The recently developed photolatent base catalysts comprise a new cure-on-demand technology, which combine light-curing capabilities with conventional (non-acrylate based) resin technologies. The key to their success is that once photoactivated, the photolatent bases undergo a $pK_a$ jump to produce \textit{in situ} base catalysts with higher potency and activity. The results are better cure efficiencies, wider process latitude and, ultimately, lower costs to manufacture adhesives.

In this paper we review how the photolatent base catalysts can be used for a number of adhesives, but with particular attention to urethane-based adhesives. It was found that the balance of pot-life enhancement and end-property development can be optimized by selecting the appropriate photolatent base and its photosensitizer.

**Introduction**

Reactive adhesive systems are well established in many industrial, technical and even do-it-yourself applications. The beauty of a reactive adhesive system lies in the fact that the actual adhesive application can be made with relatively low molecular weight materials, thus providing good processing abilities and good wetting of porous materials. With the subsequent chemical reaction (i.e., the curing of the adhesive) extremely high bond strength and performance can be achieved depending on the adhesive system. Over the past 80 years,\textsuperscript{1} various reactive adhesive technologies have been developed and commercialized; however, each technology has its advantages and restrictions. The technology of a photogenerated base catalyst provides a new dimension to reactive adhesive systems. It is designed to overcome certain limitations of conventional reactive technologies and, in some cases, can improve manufacturing economics and provide ecologic advantages.

The technology of light-induced radical curing of adhesives, which is typically based on acrylate monomers and oligomers, is widely recognized as being able to offer considerable economic and ecological advantages. These include the fast transformation of 100% solid liquid formulations (which are stable when stored in the dark under appropriate conditions) into highly crosslinked polymer networks, thus allowing for rapid further processing of the bonded structures. Due to the fast reaction of free radicals, this type of UV-curable adhesive is typically limited to applications in which the two bonding partners are in contact with each other and at least one substrate is transparent to the appropriate activation wavelength. An exception to this common processing scenario
would be UV-cured, pressure-sensitive adhesive layers or use as UV-curing potting agents or sealing materials, particularly in the electronics industry. In both cases the uncured adhesive layer is directly irradiated to form the solid self-adhesive material to the bonded structure.

As a result, this technology is used in a wide variety of well-established adhesive, assembly and coating applications. Correspondingly, a wide range of raw materials—including resin components and photoinitiators— are available for radically curing formulations, and new materials continue to be developed. Despite these advantages, the use of this technology cannot be extended into additional end uses. These limitations are inherently linked to the free-radical, crosslinking mechanism of acrylates (e.g., oxygen inhibition, shrinkage).

To overcome these limitations, light-induced cationic polymerization of adhesives, typically using cycloaliphatic-diepoxide resins, are especially well suited. The cationic curing process is initiated with suitable cationic photoinitiators (photoacid generators) to generate Lewis or Brönsted acids after UV light exposure. In contrast to the free-radical curing systems, cationic-curing adhesives have the advantage that they are not subject to oxygen inhibition. Consequently, they continue to cure after irradiation and show considerably less shrinkage. A further consequence is that the adhesive can be irradiated before joining the two substrates, thus eliminating the need for transparency of one substrate. Although these systems constitute an alternative approach in light curing, they are still not as widely used as the acrylate-based systems. The reason is due to the smaller choice of raw materials, including photoinitiators, the high price and limited availability of high-performance resin compounds, and the curing inhibition by alkali/bases coming from substrates, pigments, fillers and other additives.

The crosslinking of suitable formulations by base-catalyzed polymerization and polyaddition reactions is well known and established in many conventional adhesive applications with polyurethane and epoxy adhesives. Other available reactions include further ring-opening of epoxide groups by nucleophilic moieties such as amines, thiols, carboxylates or anhydride, and the Michael reaction of acetoacetate or malonate groups containing polyesters with acrylate oligomers. Curing of epoxides by imidazole derivatives is an example of a base-catalyzed homopolymerization reaction. With all these systems, the addition of a base catalyst results in the immediate initiation of the crosslinking process, which limits its use to two-part adhesive systems with a defined system depending on open time or pot life.

Photolatent base catalysts could be an attractive possibility to improve control over the curing process of adhesives while maintaining cure speed and the excellent properties of the cured article. Thermally blocked amine catalysts are known, but require a relatively high de-blocking temperature in order to maintain sufficient stability of the uncured material (e.g., during storage and transportation). The use of UV light to trigger the release of a base catalyst is a very attractive way to achieve optimum control of the application and the curing process.

