketone type photoinitiator has been developed for clear coat applications, which is particularly suited for curing of thin films in air[2]. This photoinitiator does show very low migration and odour in the cured coating.

- high reactivity
- curing of thin films in the presence of air
- low migration, reduced volatility and minimal odor



Furthermore, an easy-to-use broadly compatible liquid photoinitiator for solvent-borne UV systems - based on a dimeric phenylglyoxalate structure - has been developed to specifically target low yellowing, low migration and low odour issues of the cured film[3].

- easy-to-use and broadly compatible initiator
- low yellowing and high reactivity
- low migration, reduced volatility and minimal odor



A novel approach has been pursued more recently in our labs to obtain additional surface effects in UV cured coatings. The combination of surface active substituents as part of the initiating species and the modification and optimization of the chromophore gives rise to a new class of photoinitiators providing improved performance and efficiency *versus* state of the art photoinitiators along with additional effects.

The optimized balance of UV spectral properties, molecular weight, spacer functionality and choice of surface active side chains within a single initiator enables a very fast UV curing process that ultimately yields a high polymer crosslink density at the surface.

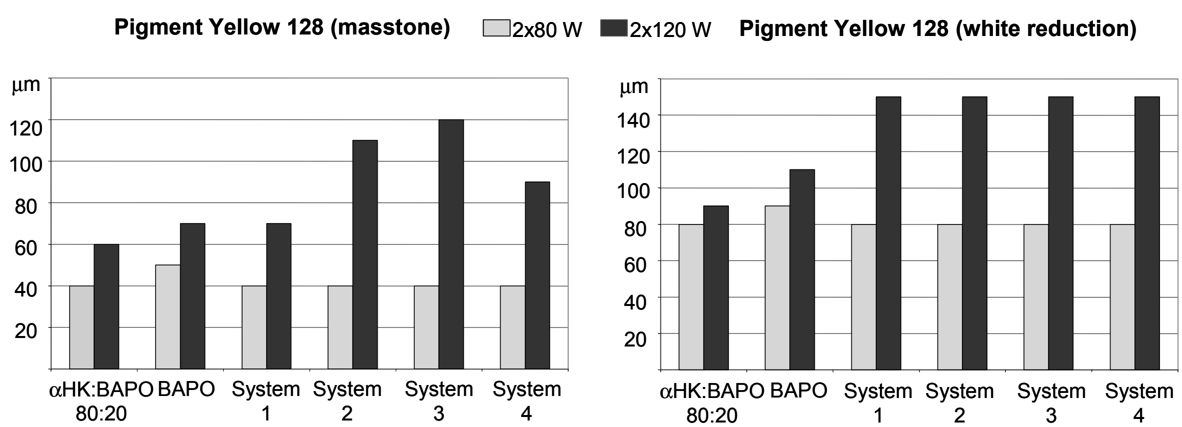
For these reasons, improved resistance from scratches and low yellowing are observed. The novel system is therefore particularly well suited for high performance applications such as automotive clear coats where the fine tuning of surface properties, like scratch resistance, is highly desirable.

Novel approaches for UV curing of colored pigmented coatings

One of the major challenges that prevent further penetration of UV curing technology into broader industrial areas is the limited curing of thick or highly pigmented coatings. To allow for proper through cure of UV-curable acrylate based resin systems, the radiation responsible for initiating the cleavage of photoinitiators needs to penetrate the entire coating film sufficiently from the surface down to the substrate. In particular yellow, orange, green and black pigments are known to significantly reduce the light transmission through a coating film in the relevant UV range due to absorption and scattering.

