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New Developments in Photoinitiators

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Summary: New developments of photoinitiators are the base for the further extension of the radiation curing technology. Three different approaches are presented: The optimized combination of a bisacylphosphine oxide photoinitiator with a suitable stabilizer package allows the UV curing of clear coatings with an excellent performance in outdoor use. The design of new oxime ester derivatives allowed the introduction of a new tailor-made photoinitiator for color filter resists applications that considerably improves the color quality of the color filter. A novel photoinitiator class capable of releasing strong amine bases opens new opportunities for expanding radiation curing into resins types that crosslink by base-catalyzed processes.

Keywords: color filter resists; outdoor coatings; photoinitiator; photolatent amines; photopolymerization

Introduction

Over the last two decades, radiation curing became a well-accepted technology with widespread use. The major reasons for this development are its unique features, which include solvent-free formulations, high cure speed, low temperature processing and a high quality of the products obtained. Considerable economic and ecological advantages are thus achieved and make radiation curing attractive for industrial applications. Especially radically polymerizing UV-curable formulations are used in a wide variety of applications. These include protective and decorative coatings on wood, metal, plastic and paper, glass fiber coatings, or UV-curable printing and ink jet inks for graphic arts. The possibility of imagewise exposure to light is the base of the manufacturing process for printing plates and electronic applications such as photoresists as well as for

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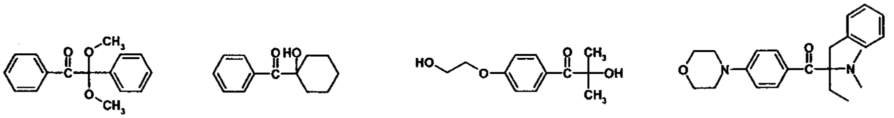
the fabrication of three-dimensional models in the stereolithographic process.

All applications require photoinitiators as a key component, which must meet the requirements of the different curing conditions and the use of the cured article. Correspondingly, a broad palette of such initiators has been developed both in academic and industrial laboratories.[1][2] Several highly efficient photoinitiators are available as commercial compounds and used in large amounts. A typical, albeit not comprehensive, selection of commercial radical photoinitiators is collected in Figure 1, together with their main application areas. Other commercial photoinitiators are also available for cationically curing formulations.



benzoin dimethylketal

wood coatings
wood fillers
flexo printing plates
etch resists

1-hydroxy-cyclohexyl-phenyl-ketone

top coats on wood, plastic or metal
overprint varnishes
adhesives

2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone

adhesives
overprint varnishes
UV powder coatings
water-based UV formulations
low volatility, low odor

2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone

offset, screen and flexo inks
solder masks
etch resists
low volatility, low odor

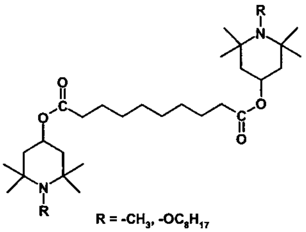
Figure 1. Typical commercially available radical photoinitiators.

Despite the large variety of available photoinitiators, novel compounds that fit even better to newly emerging applications with high demands are still needed. Improved equipment, such as novel light sources, also requires optimized compounds that make best use of the available light. Moreover, the development of novel classes of photoinitiators has to be continued in order to open new opportunities for radiation curing in fields that are not yet available to this technology. Three examples of recent developments that expand the scope of radiation curing are reported in the following.

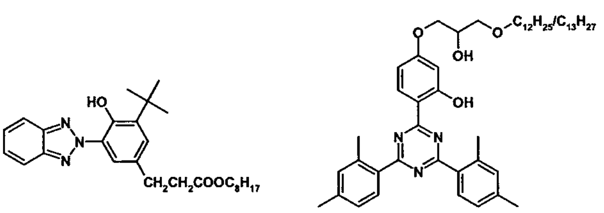
Curing of automotive coatings: Smart photoinitiator/stabilizer packages

Clear coats that form the outermost protective layer of a multi-layer automotive coating are a special challenge for radiation curing. Since the service life of modern cars is guaranteed for at least ten years, an extraordinary weather resistance of the cured coating is required. In fact, these lacquers are continuously exposed to harsh weathering conditions, suffering the action of sunshine irradiation, humidity, air pollution and temperature changes, which results in loss of gloss, delamination, blistering, cracking and color changes, if the coating is not appropriately stabilized.

From conventional outdoor coatings, it is well known that the best stabilization is obtained by the combination of two types of light stabilizers: Hindered amine light stabilizers (HALS) and UV-absorbers (Figure 2).[3] For radiation-curable lacquers, a similar stabilizer package has to be used in order to achieve the required service time.



hindered amine light stabilizers (HALS)



benztriazol (BTZ) type UV absorber

hydroxyphenyl-s-triazine (HPT) type UV absorber

Figure 2. Typical HALS light stabilizers and UV-absorbers.

The stabilizing effect of HALS compounds is attributed to the radical scavenging ability of the 2,2,6,6-tetramethylpiperidine moiety, which intercepts radicals formed during the weathering process. While this process is effective for the quenching of radicals produced in low concentration during the polymer degradation process, it does not efficiently reduce the high momentary radical concentration produced during the radiation curing process. Moreover, most HALS stabilizers are used in a captive form (N-alkyl or N-alkoxy derivatives, Figure 2), from which the active form is formed in a multistep reaction in the *Denisov* cycle.[4] Thus, the influence of HALS stabilizers on the radiation curing process can be virtually neglected.

