Novel chemistry for UV coatings

Photolatent base system optimises performance for refinish clearcoats.
Kurt Dietliker, Katharina Misteli, Tunja Jung, Patrik Contich, Johannes Benkhoft, Eugene Sitzmann.
Radiation curing offers clear economic and environmental advantages. It combines low VOC formulations and low processing temperatures with fast cure speed. Nevertheless, current systems have some well-understood limitations. The development of a new photolabile base UV curing system is described, which is particularly well suited for use in the difficult application area of refinish clearcoats. Most radiation curable coatings today are based on photoinitiated free-radical polymerisation. A wide variety of resin components and photoinitiators allows the formulation of photocurable coatings for a broad spectrum of applications. The technology does, however, have significant limitations, notably 'oxygen inhibition', which retards surface cure, and high shrinkage upon curing, which limits adhesion in some applications. Photoinduced cationic polymerisation has also been exploited. It eliminates oxygen inhibition and offers improved adhesion. Some inherent limitations and higher costs have, however, restricted the use of this technology.

Amine catalysts can also be used in UV curing
Very few photoinitiated curing processes using base-catalysed crosslinking reactions are known [1]. The photoactive compounds used rely on photolabile blocking groups for primary or secondary amines, developed as protective groups in organic synthesis [2]. A few coating applications have been reported using generated amine as crosslinkers in reactions with epoxides [3-5] or isocyanates [4, 6]. A stoichiometric quantity of photons is required in relation to the number of crosslinks to be formed, making the energy efficiency of this curing process rather low. Due to their low basicity and nucleophilicity, primary and secondary amines are less efficient as catalysts than tertiary amines. However, the photogeneration of tertiary amines is considerably more difficult. The introduction of additional photolabile substituents on the amine results in the formation of ammonium salts, while transformation of one substrate into a photolabile group gives a precursor of a secondary amine (Figure 1). Most examples of photolabile tertiary amines reported in the literature are thus salts [7-12], with a correspondingly limited solubility and low chemical stability. One of the few examples of a neutral photolabile tertiary amine is a tetramethyl guanidine precursor [13].

Vehicle finishing poses many problems for UV curing
Radiation curing offers considerable advantages for the automotive industry. However, this technology has not yet found widespread use due to some major challenges:
- Automotive topcoats are applied to complex 3-D car bodies, resulting in the formation of shadowed areas which are not fully cured.
- The distance between the lamp and the coating is larger and more variable than in conventional UV applications. The resulting low light intensity gives rise to strong oxygen inhibition in free-radical coatings.
- The long-term exterior durability of an automotive topcoat requires an optimised stabiliser package, but UV absorbers can compete with the photoinitiator for the incident light making through cure more difficult. Residual photoinitiator and unreacted unsaturated groups in the cured coating were believed to contribute to faster deterioration of UV-cured lacquers under outdoor weathering conditions. Over recent years, much work has been devoted to overcoming these difficulties. The radiation curing of OEM applications has proved to be feasible, if an optimised combination of resins, photoinitiators, stabiliser package and curing equipment is used. Features such as low VOC values, fast drying at ambient temperature which increases productivity and avoids problems with heat sensitive parts, are also very attractive for car refinish applications. Consequently, a UV curable refinish primer has recently been introduced [15].

Refinish clearcoats are especially hard to cure
The development of a radiation-curable clear topcoat for car refinish applications is a greater challenge. Such a material must offer performance similar to an OEM topcoat but also be processable under the working conditions of a bodyshop. The technology must rely on simple, low cost, mobile and flexible equipment instead of the sophisticated equipment developed for OEM use. Radiation sources are limited to lamps emitting in the UV-A/visible range which do not require extensive protective equipment for the worker. This low light intensity increases oxygen inhibition in free radical curing formulations. Consequently, a different curing mechanism is preferable. 'Dark cure' must also occur in areas that are not sufficiently irradiated, preferably at room temperature since the application of heat to a fully equipped car would offset many of the advantages of UV.