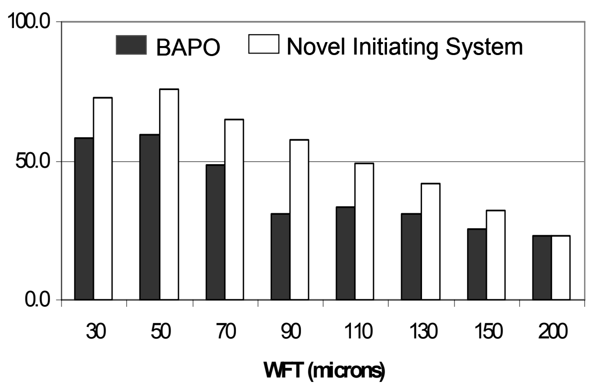
In recent years novel initiators and initiator blends have successfully been introduced, and guidelines were established[4], to improve the efficiency of UV curing of white and colored pigmented coatings. Further recent development was based on an optimized combination of commercially available photoinitiators in combination with a selection of suitable pigments[4]. Numeric simulations of through cure of these systems have been reported more recently[5]. However, breakthrough developments that significantly improve the maximum curable film thickness in pigmented coatings - in particular with respect to the most critical colors - are still missing.

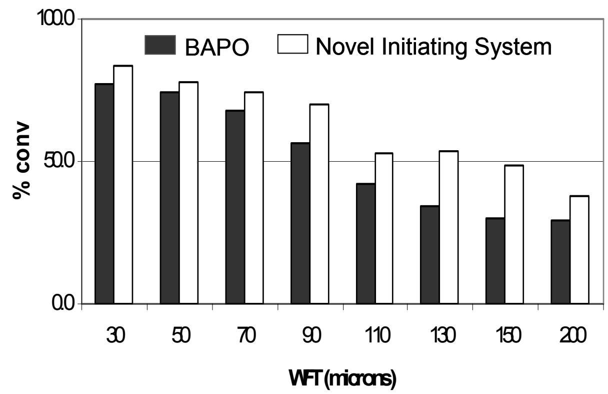
Recent investigations at Ciba Specialty Chemicals are aimed at identifying innovative solutions to overcome these through-cure deficiencies. For example, novel initiating systems – still under development - have been identified very recently allowing for significant improvements of maximum curable wet film thickness (WFT_{max}) of colored pigmented coating formulations. The relative improvement in masstone and white reduction when employing the novel initiating system *versus* commercially available state-of-the-art photoinitiators (BAPO, BAPO/α-HK blends) is illustratively depicted below (maximum curable wet film thickness achieved with novel initiating systems in yellow pigmented polyester acrylate versus commercially available photoinitiators. Left graph: 10 % PY-128; right graph: 9 % TiO2, 1 % PY-128).



Through cure and maximum curable wet film thickness were determined by measuring the conversion of double bonds *via* ATR-IR spectroscopy.

At the top surface, a conversion rate of more than 95% was observed on all samples (2 x 80W and 2 x 120 W Hg bulbs). After separation of the film from the substrate the conversion rate on the bottom side was determined (double bond conversion on the bottom (substrate) side of the cured coating film, yellow pigmented (10 % PY-128); commercially available bisacylphosphine oxide (BAPO) versus novel initiating system. Data determined by ATR-IR spectroscopy (left: 2 x 80 W, right: 2 x 120 W Hg bulbs).





The relative difference of double bond conversion at the bottom surface level clearly shows the advantage of the new initiating system at low and high lamp power settings versus the current state-of-the-art bisacylphosphine oxide photoinitiator. Currently we are continuing to further optimize these novel initiating systems to support the growth of UV curing technologies into broader industrial areas.

Novel approach for UV curing on 3 dimensional objects

UV-curable coatings have found extensive use in industrial applications where 2-dimensional objects, such as flat furniture and metal parts, papers and plastics, can be cured at high speed. If 3-dimensional substrates are coated with acrylate based UV-formulations using conventional lamp equipment for exposure, lack of curing in shadow areas may occur.