UV absorbers are designed for efficient absorption of damaging UV-A light, which is transformed into harmless thermal energy via various deactivation processes.[5] These compounds have thus a very strong absorption in a wavelength range that is most important for the excitation of UV-photoinitiators such as the compounds shown in Figure 1. Since the molar absorbance at the maximum usually exceeds that of the photoinitiator by a factor of two or more, the initiators are efficiently shielded from incident light and can hardly be activated (compare Figure 4). Thus, using conventional photoinitiators, the UV curing process becomes inefficient or even impossible at a usual coating thickness of 40-60 μm.

Photoinitiators that have an absorption extending into the visible, or compounds with a strong absorbance in the visible, are known.[1] Examples are substituted thioxanthone derivatives, such as 2-isopropyl-thioxanthone[6] or 1-chloro-4-propoxy-thioxanthone.[7] These photoinitiators allow the curing of stabilized coatings, since they can be activated with light that it not absorbed by the UV absorber. However, an absorption in the visible is synonymous with color, and a lacquer cured with such an initiator will have inherently a yellowish appearance. Discoloration is, however, not acceptable for a clear topcoat, since it would considerably influence the appearance of the automotive coating.

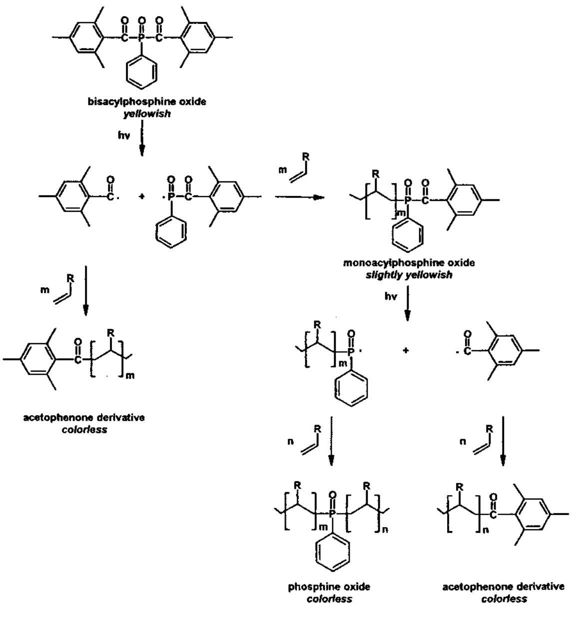


Figure 3. BAPO photoinitiator: Photocleavage and initiation.

This dilemma can only be resolved, if a photoinitiator that undergoes efficient bleaching of the long wavelength absorption is used. Such compounds have recently been developed for the curing of white-pigmented coatings, where the rutile-type titanium dioxide pigment filters off UV light, similar to the effect of an UV-absorber. These photoinitiators are based on a bisacylphosphine oxide (BAPO) structure and have a long-wavelength absorbing chromophore, which is attributed to an nπ* transition that is red-shifted by conjugative carbonyl-phosphinoyl-carbonyl interactions. After excitation with light in the near UV/visible, the excited triplet state undergoes cleavage of the carbon-phosphorous bond, thereby producing two highly efficient initiating radicals (Figure 3).

Since this photoreaction results in the cleavage of the chromophore, the photoproducts have a blue-shifted absorption, and bleaching of the long-wavelengths absorption band is observed. The addition product obtained from the benzoyl-phosphinoyl radical has a monoacylphosphine oxide (MAPO) structure, which after absorption of a second photon can undergo another cleavage reaction. The newly formed radical pair can in turn again initiate the polymerization process, thereby producing products that absorb only light in the UV. Thus, these photoinitiators are capable of producing four initiating radicals and concomitantly undergo efficient bleaching, resulting in a colorless coating.

A comparison of the UV spectra of benzotriazol (BTZ) and hydroxyphenyl triazine (HPT) UV absorbers reveals that the latter compounds have a stronger absorbance, but a slightly blue shifted maximum with a steep long-wavelengths edge. While BTZ-type absorbers give excellent results in wood coatings by absorbing light harmful for lignin, HPT-type UV absorbers in a clear topcoat are well suited for the protection of pigments against fading. Due to their blue-shifted absorption edge, the combination of this UV-absorber class with BAPO photoinitiators allows for the most efficient absorption of light by the photoinitiator and hence for efficient curing. Advantageously blends of BAPO photoinitiators with suitable α-hydroxyacetophenone photoinitiators are used. The latter compound guarantees a fast surface cure even in the presence of the UV absorber, and allows for the most cost efficient curing.

While the efficient curing of stabilized clear lacquers is thus possible using the BAPO/α-hydroxyketone photoinitiator package, it had to be proven that the performance of the coatings thus obtained is at least equal to that of a conventional automotive coating during outdoor exposure. In fact, the presence of photoinitiator fragments in a cured coating had for a long time been considered as inherently reducing the lifetime of the coating.

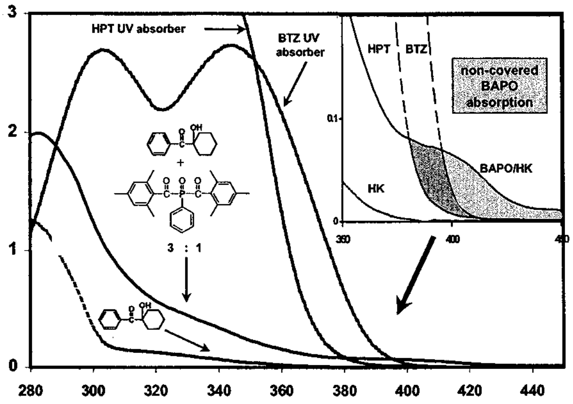


Figure 4. UV spectra of UV absorbers and photoinitiators.
Inset: Absorption of a BAPO/α-hydroxyketone blend not covered by the UV absorbers.

