

Photolatent Tertiary Amines – A New Technology Platform for Radiation Curing

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Abstract: The lack of efficient photolatent amine catalysts has so far prevented the use of base-catalyzed formulations in radiation curing. The development of two new photocatalysts which release 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or tertiary amines upon irradiation opens new opportunities for this technology. Photolatent DBN is used for crosslinking processes where strong bases are required as catalyst, such as coatings crosslinked via the Michael addition reaction, while a tertiary amine efficiently catalyzes reactions involving more acidic compounds. A UV-A curable car refinish clear lacquer has been developed as a first example of a commercial formulation using a photolatent amine as catalyst.

Keywords: Radiation curing · Photolatent DBN · Photolatent tertiary amine · UV curable coatings · UV curable car refinish lacquer

1. Introduction

Nowadays radiation curing is a well-established technology that has enabled an increasingly large number of industrial uses. Driving forces for this development are the unique features of this process, which allow the realization of considerable economic and ecological advantages. UV-curable lacquers are so-called 'high-solid' formulations containing a large amount of high molecular oligomers and reactive diluents which become part of the polymer network after curing, but no or only very little amount of solvents. The correspondingly low emission of volatile organic compounds (VOC) makes this technology compatible with increasingly stringent legal regulations with regard to air pollution. Use of light as the trigger gives full control over the curing process, combining a long shelf

life of the ready-to-use formulation when stored in the dark with a rapid 'cure on demand' when exposed to light. This feature translates into easy handling, little loss of materials and a high productivity, thereby reducing the manufacturing costs. Since no heat is applied, curing on temperature-sensitive materials is possible. Besides these processing advantages, the superior quality of the finished products regarding properties such as gloss, durability or abrasion resistance, or the high resolution achieved in imaging applications, are other advantages of outmost importance for industrial use.

Since the very beginning of radiation curing, most applications are based on materials cured by radical polymerization.^[1] An advantage of radical polymerization is the very rapid reaction rate, which allows the crosslinking process to be performed within fractions of a second at ambient temperature. Accordingly a wide variety of oligomers and reactive diluents as well as radical photoinitiators are commercially available,^[2] allowing the formulation of coatings, inks or resist materials with a broad range of properties.

Cationic photopolymerization of epoxides, oxetanes or vinyl ethers using sulfonium and iodonium salts photoinitiators^[3] is another radiation curing technology offering advantages such as no oxygen inhibition or improved adhesion on various substrates. Due to some limitations, cationic photopolymerization has found less use than radical UV curing.

Although efficient systems curing by radical or cationic polymerization are avail-

able, an important step for the further dissemination of this environmentally friendly technology is the opening of new opportunities for radiation curing. In the following account, we report on the development of a new radiation curing technology platform based on photolatent amines.

2. Photolatent Amines in Radiation Curing: State of the Art

Base-catalyzed crosslinking processes are widely used for conventional coating applications, such as the base-catalyzed addition reaction of polyols to polyisocyanate providing polyurethanes,^[4] ring-opening of epoxides by nucleophiles such as amines, thiols, carboxylates or anhydrides,^[5] or Michael reaction of acetoacetate or malonate groups containing polyesters with acrylate derivatives in the presence of a strong base.^[6,7] These systems have to be handled as two-component formulations that must be applied within a short time after mixing, which makes their use unpractical for many applications.

Despite the attractive properties of base-catalyzed formulations, they have so far not yet been intensively exploited for radiation curing. However, the use of light as trigger for the curing process can be expected to add extra value for many applications, such as the development of one-component formulations with a long shelf life, or, alternatively, two-component systems that can be more easily processed due to an extended working window. In both cases rapid cur-