**Base Catalysis and Adhesives**

Base-catalyzed reaction mechanisms that might be considered for adhesive curing applications are shown in Figure 1. In industrial applications, the most commonly used are the polyl/isocyanate and the epoxy/thiol mechanism.
between long open time and a fast curing process becomes very important. The manufacture of film or foil laminates requires a certain working window of the adhesive in order to maintain consistent coating parameters such as viscosity, coating weight and coating appearance. A short open time has the advantage of fast curing in the final structure but at the same time bears the danger for a step viscosity increase of the adhesive in the supply lines and in the coating reservoir. Besides the above mentioned difficulties it can also lead to clogging or buildup of crosslinked adhesive in the coating line—especially in case of unexpected line stops or general downtime. A longer open time avoids these issues but also extends the time to reach sufficient bond strength for further converting of the laminate respective of its end use. With food packaging laminates, health and safety compliance also has to be considered and reactive components need to be fully incorporated into the crosslinked structure or transformed into non-migrating species. In large assembly applications, similar issues occur which lead either to unequal bonding performance (too short open time) or excessive curing or quarantine time.

The technology of a photogenerated base catalyst can overcome some of the aforementioned contradictions and offers considerable economic and ecological advantages.

**Development of a Strong Photolatent Base Catalyst (PLB)**

Many base-catalyzed crosslinking reactions require amines with well-balanced basicity and nucleophilicity properties. These factors and steric hindrance strongly affect the efficiency of amine bases in isocyanate reactions. The addition of weakly acidic acetoacetate or malonate derivatives to acrylic double bonds in a Michael addition reaction is efficiently catalyzed by amine bases such as tetramethyl guanidine, 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. These amidine-type bases are three to four orders of magnitude more basic than tertiary amines (Table 1). Thus, it was considered attractive to develop photolatent amines that produce an active catalyst providing the properties of an amidine base.

A challenge in the design of a photolatent tertiary amine is the fact that the introduction of a photocleavable substituent on nitrogen results in the formation of ammonium salts. This concept has been used for most photolatent tertiary amines reported so far, but results in compounds with a correspondingly limited solubility and stability in formulations of low polarity and, thus, is of limited practical use.

The amidine structure allows for an attractive alternative approach to photolatent structures. Since the exceptionally high basicity of these compounds is attributed to the conjugative interaction of the two

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**Table 1**

<table>
<thead>
<tr>
<th>trialkylamines</th>
<th>guanidines</th>
<th>amidines</th>
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</thead>
<tbody>
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<td>trimethylamine</td>
<td>1,1,3,3-tetramethylguanidine</td>
<td>1,5-diazabicyclo-[4.3.0]-non-5-ene</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>pKₐ = 12.5</td>
</tr>
</tbody>
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**Figure 2**

**Concept of photolatent DBN**

- **Strong amine base, pKₐ = 13.5**
- **Amine base, pKₐ = 9**
- **PLA**
- **Photo-induced removal of PRG with concomitant oxidation**
- **Elimination of amidine double bond**
- **Introduction of photo-removable group (PRG)**
nitrogen atoms via the carbon-nitrogen double bond, elimination of this double bond results in structures with isolated secondary and tertiary amine groups, possessing a correspondingly lower basicity. Such amines 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 using a suitable photoremovable group (PRG). An advantage is that the photolatent amines thus obtained are neutral organic compounds. This concept is illustrated in Figure 2 for photolatent 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) which has been mainly used in this study.

In this concept, both the latent PLB and the active form DBN of the catalyst are amines, albeit of very different activity. The pKₐ values of both the photolatent and the active amine of the structure PLA were calculated¹⁵ and provided a ΔpKₐ of approximately 4.5 units between the latent amine PLA (pKₐ = 8.96) and DBN (pKₐ = 13.41). The fact that the basicity of the photolatent form is similar to tertiary amines suggests that it might show some activity in reactions that can be catalyzed by simple tertiary amines.

Extensive investigations on different PRGs revealed that compounds with this property are obtained when suitable substituted allyl or benzyl groups are used.¹⁶ The photochemically induced introduction of the amidine conjugation can be rationalized by a photo-induced cleavage of the allylic or benzylic carbon-nitrogen bond (illustrated for a benzyl substituted photolatent amine in Figure 3). The radicals formed in this reaction are not efficient initiating species for radical reactions, since they are highly stabilized allyl or benzyl-type and non-reactive nitrogen-centered radicals.¹⁸

These radicals preferentially undergo hydrogen abstraction reactions, which preferentially occur from tertiary carbon atom in the amine cleavage product activated by the two amino substituents. This hydrogen transfer results in the regeneration of the amidine double bond in DBN. This hypothesis is supported by ¹H-NMR-CIDNP studies showing an emission type signal for the benzylic protons in the PRG group after the cleavage reaction, thereby supporting a radical precursor. Scrambling of deuterium from the aminal position in PLA to the PRG is also in agreement with the proposed mechanism.

As expected, various properties of PLA can be optimized without affecting the active amine catalyst formed by a suitable design of the PRG in order to meet different requirements. As an example, the absorption spectra of these types of photolatent bases can be tuned over a wide range by

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**Figure 3**

Photo release of DBN from N-benzylated precursors

**Figure 4**

Absorption spectra of PLB-1 through PLB-4 (continuous lines) and ITX (dotted line)
changes in the substitution pattern on the benzylic moiety. The absorption spectra of four derivatives (PLB-1 through PLB-4) are shown in Figure 4.