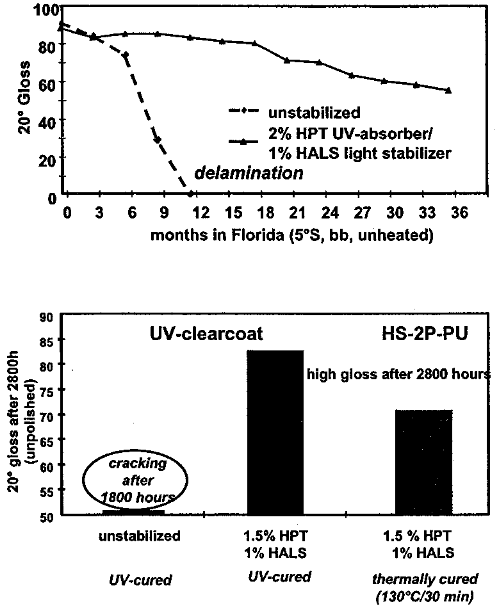


Figure 5. Top: Outdoor exposure of a UV-curable clear coat over a silver metallic basecoat. Down: Xenon weatherometer (CAM 180) exposure of a high-solid two-pack polyurethane lacquer and a UV-cured clearcoat.

Extensive testing, both under artificial weathering conditions and upon Florida exposure, showed that the light cured clear coating is at least as stable as a conventional lacquer (Figure 5). Thus, the optimized combination of light stabilizers with photoinitiators gives smart additive packages that allow for automotive coatings to combine an efficient radiation curing with excellent outdoor performance.[8] The design of such packages in combination with recent developments in the curing equipment, which allows regular irradiation even of complex three-dimensional shapes, will result in a fast acceptance of the highly productive and ecological radiation curing technology in automotive applications.

Further work on BAPO photoinitiators is necessary in view of an even better performance and new applications. Key to a successful optimization of a photoinitiator is the understanding of the photochemistry and the initiation step. A versatile tool for studying these processes is time-resolved electron spin resonance (TR-EPR). In contrast to time-resolved laser flash spectroscopy, this method can not only follow the build-up and decay of radicals over time, but also provides plenty of structural information on the species observed. The fact that phosphorous centered radicals exhibit a large hyperfine coupling (hfc) in the range of 20-40 mT further facilitates the interpretation of the spectra, since the two resonance lines of the phosphorous doublet are well separated from the signal of the benzoyl radical and resonances of products obtained by the addition of the initiating radicals to acrylic double bonds.

It is well known that the magnitude of the phosphorous hfc reflects the hybridization of the phosphorous radical. A lower coupling constant is synonymous to a flatter configuration and thus to a higher p-character of the orbital carrying the radical electron. This electronic effect translates into a lower reactivity of the radical in addition reactions.[9] In fact, when the addition rate constants of different phosphinoyl radicals are plotted against the corresponding hfc values, a reasonable correlation is observed (Figure 6). Strong deviations are only found for radicals that exhibit strong steric hindrance, which overwhelms the electronic effect. Since the hfc is easily extracted from EPR spectra, even without time resolution, a versatile tool for structure-reactivity correlations is at hand.

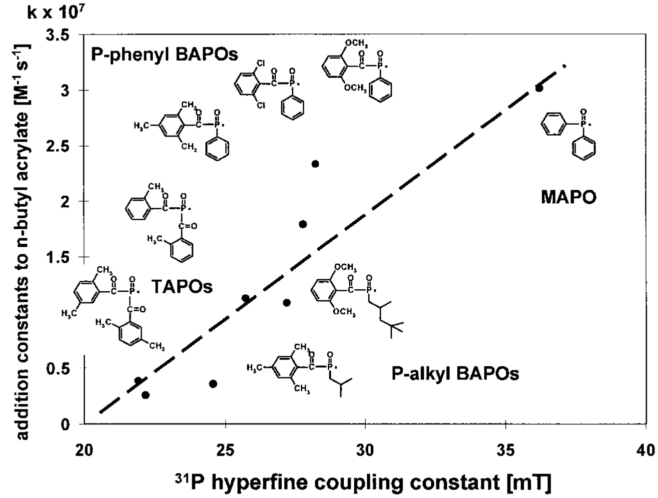
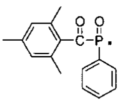
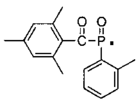
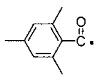


Figure 6. Addition rate constants k_{add} as function of the phosphorus hyperfine coupling constants.

TR-EPR spectra contain information that principally allows the quantitative determination of addition rate constants. However, quantitative treatment of EPR spectra is not trivial, since the signal intensities are not proportional to the radical concentration due to the occurrence of polarization effects that strongly influence the signal intensity.