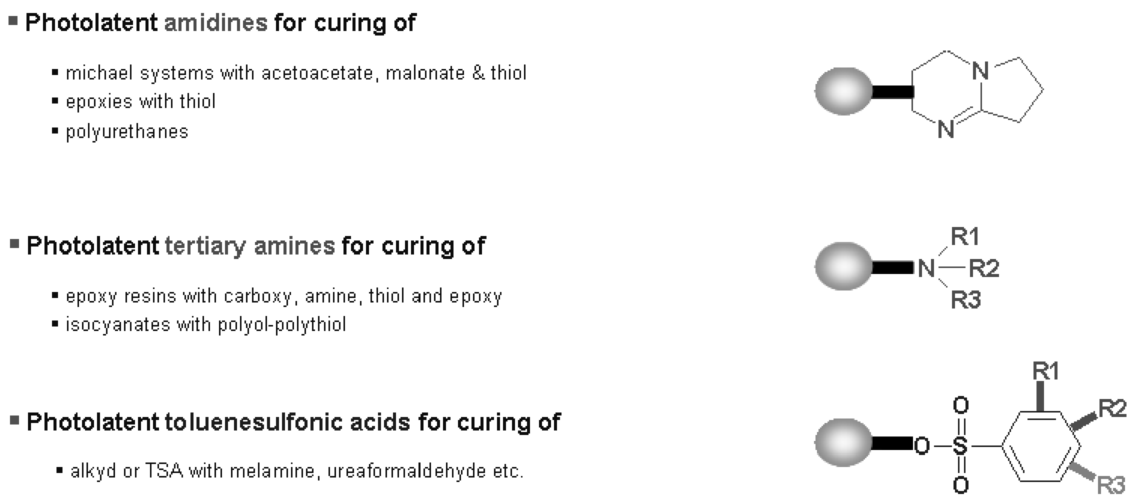
Different strategies are being developed to overcome shadow cure effects. For example, so called Dual Cure Systems (which involves a UV-curing and a thermal curing step) have been developed. Another innovative approach involves PlasmaCure™ as a workable solution[6]. The key features along with the plasma curing of a real size car body are depicted below.

- scratch and mar resistance
- excellent appearance and durability
- faster processes at room temperature
- high adaptability in current automotive industry line set up
- curing of assembled car body with parts
- optimized coating process
- low or no solvent emission

Novel Photocataysts: Photolatent Acids and Bases

Recently the development of photolatent bases suitable for application in industrial coating processes has been reported[7]. This novel technology is aimed at taking the well known benefits of photocuring processes - providing full control over the curing process – into alternative as well as standard coating systems. Additionally, photolatent catalyst technologies can overcome the intrinsic barriers associated with "conventional" radical photo-polymerization processes.

In the past, traditional two-component coatings resins required the addition of a catalyst immediately before use. The curing reaction began as soon as the catalyst was added, restricting the time during which the coating could be used and necessitating the disposal of leftover paint or varnish. Photolatent catalysts remain stable in the coating until irradiated at the appropriate wavelength: only then is the catalyst released to initiate the crosslinking reaction immediately. Below a set of photolatent catalyst technologies is depicted which are currently being further developed.



The blocked catalysts are suitable for base- or acid-catalyzed crosslinking mechanisms and realize photocuring of conventional resin systems for coatings and other industries which have hitherto been inaccessible for radiation curing[8, 9, 10].

More recently, the first UV clear coat for automotive refinish industry has been developed in a joint cooperation[11]. The active catalyst – a photolatent base – is efficiently released under UV-A exposure, for example, by employing UV fluorescent lamps. Main features of the novel clear coat system are:

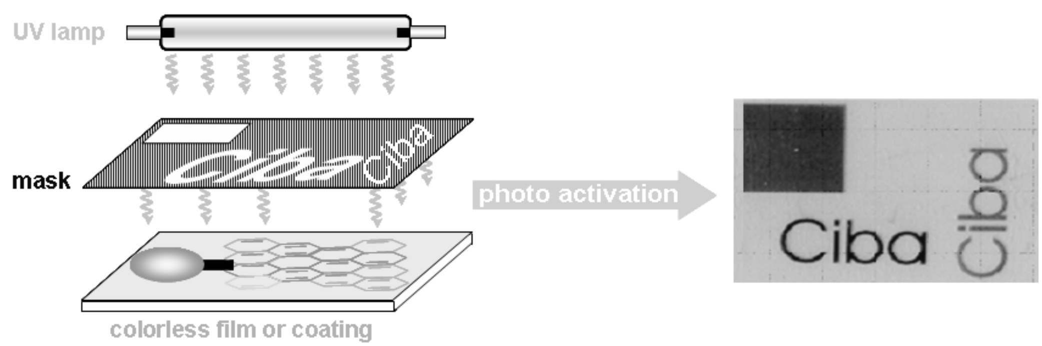
- Fast curing under fluorescent lamps at room temperature.
- Little susceptibility for parameter changes (lamp distance).
- Good high gloss appearance and durability.
- Fast and proper curing in shadow areas.
- Increased potlife of ready to cure formulation.