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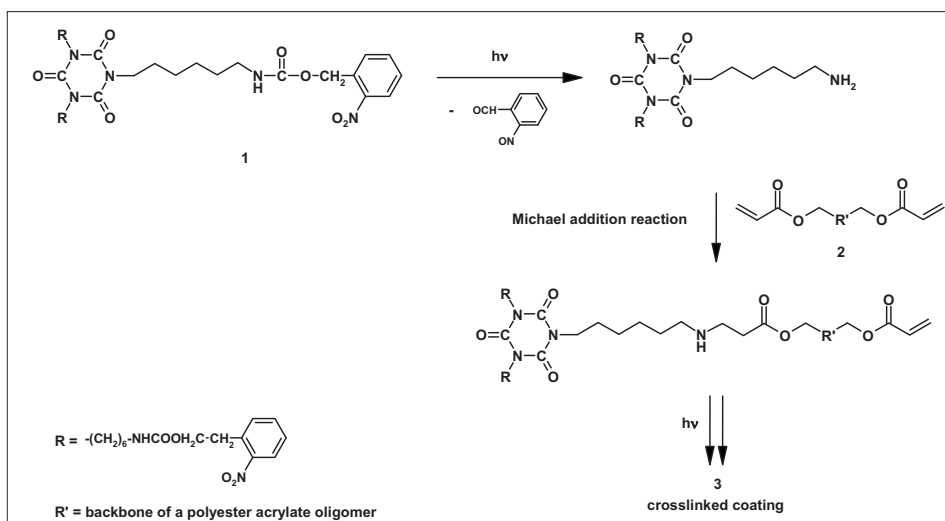
ing at low temperatures would occur after exposure to light.

The marginal use of radiation curing for base-catalyzed formulations is mainly due to the lack of suitable photolabile amine catalysts. The use of photochemically removable protective groups for amines and amino acids is well known in the domains of synthesis and biochemistry (often referred to as 'caged amines' in this context^[8]). A few photolabile amines developed in this field have actually been exploited for use for radiation curing. For example, *ortho*-nitrobenzyl carbamates^[9] or 3,5-dimethoxy- α,α -dimethylbenzyl carbamates^[10] were investigated for resist applications, while O-acyloximes were studied as precursors for benzyl amine.^[11]

A feature of these systems is that primary, or possibly secondary amines are formed upon irradiation. These amines undergo efficient addition or condensation reactions with a variety of functional groups. An example is the trifunctional *ortho*-nitrobenzyl carbamate **1** that is easily prepared from a triisocyanate precursor. Irradiation of this compound in a coating formulation containing an acrylate oligomer **2** results in the rapid Michael addition of the photogenerated primary amino groups with the acrylic double bonds producing a crosslinked polymer network **3** (Scheme 1).^[12]

Coating formulations are of low viscosity in order to facilitate application on the substrate, and consequently a relatively large number of crosslinks has to be formed in order to achieve complete cure. In the crosslinking process shown in Scheme 1, one photon is used for the formation of one or possibly two crosslinks. A curing process that requires almost stoichiometric amounts of photons is of low efficiency regarding the applied light energy. This is in contrast to formulations curing by radical polymerization, where the radicals formed upon photochemical cleavage of the initiator induce the polymerization of a large number of acrylic double bonds in a thermal chain reaction. This 'thermal amplification' of the photochemical event allows complete cure to be achieved with a low dose of light energy, making radiation curing attractive as an industrial application of photochemistry.

Thus photolabile primary or secondary amines are not useful for coating applications. Tertiary amines that can act as catalysts in thermal crosslinking reactions are much more attractive for this use. The photogeneration of tertiary amines is, however, considerably more difficult than that of primary or secondary amines, and only a very limited number of photolabile tertiary amines has been reported in the literature. Introduction of a photolabile substituent on the nitrogen of a tertiary amine results in the formation of ammonium salt derivatives,^[13] which are usually of low solubility



Scheme 1. UV curable coating formulation based on a photolabile primary amine crosslinker and a polyester acrylate binder

Table 1. Amines suitable as catalysts for crosslinking reactions (pK_a in aqueous solution^[4,17])

trialkylamines	guanidines	amidines	
trimethylamine	1,1,3,3-tetramethylguanidine	1,5-diazabicyclo[4.3.0]non-5-ene	1,8-diazabicyclo[5.4.0]undec-5-ene
$\text{pK}_a = 9.8$	$\text{pK}_a = 13.6$	$\text{pK}_a = 12.7$	$\text{pK}_a = 12.5$

and thermal stability in most formulations. A photolabile tertiary amine useful in technical applications should therefore preferentially be a neutral compound. Only a few compounds of this type have been reported so far.^[14]