Table 1. Addition rate constants of phosphinoyl and benzoyl radicals simultaneously determined by TR-ESR line-width analysis.

			
k_{add} [$Mol^{-1}s^{-1}$]	$7.65 \cdot 10^6$	$0.80 \cdot 10^6$	$0.52 \cdot 10^6$
k_{add} [$Mol^{-1}s^{-1}$][1]	$8.67 \cdot 10^6$	$0.92 \cdot 10^6$	not available

[1] Measured by laser flash spectroscopy.[10]

Careful analysis of TR-EPR spectra revealed that the line-width of the EPR resonance lines is not influenced by these polarization effects, but only depends on the concentration of the monomer. Hence EPR line-width is a useful parameter for the quantitative determination of radical to monomer addition rate constants.[10] Comparison of the results obtained by this method with rate constants measured by laser flash spectroscopy [10][11] showed a good agreement, thus proving the utility of the line-width method. A clear advantage of the latter is the possibility to observe the phosphinoyl and the benzoyl radical simultaneously, allowing the concomitant determination of both addition rate constants from one spectrum (Table 1). This is not possible by laser flash spectroscopy, since the weak absorption of the benzoyl radical is completely covered by the much more intense signal of the phosphinoyl radical. Thus, this new method for the analysis of TR-EPR spectra is a powerful tool for the further optimization of BAPO photoinitiators.

A photoinitiator designed for color filter resist applications

Flat panel displays are nowadays in widespread use in many devices such as notebook computers. The displays include numerous high-tech optical and electronic elements, such as a back light system with the necessary optical tools, a glass plate carrying thin film transistors for the pixel electrodes, a layer containing switchable liquid crystals, and optical compensators and polarizers.

One important part in this build-up is the color filter, which consists of transparent pixels of the three basic colors blue, red and green embedded in a black matrix frame. Three pixels of each basic color, which can be individually addressed via the pixel electrodes, make up for one color dot on the screen.

The colored pixels as well as the black matrix are produced by photolithography techniques using blue, red and green pigmented resist materials as well as a black matrix resist. Photolithography is thus a key technology in the fabrication of flat display panels, and the availability of suitable photoinitiators is of outmost importance.

As for all applications aimed at a high production rates, a high photospeed, measured as photosensitivity, i.e. the minimum irradiation dose required to achieve full cure, is essential for a photoinitiator to be used in color filter resists.

In addition, several requirements that are specific for color filter applications have to be fulfilled. Since the features of the color pixel are relatively large in size, the negative resist technology using light in the near UV/visible range can be used without affecting the resolution. This wavelength range is also most suitable for the curing of pigmented formulations, which are sufficiently transparent in the near UV region. A mask aligner equipment using the i- (365 nm), h- (405 nm) and/or g-line (436 nm) for exposure is commonly used. In contrast to other resist applications, the irradiation is performed by proximity exposure. As a consequence, the resist surface is exposed to atmospheric oxygen during the irradiation step and therefore low oxygen sensitivity of the photoinitiator is an important requirement.

Most important for a color filter resist, however, is a cured material that has the highest transparency possible in the wavelength range of the corresponding color. This is extremely important for the performance of the color filter, since it allows to achieve the exact color shade and a high brilliancy. For the photoinitiator for use in the blue color filter resist, this requirement means that no photoproducts absorbing above 400 nm must be formed upon irradiation, and no discoloration by the photoinitiator or its photoproducts must occur during the thermal treatment in the postbake step, which may require temperatures in the range of 220°C for up to 30 minutes.

Suitably substituted 4-(2-arylethenyl)-2,6-trichloromethyl-1,3,5-triazine derivatives have been frequently used in this application besides α-aminoketone derivatives such as 1-(4-morpholinophenyl)-2-dimethylamino-2-benzyl-butan-1-one. The trichloromethyl triazine derivatives are efficient photoinitiators, which have strong absorption maxima in the near UV that can easily be adjusted by a suitable substitution pattern. However, when used in a blue color filter resists, the red-shifted absorbance and the discoloration observed upon thermal exposure result in resist materials that are not optimal regarding transparency. Furthermore, since chlorine ions are produced upon irradiation, hydrogen chloride can be formed as by-product that possibly corrodes the processing equipment and may be harmful in a liquid crystal display. α-Aminoketone photoinitiators are less reactive and have also a tendency for the build-up of some yellowing.

In view of the drawbacks of the photoinitiators in use, new compounds that could overcome these limitations were investigated. Evaluation of several substance classes revealed the most interesting results for *O*-acyl-α-oximino ketones. The photoreactivity of these compounds is well known and has for the first time been noted by Werner,[12] who observed the daylight-induced decomposition of *O*-benzoyl benziloxime during his studies on the Beckman rearrangement. The use of *O*-acylated oximinoketones as photoinitiators has for the first time been reported at the very beginning of industrial photopolymerization,[13] and one compound was commercially available during some time.[14] However, due to the reported low shelf life stability[15] and the introduction of more efficient photoinitiators, such as benzil dimethylketal or α-hydroxy ketone derivatives, for coating applications, interest in this substance class faded and little use was reported for more than twenty years. It was only recently that some new interest in its photoinitiator reactivity and fragmentation mechanism was manifested by two independent studies.[16][17]