The key advantages of this novel technology comprise flexibility in having different technologies at paint shops and economy & ecology, such as less waste and increased throughput (5 min at room temperature *versus* 30 min at 60 °C).

This innovation brings all the advantages of light-triggered hardening to a wide range of new coating resins useful for applications extending from wood varnishes to automotive repair finishes. Photolatent bases allow coating manufacturers to fine-tune their products, to make the curing process economically more attractive by reducing curing time from hours to minutes and eliminating waste formation due to premature gelling of the formulation, and to select the required wavelength to initiate the reaction. Furthermore, perfectly uniform illumination is no longer required, because the curing effect ultimately extends even into shadow areas. This gives the industry the chance to rethink the whole range of coatings resins, improving efficiency, quality and environmental performance.

Photoindicators: Photolatent Colorants

Novel photo-induced effects (triggered by UV-Vis light) that are not necessarily involving the generation of initiators for curing have been investigated recently in our labs. For example, a range of novel additives that are colorless (pre-chromic) and thermally stable is currently under development. Only when irradiated with the appropriate wavelength, the color is developed instantaneously, within fractions of seconds. Irradiation can be performed with full exposure or through a photomask, providing either a full colored article or an image in the carrier material. The method is especially suitable for instantaneous in depth coloring of a coating composition, which has the advantage that the image obtained, cannot be removed without disturbing the coating. The concept of photocoloration and image formation through a mask on a thermally cured coating system (1 % in thermo-setting melamine – acrylate; curing at 130°C for 30 min) by UV exposure (2 x mercury lamps, 80 W/cm, 10 m/min) along with the key features of this technology is depicted below.



- Thermally stable prechromic coatings.
- Smooth, continuous color change on sunlight exposure.
- Instantaneous *“on demand”* coloration on UV exposure.
- Image formation through mask on conventional inks, coatings and objects.
- *In situ* mass coloration of UV curable formulation or thermo-cured coating film (TSA).
- Variety of prechromic”colorants“ available.

The pre-chromics can be incorporated and cured in conventional baking systems without any color formation since the latent, colorless system is stable under thermal curing conditions. On exposure to UV radiation a wide range of colors can be obtained instantaneously. The photoprocess can be triggered using standard UV irradiation conditions, such as medium pressure mercury bulbs. In addition UV lasers can be employed to generate writings or images without the need of a photomask and the system is therefore suitable for brand protection of coated substrates. The slow color formation under long-wave UV exposure can be exploited as a sensitive dosimeter for UV exposure.

Due to the immediate and intense color formation under conventional UV curing conditions the photolatent colorants are also useful as processing aids (UV indicator) in UV curable formulations to visualize the degree of UV exposure and through cure in UV curing processes in coatings, adhesives and for the formation of 3D objects.

Photoscents: Photolatent Fragrances

The effect of photo-induced release of fragrances is well known. Most precursors of fragrances or the actives themselves are volatile and therefore the desired effect diminishes quickly under ambient conditions, especially at elevated temperatures. For example, when employed in substrates which undergo further processing at elevated temperatures - such as the curing process of a coating layer - many (pro)fragrances are unstable or disappear quickly. To prolong olfactory perception, new systems have to be developed which are stable to the processing conditions, which thus allow a controlled, slow and long lasting release of the active fragrance.

Several concepts have recently been reviewed by Hermann et al.[12], that are relevant to this topic. For example, one is the controlled delivery of fragrances from polymer substrates *via* thermal or photochemical release. Another fragrance control concept uses encapsulation techniques. However, a single, unique release mechanism would be highly desirable since it would also allow the liberation of well defined scents composed of a blend of many individual components at the same rate.

Recent developments in our labs have targeted and optimized pro-fragrances that can be delivered on demand by activation with appropriate UV-visible light. The concept and key features are depicted schematically below.