3. Development of New Photolabile Tertiary Amines for Radiation Curing

The efficiency and scope of application of a tertiary amine catalyst strongly depends on its chemical structure. For instance, the basicity and steric hindrance of tertiary amines are considered to be the two main factors influencing the rate of isocyanate reactions.^[15] Simple tertiary amines are sufficiently basic for deprotonation of compounds of high acidity and thus *e.g.* capable of catalyzing the crosslinking of epoxides with carboxylates.^[16] Amidine-type bases are by 3–4 orders of magnitude more basic than tertiary amines (Table 1) and therefore useful as catalysts for reactions such as the Michael addition of weakly acidic acetoacetate or malonate derivatives to acrylic double bonds. This reaction is ef-

ficiently catalyzed by tetramethyl guanidine (TMG), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,5-diazabicyclo[5.4.0]-undec-5-ene (DBU), but not by simple tertiary amines.^[6]

It is therefore important to develop photolabile amines that release an active catalyst with the right combination of basicity and steric constraints meeting the requirements of the crosslinking reaction. To this end, two novel concepts for the blocking and photogeneration of tertiary amines have been developed and will be discussed in the following.

3.1. Latency Control via Photo-induced Oxidative Introduction of an Amidine Double Bond: A Photolabile Strong Amine Base

The exceptionally high basicity of amidine-type tertiary amines is attributed to the conjugative interaction of the two nitrogen atoms *via* the carbon–nitrogen double bond. Elimination of this double bond results in structures with isolated amine groups possessing a correspondingly lower basicity. Such compounds can be used as latent precursors for the much stronger amidine base, if it is possible to

introduce the double bond by a photoinitiated oxidation reaction.

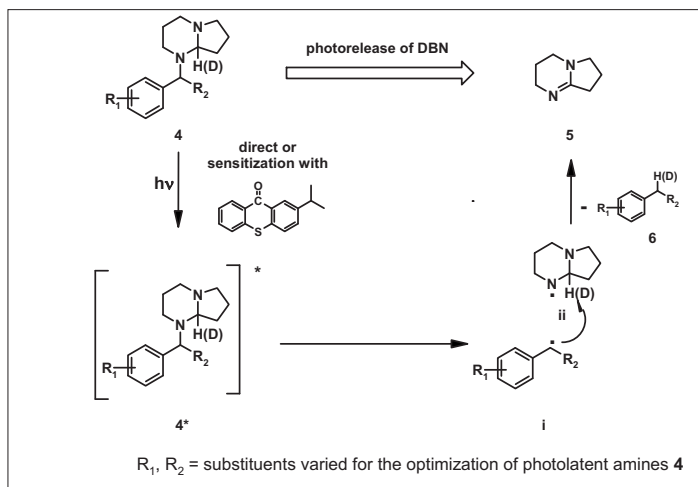
Compounds with this property are obtained, when the reduced form of amidine derivatives such as DBN or DBU is alkylated with suitably substituted allyl^[18] or benzyl groups (compounds **4**, Scheme 2).^[19]

Although the photochemistry of these compounds has not yet been fully elucidated, cleavage of the benzylic carbon–nitrogen bond is assumed to be the primary photochemical reaction. Both the resonance-stabilized benzyl radical **i** and the N-centered radical **ii** do not efficiently add to acrylic double bonds,^[20] and compounds **4** can therefore not be used as radical photoinitiators. This is important when these photolabile amines are used as catalysts for Michael addition reactions, where the formulation contains an acrylated oligomer that must not undergo radical homopolymerization.

Instead, the primary radicals undergo hydrogen transfer reactions which, in the case of the aminyl radical **ii**, results in the introduction of the amidine double bond of DBN (Scheme 2). This mechanistic hypothesis is supported by results obtained with a derivative of **4** deuterated in the 6-position of the 1,5-diazabicyclo[4.3.0]nonane moiety, where partial transfer of deuterium into the benzyl derivative **6** was found. Furthermore, ¹H-CIDNP spectra obtained upon irradiation of a solution containing **4** with a medium pressure mercury lamp show a resonance with emission polarization at 2.3 ppm, indicative for a benzylic proton formed from a radical precursor.^[21]

The absorption spectra of the photolabile bases **4** can be tuned over a wide range by changing the substitution pattern on the benzylic moiety. The two derivatives selected in view of their excellent overall performance for further development have an absorption that is limited to the short UV. However, sensitization of **4** by compounds such as substituted benzophenone or thioxanthone derivatives is possible and allows an easy tuning of the absorption of the initiating system to the requirements of the application in terms of cure speed and yellowing (Fig. 1).