The compounds reported in the literature did not meet the requirements for color filter resist applications. Firstly, a more red-shifted absorption was required in order to allow the curing of the pigmented resist material. The introduction of a phenylthio substituent in the *para*-position of the aryl ketooxime structure provided the necessary shift of the main absorption band into the near UV range. An alkyl substituent at oxime group is known to result in a higher reactivity than an aryl group.[16][17] By the introduction of an alkyl substituent of a higher chain length in combination with a benzoyl ester on the oxime, the best thermal stability was achieved which is sufficient to withstand the thermal exposure during the postbake step. In parallel, the introduction of the relatively large substituent in all positions is an additional advantage, since it increases the molecular weight and thus reduces the volatility of the compound. This is important in color filter applications, since the prolonged exposure of the resist formulation to elevated temperatures during the predrying process can result in undesirable loss of photoinitiator. Thus, 1-[4-(phenylthio)phenyl]-1,2-octandione-2-*O*-benzoyloxime (Figure 7) was identified as the most versatile compound for the target application.[18][19]

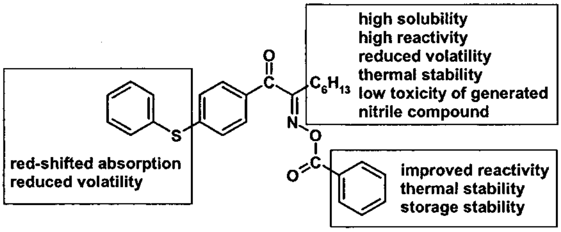


Figure 7. 1-[4-(Phenylthio)phenyl]-1,2-octandione-2-*O*-benzoyloxime.

The absorption spectrum of the new photoinitiator is compared to those of a typical trichloromethyl triazine and an α-aminoketone in Figure 8. The absorption maximum of the new initiator is in the same range as that of the α-aminoketone, but less red shifted than the triazine spectrum which has an absorption band tailing up to 450 nm.

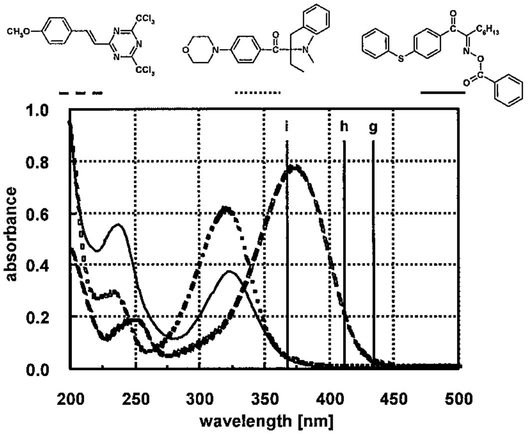


Figure 8. Absorption spectra of 1-[4-(phenylthio)phenyl]-1,2-octandione-2-*O*-benzoyloxime, 4-[2-(4-meth-oxyphenyl)-ethenyl]-2,6-trichloromethyl-1,3,5-triazine and 1-(4-morpholinophenyl)-2-dimethylamino-2-benzyl-butan-1-one (0.001% by weight in acetonitrile).

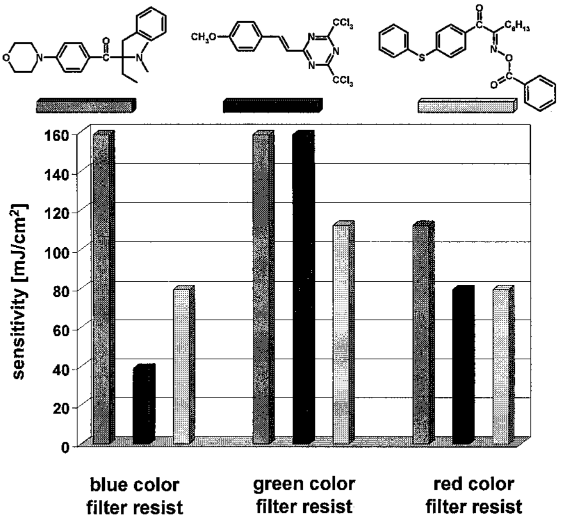


Figure 9. Photosensitivity of 1-[4-(phenylthio)phenyl]-1,2-octandione-2-*O*-benzoyloxime in a blue, green and red color filter resist formulation.

Not surprisingly, the latter compound shows the highest photosensitivity in the blue resist formulation (Figure 9). This is due to the fact that the blue pigment has a strong absorption around 350-400 nm, which considerably reduces the light available for the α-aminoketone or oxime ester photoinitiators absorbing in the same region. In contrast, the red-shifted absorption of the trichloromethyl triazine extends into longer wavelengths, which are less shielded by the pigment.

Despite this less favorable absorption, the new compound provides an excellent performance in the blue resist formulation and exceeds the α-amino ketone photoinitiator albeit a lower absorbance at the same weight concentration. This finding can be attributed to both specific features of the photochemistry of oxime esters and the conditions under which the curing process occurs. The resist formulation is in fact a tack-free material even before crosslinking by the photopolymerization process takes place. Thus, the photochemistry and the curing reaction occur in a medium of much higher viscosity than in a coating application. After the photoinduced cleavage of the N-O-bond, the carbonyloxy radical formed undergoes a very fast loss of carbon dioxide (Figure 10). The extrusion of this stable molecule prevents the recombination of the primary radicals, a deactivation pathway that becomes important for α-cleavage type photoinitiators in formulations of high viscosity, and which lowers the efficiency of these initiators under the specific conditions. Similarly, the fast fragmentation of the iminyl radical to give a nitrile and a benzoyl radical additionally inhibits the recombination reaction and further contributes to the high reactivity of the new photoinitiator, since the benzoyl radical thus formed is known to be a very efficient initiating radical.