For practical applications, use of compounds PLB-1 or PLB-2 (possessing an absorption that is limited to the UV-B spectral region) was found to be most useful both in view of the application properties and the synthetic access. The spectral sensitivity of the photolatent amine can easily be extended to longer wavelengths by the use of a sensitizer. In the course of an extensive evaluation, several types of aromatic ketones, such as substituted benzophenone derivatives or thioxanthones, were found to be most useful as sensitizers. The combination of both photobase generators with suitable sensitizers thus allows an easy tuning of the absorption characteristics of the initiating system to the requirements of the target application (Figure 4).

Experiments and Results

In order to show and confirm the basic concept of photolatent base catalysts, a series of exemplary adhesive systems have been formulated, modified and tested. Focus was laid on basic incorporation of the photolatent base, pot-life stability and development of bond strength over time.

Photolatent base PLB-1, in combination with benzophenone as photosensitizer, was incorporated into a solvent-borne 2K-PUR laminating adhesive formula. To assess the efficiency of the photolatent DBN, the adhesive was used to laminate a 36-micron polyester film against a 30-micron biaxially-oriented polypropylene (BOPP) film and the bond strength was determined in the T-peel mode. The reference and the modified adhesives were wet coated to the polyester film, dried and the resulting dry film thickness of approximately 20 micron was laminated to BOPP film using a ChemInstruments bench-top laminator. Subsequently, the laminate was exposed to the UV radiation (IST-Metz, 2 medium-pressure mercury lamps with 100 W/cm at 5 m/min belt speed) through the BOPP side and the bond strength was measured with a tensometer after different times.

The results in Figure 5 show that the system with the photogenerated DBN catalyst builds quicker cohesive strength and already changes failure
mode to adhesion failure after six hours. The adhesion continues to increase and leads to tearing of the polyester after 48 hours (material failure). Even after 48 hours, the non-catalyzed reference system still exhibits peel strength similar to the photocatalyzed system after six hours.

As described earlier, viscosity stability during the coating process is of high importance to the adhesive user. Figure 6 shows the viscosity development over time of a solution-based, 2-K polyurethane adhesive. The non-modified reference shows stable coating viscosity over at least 72 hours when stored in a dark environment. Modification with PLB-3 can maintain similar pot-life stability, whereas the catalytic effect of PLB-1 leads to a four times higher viscosity within the same time period.

In a further series, the bond strength development in a thiol/isocyanate adhesive system was observed. The photolatent tertiary amine PLB-4 was incorporated into the adhesive at 0.4%, applied to and laminated with a 75-micron BOPP film. Bond strength in the T-Peel mode of the UV-irradiated sample (two medium-pressure mercury lamps with 100 W/cm at 5 m/min belt speed) was compared to the non-irradiated and the reference laminate. Figure 7 shows the highly catalytic tertiary amine with which the maximum bond strength is reached almost immediately (approximately 12 minutes). In the latent, non-irradiated form, PLB-2 shows slower catalytic behavior and maximum strength is reached after eight hours. Within the same period of time, the non-catalyzed system only reaches approximately 55% of the maximum strength.

The pKₐ of the released base catalyst determines which reactions can be considered for evaluation. With a large pKₐ difference between the photolatent and the free base form, typically a storage stable system with fast reaction is feasible. A system with a small pKₐ difference, on the other hand, has the advantage in that it might then catalyze the reaction also in dark or in shadow areas; however, its stability/reactivity ratio has to be carefully evaluated and is only suitable for two-component systems. Figure 8 illustrates the pKₐ relation between the photolatent and the photo-released base.

**Conclusion**

The development of new photolatent base catalysts that release amidine-type catalysts open new opportunities for radiation curing of conventional adhesive systems, allowing the light-triggered-on-demand curing of formulations catalyzed by strong DBN-type bases. Different application modes are possible, depending on the involved cross-linking...
chemistry as well as the adhesive application and bonding process. Components that react even in the absence of a catalyst must be used as two-component formulations, but significantly improved balance between a long pot life and fast curing provide considerable advantages for the end-user in the form of easier handling, fewer losses and a higher throughput.

Resin systems that do not react in the absence of a base catalyst can be handled as one-part systems, with an extended shelf life up to several months in the dark while providing fast cure-on-demand after light exposure. The use of photosensitizers has proven to be a useful tool for the optimization of the light sensitivity to light curing conditions.

The careful selection of a photolatent base producing an appropriate catalyst is crucial for efficient curing. Research and application work on photolatent bases is continuing, aiming at further expanding the scope of this new technology platform that is complementary to the existing UV-curing processes while providing new possibilities for light curing.

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