The photoinduced transformation of **4** into **5** induces a significant increase of basicity from $pK_a = 8.96$ ^[22] for **4** to $pK_a = 13.41$ ^[22] for DBN **5**. The novel photolabile base **4** has been evaluated for the curing of a variety of different resins. Examples are formulations crosslinked *via* a Michael-type addition of a CH-acidic moiety to a acrylic double bonds, which have been known for a long time to give coatings of excellent quality.^[4,6,7] Upon addition of DBN to such a formulation, a tack-free coating is obtained in less than one hour, however at the expense of a sufficient potlife of the ready-to-use mixture.



Scheme 2. Photorelease of DBN from N-benzylated precursors **4**

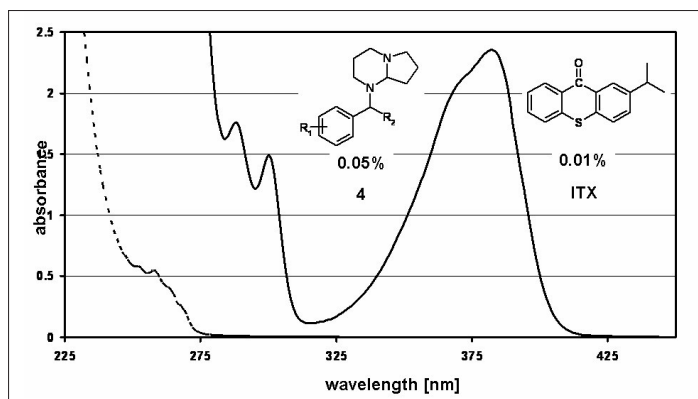
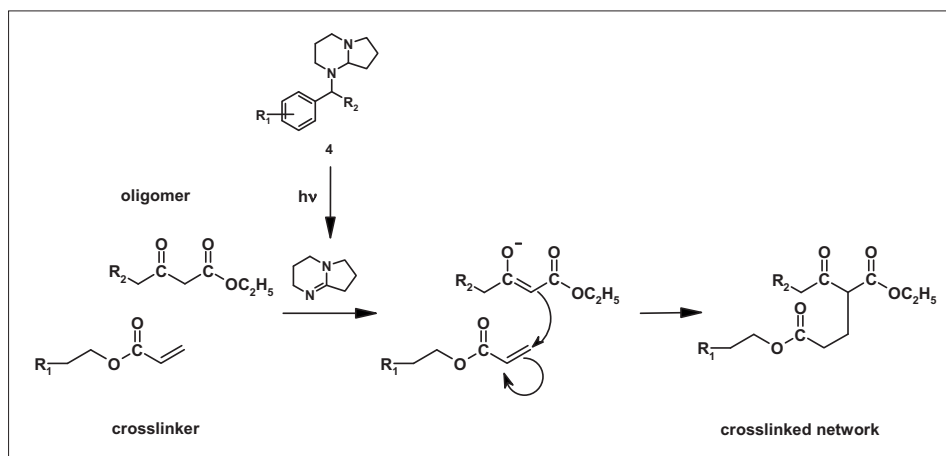


Fig. 1. Absorption spectra of photolabile amine **4** and ITX



Scheme 3. Crosslinking *via* Michael addition photoinduced by photolabile amine **4**

The use of the photolabile DBN **4** allows the development of one-pack Michael formulations with a shelf life in the dark of up to nine months (Scheme 3). In fact, the basicity of the latent amine is not sufficient to catalyze the Michael addition reaction.^[6] Only when DBN is generated upon irradiation, crosslinking is initiated and leads to tack-free coatings within a short time. The

progress of this reaction can be followed by IR spectroscopy, which allows the decrease of the acrylate double bonds to be monitored over time by measuring the absorbance of the C=C stretching vibration at 1410 cm^{-1} . By this technique it could be demonstrated that, using 2-isopropyl thioxanthone (ITX) as sensitizer, approximately 80% of the acrylic double bonds have reacted within