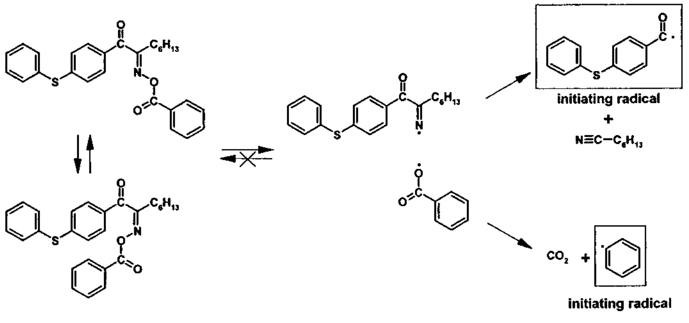


Figure 10. Photochemistry of 1-[4-(phenylthio)phenyl]-1,2-octandione-2-*O*-benzoyloxime.

On the other hand, oxime esters are known to undergo upon irradiation (E/Z)-isomerization on the oxime moiety, a process that wastes excitation energy and thus lowers the initiating efficiency of these compounds (Figure 10).[17] This process is assumed to be of less importance in a viscous resist formulation due to the more restricted mobility, and hence the initiation efficiency should be higher under these conditions. Thus, the viscous medium of a color filter resist is expected to favor an efficient photocleavage of the new initiator, while it hampers that of an α-cleavage photoinitiators. This interpretation is supported by the fact that the new compound is less efficient than α-amino ketones when used as a photoinitiator for blue printing inks, which have a much lower viscosity than the resist material.

The photosensitivity obtained with the oxime ester photoinitiator in green and red color filter resists (Figure 9) and even in the black matrix formulation is also excellent. Green and red pigments have a considerable absorption around 400 nm, which reduces the absorption efficiency of the trichloromethyl triazine photoinitiator as compared to the blue pigmented formulation. In these applications, the new initiator hence equals or outperforms the trichloromethyl triazine compound due to its highly efficient photochemistry. In these formulations, a further improvement can be achieved, when a sensitizer, such as a thioxanthone or 4,4'-diethylaminobenzophenone, is added. A similar boost in photosensitivity is also observed in the blue resist formulation. However, the yellowing induced by these sensitizers prevents their use in a blue color filter resist application.

The improved transparency obtained with the new photoinitiator is in fact the outstanding advantage in the blue color filter resist.[19] This effect is shown in Figure 11, where the transparency of a blue color filter resist formulation is shown before and after irradiation and after a postbake at 220°C for 30 minutes. While the red shifted absorption of the triazine photoinitiator is an advantage for the curing process, it is clearly a disadvantage for the performance of the resist material after curing. The transmittance in the critical region between 400 and 440 nm is lower before irradiation due to the inherent absorption of the photoinitiator. While a weak photobleaching is observed during the irradiation step, a significant increase in the absorbance occurs between 430 and 500 nm during the harsh postbake conditions. This is in contrast to the performance of the oxime ester photoinitiator. A formulation containing this photoinitiator shows practically no decrease in transmission during the whole fabrication process. The significantly improved color quality in combination with an excellent photosensitivity is thus the major reason that led to the fast acceptance of the new initiator in this application.

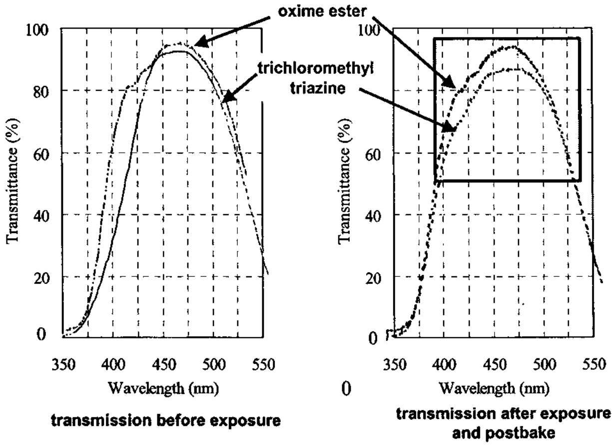


Figure 11. Comparison of transmittance between 400 and 500 nm of the resist material before exposure and after exposure (200 mj/cm^2) and postbake treatment (220°C, 30 min).

This compound is thus a typical example for a high performance photoinitiator that has been tailor-made to meet the specific requirements of a target application. While the conventional α-cleavage type photoinitiators remain the workhorses for a wide variety of well-established application, such highly specialized photoinitiators are more and more required for use in advanced materials and applications.

Photolatent amines: A new opportunity in radiation curing

Radical and, to a lesser extent, cationic photoinitiators are well established and will be further developed to tailor-made compounds and optimized multipurpose blends. However, other crosslinking reactions than radical polymerization or acid-catalyzed polymerization and polycondensation are well known in the manufacturing of coatings. Examples are crosslinking processes catalyzed by bases such as amines, which are widespread used in conventional, mostly two-pack applications. These curing procedures have hardly been transformed into light-triggered processes, despite the obvious advantages of such reaction conditions providing features such as an extended pot life, cure on demand or the possibility for imagewise exposure.