- Thermally stable and durable coatings providing long lasting pleasant aroma.
- Instantaneous scenting, which is long term and re-activatable.
- Triggered by UVB, UVA and daylight.

Thermally stable slow release systems that also do not affect the standard coating performance (such as gloss, durability, discoloration etc.) are currently under development. These systems will allow one to scent objects when desired and on demand, e. g., to conceal initial coating malodour or deliver long-term and distinct scents from furniture, deco coatings, inks, packaging etc.

Outlook

Innovation in radiation curing technology is ongoing. Recent developments at Ciba Specialty Chemicals were targeted at specifically improving or managing the limitations of this technology. With this commitment we actively support the expansion of light curing technology in all industrial application areas. Such effort helps to expand horizons into new areas – such as the discovery of novel photo-induced effects that goes beyond simple photocuring. The future thus hold great promise for even more innovation as these new effects become further developed and are exploited for specific applications.

Literature

[1] Burglin, M.; Köhler, M.; Dietliker, K.; Wolf, J.-P.; Gatlik, I.; Gescheidt, G.; Neshchadin, D.; Rist, G. *RadTech USA 2000, Conference Proceedings*, Baltimore 2000, p. 577.

[2] Fuchs, A.; Bolle, T.; Ilg, S.; Hüsler, R. *RadTech Europe 2003, Conference Proceedings*, Berlin, 2000, p. 505-511; Fuchs, A.; Richert, M.; Biry, S.; Villeneuve, S.; Bolle, T. *NIP19: International Conference on Digital Printing Technologies 2003*, p. 268-271.

[3] Bolle, T.; Peter, W.; Fuchs, A.; Hüsler, R. „New Low Emission Photoinitiators for Coatings and Inks“ *RadTech Asia 2003, Conference Proceedings,* Yokohama, December 9.-12., 2003.

[4] Pigments/Photoinitiators: Guidelines for UV Curing of Pigmented Coatings, Ciba Specialty Chemicals, Basel 2002.

[5] Frey, T. „Modellbetrachtung zur Durchhärtung pigmentierter UV-härtender Lacke“, 4. Esslinger Oberflächenseminar, September 2004; Frey, T. “UV Meets Colour: A Numerical Simulation of the Through-Cure of Pigmented UV Coatings” *RadTech Europe 05, Conference Programme*, Barcelona, 2005.

[6] Jung, T.; Simmendinger, P.; Tobisch, W. *European Coatings Journal*; 2005, p. 138-143; Jung, T. “UV-Plasma Curing: Capture the Third Dimension” *RadTech Europe 05, Conference Programme*, Barcelona, 2005.

[7] Dietliker, K.; Jung, T.; Benkhoff, J. “Photolatent Amines: New Opportunities in Radiation Curing” *RadTech USA e¦5 2004, Conference Proceedings,* May 2-5, 2004; Jung, T.; Dietliker, K.; Benkhoff, J.; *Farbe & Lack*, 2003, 109, p. 34-41.

[8] Noomen, A. *Prog. Org. Coatings* 1997, 32, p. 137; Erdle, W.; Vogel, K.-H.; Tinsley, R.; *Farbe & Lack* 2004, 2, p. 22.

[9] Barton, J. M. *Adv. Polym. Sci.* 1985, 72, 11; Birbaum, J.-L.; Kunz, M.; Kimura, A.; Kura, H.; Oka, H.; Nakashima, H*, Eur. Pat. Appl. 898202 A1* (1999).

[10] Benkhoff, J.; Dietliker, K.; Jung, T. *Athens Conference on Coatings Science and Technology, Conference Proceedings,* July 7-11, 2003, p. 35-48.

[11] Dietliker, K.; Jung, T.; Benkhoff, J., Sitzmann, E. *8th Nürnberg Congress 2005, Conference Proceedings*, Nürnberg 2005, p. 145.; Dogan, N.; Klinkenberg, H.; Frings, S.; Reinerle, L., Wijnands, H. A. *8th Nürnberg Congress 2005, Conference Proceedings*, Nürnberg 2005, p. 155.

[12] Hermann, A. “Photochemical fragrance delivery systems based on the norrish type II reaction – a review” *The Spectrum*, Volume 17, Issue 2, 2004, p.10-19.