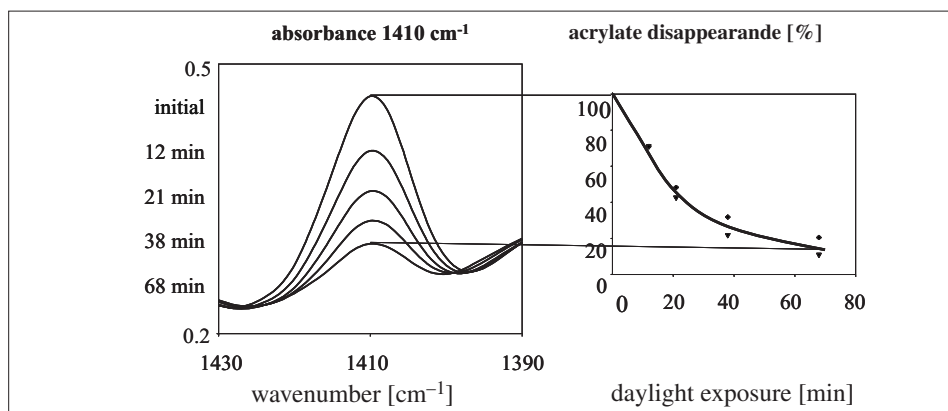


Fig. 2. Acrylate conversion in the photoinduced Michael reaction (monitoring by IR spectroscopy)

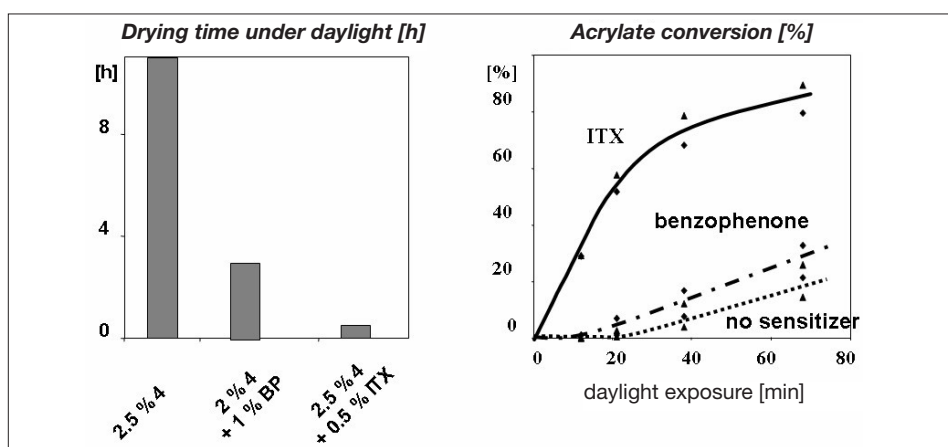


Fig. 3. Comparison of drying time measured with the drying recorder from Byk-Gardner and acrylate conversion determined by IR spectroscopy.

one hour upon irradiation with artificial daylight, which simulates constant natural light conditions and has an accordingly low light intensity (Fig. 2).

For further testing, the formulation was applied with a slit coater on 30 cm long glass plates. Curing of the samples was monitored using a drying recorder from Byk-Gardner, where a needle is moving during 24 h with constant speed over the whole length of the coated substrate. Evaluation of the trace in the coating allows an assessment of the curing process. The formation of a tack-free surface with no further dust uptake is considered crucial in practical applications, even if the crosslinking is going on in the dark for several hours until full through-cure is achieved. Thus, the time to achieve a tack-free surface was used as measure for the performance of the photolatent amine.

As shown in Fig. 3, the acrylate conversion observed by IR correlates well with the drying time of the coating as measured by the Byk recorder. Since the photolatent base absorbs light only in the UV-B, no tack free coating is obtained even after eight hours of irradiation with artificial daylight. Very little conversion of acrylate double bonds is observed by IR analysis under the same

conditions. Cure speed is significantly improved by the addition of benzophenone or ITX as sensitizers. Using ITX, a tack-free coating is obtained at room temperature in less than one hour, with a concomitant conversion of approximately 80% of the acrylic double bonds according to IR analysis.

In an extended evaluation it was shown that other crosslinking reactions can also be catalyzed by the latent catalysts **4**. These include the Michael addition of thiols to acrylates, addition of alcohols to isocyanates to give polyurethane resins, the curing of epoxide/thiol based formulations, or the base-catalyzed polycondensation of alkoxysilane-terminated organic polymers in the presence of humidity.^[23]

3.2. Latency Control via Photo-induced Steric Release: A Photolatent Tertiary Amine for a UV-A Curable Car Refinish Clear Coat

While radiation curing is typically performed by trained operators using specialized equipment in a factory, new applications are currently emerging, which require curing under simple working conditions by non-specialized workers. A typical example is car refinishing, where a repair lacquer has

to be cured in the body shop environment. If radiation curing is to be used for such an application, the curing process must be performed using simple low-cost equipment under conditions that are safe for the work force. This means use of harmless UV-A bulbs of weak power, mounted on a simple rack or used as hand-held lamps at variable distances from the coating to be cured. In the case of formulations curing by radical polymerization, the correspondingly low light intensity applied to the coating would result in insufficient cure due to oxygen inhibition. A curing mechanism that is not inhibited by oxygen is thus advantageous for curing under these conditions.