An analysis of the literature revealed one important reason for this finding: Only a few types of photolatent amines have been reported so far. The photoactivity of these compounds is mostly based on the known methodology of photolatent protective groups for amines used in synthetic chemistry, which produces primary or secondary amines upon irradiation.[20-25]

While these compounds have been used as photodeblockable crosslinkers for coating materials[26][27] or in tailor-made resist formulations,[28-30] most examples suffer from a drawback that prevents a more general use: primary or secondary amines are in fact not very strong bases and rather good nucleophiles. These properties are useful for crosslinking processes, e.g. based on the Michael addition of a photoreleased amine to an activated double bond.[31] However, they do not allow for a reaction that is truly catalyzed by the photochemically generated amine. Hence, in most reported systems, one photon is required per crosslink formed, compared to several hundred or more crosslinks obtained per photon in a radical photopolymerization. Curing processes based on photolatent primary amines are thus not energy efficient and therefore of little interest for most industrial applications where the economy of the process is an important issue.

Tertiary amines are generally more suitable as catalysts. However, reports on the photogeneration of tertiary amines are rare, and only very few systems useful for radiation curing are known.[32-35] Furthermore, the most efficient base catalysts used in conventional crosslinking reactions are strong amines such as guanidine or bicyclic amidine bases. These compounds are e.g. known to be efficient catalysts for the Michael reaction, while conventional tertiary amines are hardly active under these conditions.[36] Only two patents reporting a photocatalyst that was claimed to produce a guanidine or amidine base have been reported.[37][38]

In view of this lack of suitable photolatent amines, it was attractive to set out for the development of new compounds that can produce strong, non-nucleophilic amines useful as true catalysts.

In compounds such as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,8-diazabicyclo[5.4.0]undec-5-ene (DBU), the bicyclic amidine functionality possessing a strong conjugative interaction between the two nitrogen atoms is responsible for the high basicity. Therefore this structural feature had to be suitably modified in the latent form in order to reduce the basicity. Decoupling of the conjugative interaction by the reduction of the carbon-nitrogen double bond is a possible approach to this goal, since it transforms the amidine into amine functionalities. Thus, the 1,5-diazabicyclo[4.3.0]nonane structure was selected as the latent form of the amine.

Evaluation of a series of photodeblockable groups revealed that benzylic substituents on nitrogen(5) are easily accessible and efficient blocking groups that are removed upon irradiation with UV light.[39] The absorption spectra of the compounds can be tuned to different wavelengths by the introduction of suitable substitution patterns. Furthermore, detailed investigations revealed that the photocleavage reaction can be sensitized by substituted benzophenone or thioxanthone derivatives, allowing to use light in the near UV/visible range for the curing process. In view of these findings, 5-benzyl-1,5-diazabicyclo[4.3.0]nonane was selected as the most versatile compound for a variety of applications.

Although the photochemistry of this compound has not yet been elucidated in detail, it is supposed that homolytic cleavage of the benzylic carbon-nitrogen bond is the photoreaction taking place after excitation of the molecule (Figure 12). The primary radical pair formed can undergo a disproportionation reaction, which via hydrogen abstraction adjacent to the amino-centered radical results in the formation of the amidine double bond and thus in the release of DBN. This hypothesis is supported by the finding that upon irradiation of the benzylated 1,5-diazabicyclo[4.3.0]nonane derivatives deuterated at the 6-position, the deuterium atom was found scrambled on the benzyl part.

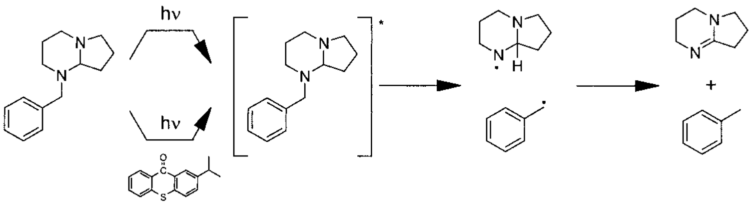


Figure 12. Proposed mechanism for the photoinduced release of DBN from 1,5-diazabicyclo[4.3.0]nonane.

The efficiency of the photolatent DBN derivative as a curing catalyst was probed in different applications. Automotive refinish clear lacquers, consisting of a polyisocyanate and a polyol-based component, are an example of high industrial interest. Due to the reactivity of the alcohol with the isocyanate groups, which results in slow gelation even at room temperature, such lacquers have to be used as two-pack systems. After mixing of the components, the "ready-to-use" formulation has a limited pot life. The "working window", i.e. the time during which the formulation can be applied on the carrier material, is usually defined as the time to doubling of the initial viscosity. For a polyisocyanate/polyol formulation this working window is usually in the range of several hours.

Addition of a catalyst, such as dibutyltin dilaurate (DBTL) or an amidine base to the formulation results in a considerable acceleration of the crosslinking process. At the same time, however, the catalyst reduces the pot life of the "ready-to-use" formulation, and the "working window" is thus shortened to less than two hours (Figure 13). Hence the design of these lacquers has always to compromise between a long working window, required for the convenience of an efficient application, and a fast cure speed desirable for the economy of a high through-put.

The use of the photolatent DBN catalyst does not allow formulating a one-pack system either, since the inherent reactivity of the two components is maintained. However, the working window of the ready-to-use formulation, both with and without 2-isopropyl thioxanthone added as a sensitizer, is considerably extended to a full working day. These values match or even exceed that of the uncatalyzed formulation, thereby considerably increasing the ease of handling (Figure 13).

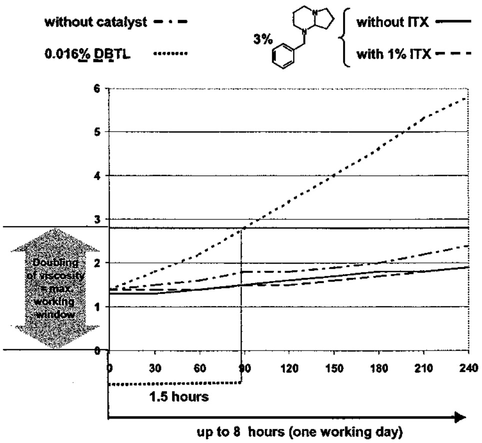


Figure 13. Pot life of "ready-to-use" polyurethane formulations containing no catalyst, DBTL catalysts and the photolatent DBN catalyst with and without ITX.

Curing was performed using artificial daylight provided by fluorescent lamps. These conditions were selected in order to simulate processing conditions that can be applied in a body shop. In fact, only radiation sources emitting no harmful UV radiation of shorter wavelengths that can be used without the need for protective measures are acceptable for such an application. For a sufficient response to light of these wavelengths, 2-isopropyl thioxanthone was added as a sensitizer.

The reactivity of the formulations was determined using a drying recorder from Byk-Gardner that allows following the curing process of a coating applied on a glass plate over a time of 24 hours. The application results show that, using the new photolatent DBN derivative in combination with the thioxanthone sensitizer, curing is achieved almost within the same time as with conventional non-blocked catalysts (Figure 14). The advantages of the radiation curing strategy is the combination of a long working window, which allows for a more efficient application, with a curing process that can be initiated "on demand" by irradiation and proceeds with a speed similar to that of a system using a conventional catalyst.

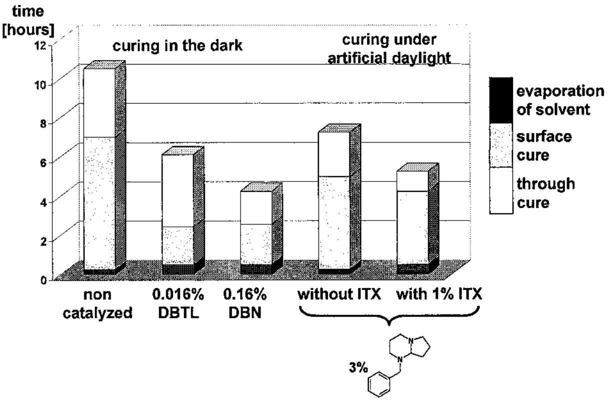


Figure 14. Drying time of a two-pack polyurethane formulation (a) without catalyst, (b) with a conventional catalyst (DBTL) and (c) the photolatent base with and without 2-isopropyl-thioxanthone.

It should be mentioned that the photolatent DBU was used in higher concentrations than the non-blocked catalysts. This is necessary due to the fact that the photolatent catalyst is not completely deprotected upon irradiation, so that the concentration of the active catalyst is always smaller than the applied concentration of the latent catalyst.

Cure speed for these formulations is measured in hours and not in seconds or less as usual in radiation curing using radically polymerizing systems. This is not due to the efficiency of the photoinitiator, but to the chemistry of the crosslinking process, which is inherently much slower than a radically curing system. Hence photopolymerization enters into applications with new application profiles, where a high cure speeds is not an issue. Nevertheless, the use of the radiation curing technology brings considerable advantages to the end user in view of optimizing the efficiency and economy of the process.

A variety of other crosslinking processes are also available to radiation curing using the photolatent amidine. A non-comprehensive selection of possible formulations is shown in Figure 15. Crosslinking mechanisms typically are base-catalyzed additions of various types of nucleophiles on acrylates in a Michael reaction, but also the base-catalyzed homopolymerization of epoxides. Hence these new photolatent bases are designed for opening new application areas for radiation curing. Currently in an early phase, this novel technology will be further expanded by the development of more reactive photobases and suitable resin systems.

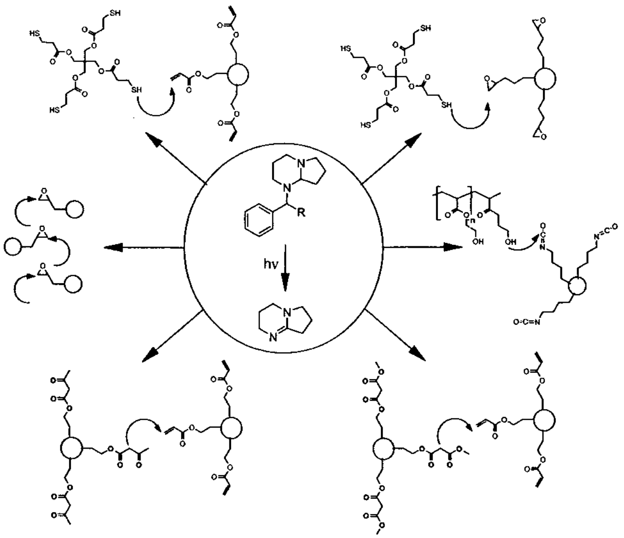


Figure 15. Resin types curable by the photolatent base technology.

Conclusions

While efficient photoinitiators are available for many well-established applications in radiation curing, new developments in photoinitiators are aimed at overcoming existing limitations and opening novel opportunities for this technology. In some cases smart combinations of photoinitiators with other additives can provide new solutions, while the development of tailor-made new compounds is necessary to meet the demanding requirements of other applications. Finally, the introduction of novel classes of photoinitiators strives for the extension of the radiation curing technology into new resin chemistries and thus opens the possibility for applications that were not available before.

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