Clear coats based on a polythiourethane network have excellent properties for use as topcoats in car refinish applications. These coatings are used as two-component systems, consisting of a thiol functionalized binder and a polyisocyanate crosslinker. While the two components undergo only a very slow crosslinking in the absence of a catalyst, the reaction becomes very rapid in the presence of tertiary amines. A fully cured coating is obtained within a few minutes, a very attractive feature in view of high productivity. However, the concomitant very short pot life of the ready-to-spray formulation prevented practical use so far. An acceptable balance between sufficient pot life and high cure speed can only be achieved when a latent amine catalyst is used that can be activated on demand by irradiation with UV-A light.

The thiol/isocyanate addition reaction is catalyzed by simple tertiary amines and does not require the high basicity of amidine-type bases. A former study on the use of α -amino ketones as radical photoinitiators in resist applications had revealed that the amine-containing photocleavage products obtained reduce the temperature required for the thermal post-baking step by approximately 70 °C.^[24] This effect has been attributed to an increased catalytic activity of the amine in the cleavage product. The low efficiency before photocleavage is due to steric shielding of the amine by the bulky substituents in the α -position and to electronic interactions between the carbonyl group and the nitrogen atom. Upon irradiation, the compound undergoes an efficient Norrish Type I cleavage reaction, which removes the benzoyl substituent from the α -position. In the absence of acrylic double bonds, the α -aminoalkyl radical formed is further transformed *via* hydrogen abstraction into a tertiary amine of higher basicity and less steric shielding than the starting material.

This light-triggered change in catalytic efficiency was thus exploited for the curing of the thiol isocyanate lacquer. The radical photoinitiator **7** used in the resist application as well as other α -amino ketone radical

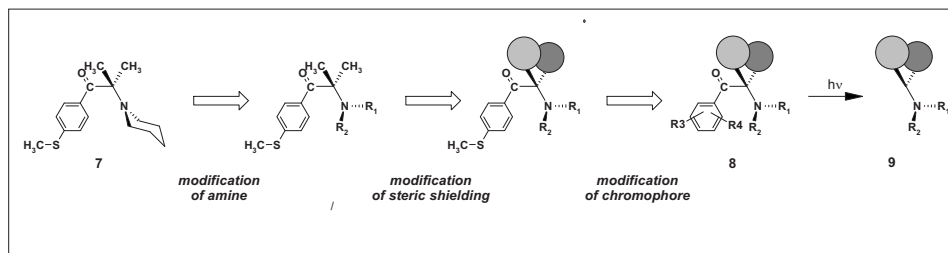
Scheme 4. Development of the photolatent base **8** from the α -amino ketone photoinitiator **7**

Table 2. Shelf-life stability of a polythiol/polyisocyanate formulation in the presence of amine catalysts

catalyst	potlife	comment
none	36 h	double viscosity
0.33% 8 (latent)	18 h	double viscosity
1% 8 (latent)	4 h	double viscosity
0.15% 9 (active)	<2 min	gelled ^a

^aTime to double viscosity could not be determined due to very rapid gelling.

photoinitiators^[1] turned out not to be suitable for this application. Only a moderate cure speed was achieved with some derivatives, while others imparted considerable yellowing to the cured coating, which is not acceptable for a clear coat application.

In search of an efficient photolatent base catalyst, a wide range of new α -amino ketones were therefore evaluated. As expected, the curing efficiency strongly depends on the structure and basicity of the amine formed. Compounds possessing other types of amino groups than **7** were found to be more efficient as latent base catalysts, and modifications introducing larger substituents at the α -carbon atom further improved the pot life stability of the formulation.

Most challenging was the design of a chromophore that allowed activation with long wavelengths UV-A light without imparting yellowing to the cured coating. α -Aminoketone photoinitiators are known to give considerable yellowing and are thus used as radical photoinitiators only in application where this is no issue. Careful modifications of the chromophore finally led to the best compromise between high initiation efficiency under near UV irradiation and a very low yellowing. Combination of all optimized structural features provided a new photolatent tertiary amine **8** that is suitable for use in the two-component car refinish lacquer (Scheme 4).

As for the photolatent DBN derivative **4**, both the latent and the active form of the photocatalyst **8** are tertiary amines, albeit of significantly different catalytic efficiency. This is illustrated by measurements of the pot life of a ready-to-use model formulation containing either the latent **8** or the active amine **9**. The active tertiary amine catalyst

9 was independently synthesized for these studies and is identical to the amine produced by the photochemical reaction. Pot life is defined as the time to doubling of the viscosity of the coating, which is the range of viscosity in which the lacquer can be applied to the substrate using standard application techniques. The results are shown in Table 2.

The two-component formulation without any catalyst has an intrinsic stability of 36 h at room temperature. If 0.33% of the photolatent amine **8** is added, shelf-life stability is reduced by a factor of two, while a further increase of the latent catalyst concentration to 1% decreases the shelf life to 4 h. This is proof for the weak, but measurable catalytic activity of the latent amine. In the car refinish application, this is a versatile feature, since it guarantees for sufficient dark cure even in regions on the three-dimensional car body that were not sufficiently irradiated.

If only 0.15% of the active amine catalyst **9** is added, the formulation gelled com-

pletely in less than 2 min at room temperature, showing the very high efficiency of amine **9**. A change from 18 h for **8** to less than 2 min pot life for **9** corresponds in fact to an increase of the catalytic efficiency by a factor of more than 500.

By varying the concentration of the photolatent base, an optimum balance between shelf life, dark curing and curing after irradiation can be achieved. Thus, a two-component car refinish lacquer could be developed which, after mixing of all components, gives a ready-to-spray formulation with a guaranteed pot life of 8 h. This corresponds to one working day and is by far sufficient for this application, where handling of two component formulations is an established procedure. Thus, with the exception of simple UV-A radiation sources as shown in Fig. 4, existing body shop equipment can be used for this application.^[25]

Besides the outstanding quality of the cured lacquer, main advantages of the new car refinish formulation are the low VOC values meeting the most stringent legal requirements, and a significant increase in productivity. In fact, a comparison of a conventional two-component car refinish lacquer with the new system showed a reduction in cure time from 30 min for thermally curing lacquers (including heating up to 60 °C and cooling down to room temperature after curing) to only 5 min for the radiation cured lacquer.^[25] Not surprisingly, this new technology has been well accepted by the end users and is the first example of the use of a photolatent base catalyst in a commercial application.^[26]

4. Conclusions

The development of photoinitiators that release tertiary amines or amidine-type catalysts has resulted in a first commercial application using a photobase in a car refinish lacquer. Since a wide variety of base curable resins are known, new applications using this technology are expected to be developed in a near future. The availability of suitable photolatent bases producing ap-

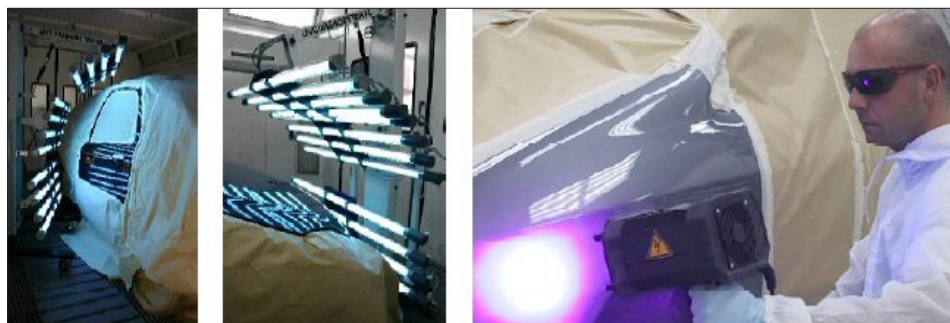


Fig. 4. Curing of the car refinish lacquer (AUTOCLEAR[®], Akzo Nobel Sikkens) in a body shop: a) and b) Mobile UV-A irradiation sources on a rack; c) Hand-held UV-A lamp (Source: Akzo Nobel Car Refinishes)

appropriate catalysts for different crosslinking mechanisms is an important condition for success. Research on photolatent bases is therefore continuing, aiming at providing complementary catalysts that can further expand the scope of this technology.

The characteristics of the curing process and the properties of the cured coatings are different from that of established formulations curing by radical or cationic polymerization. Thus, this new technology platform is complementary to the existing UV-curing processes and opens new possibilities for radiation curing.

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