Thiol-isocyanate chemistry avoids oxygen inhibition
An efficient solution to these problems requires a new resin and initiator chemistry. A suitable resin chemistry has recently been developed [16], based on a two-component system crosslinked by the addition of thiol groups to isocyanate functionalities. After mixing, the formulation undergoes slow crosslinking in the dark even in the absence of a catalyst. In the presence of an amine catalyst, full cure is achieved within a few minutes at room temperature. This is very attractive in terms of high productivity, but makes handling and application very difficult.

Only a photolabile photoinitiator, allowing the catalyst to be activated after application, can provide the required control over the curing process. This paper reports on the development of the catalyst, while a later paper will focus on the use and performance of the formulation in car refinish applications [16].

Photolatent amine must meet several requirements
The processing and application conditions already discussed define the requirements for the photolatent amine:
- Activation must occur under UV-A light;
- UV absorbers should not affect the efficiency of the initiator;
- Efficient photoreaction is needed to give fast curing at low light intensities;
- The amine produced must be an efficient catalyst for the crosslinking reaction;
- The catalyst must not cause yellowing after cure or upon long-term exposure.

In contrast to conventional photoinitiators, the latent form of the catalyst need not be completely inactive, since moderate catalytic activity improves dark cure. Hence a compound possessing an optimum balance of reactivity in the latent and non-latent forms had to be developed.

Two main factors affect amine efficiency

The efficiency of an amine catalyst depends primarily on its basicity and steric hindrance [17]. Two novel concepts for the blocking of tertiary amines by photolabile groups have recently been developed: photoinduced oxidative introduction of an amidine double bond and photoinduced steric release [14].

The first concept has been proved to be useful for compounds liberating strong bases such as DBN or DBU [18]. Photoinduced steric release has been used for tertiary amines to catalyse the ring-opening addition of carboxylates to epoxides [19].

An initial evaluation revealed that tertiary alkyl amines are the most suitable catalysts for thiol-isocyanate crosslinking. Therefore, research was focused on developing photolatent tertiary amines which utilise the steric release concept.

Steric uncoupling changes molecular configuration

New compounds were developed, based on α-amine acetoephonene structures [20, 21] possessing a highly crowded quaternary carbon atom in the α-position to the nitrogen atom. Calculations performed on one compound, 1-(4-methylthio-phenyl)-2-methyl-2-(morpholin-4-yl)-1-propanone (PLA-1), suggest a folded conformation in which the activity of the amine is hindered by the shielding effect of the benzoyl moiety [19].

The benzoyl group can be removed by an efficient Norrish Type I cleavage that produces an α-aminoalkyl radical [22]. Since the formulation does not contain radically polymerisable groups, stabilisation of the radical occurs via hydrogen abstraction, which is greatly facilitated by the thiol functionalities in the resin.

This photoreaction efficiently generates a new tertiary amine that is sterically much less crowded. Calculations for the amine thus formed from PLA-1 (designated A-1) indicate a stretched conformation in which the nitrogen atom is accessible for reactions (Figure 2). Thus, this transformation meets all the requirements of the steric release concept.

Oxygen inhibition is not an issue since no radical chain reaction is involved in the curing process.

Efficiency and yellowing effects studied

Several classes of photolatent amines were evaluated. Their curing efficiency strongly depends on the structure and basicity of the amine produced. For example, amine A-1 formed from PLA-1 efficiently catalyses the carboxylate-epoxide reaction [19], but is a poor catalyst for the crosslinking investigated here.

Compounds possessing other types of amino groups and a higher steric hindrance were found to be more efficient (Figure 3). The absorption of the substituted benzoyl group allows for efficient activation with UV-A light, and fast curing of the formulation upon irradiation was observed.

Most α-amine ketone photoinitiators impart yellowing to the cured coating. Hence another challenge was the development of a photolatent moiety that gives no yellowing. Finally, suitable modifications to the chromophore allowed the combination of high initiation efficiency under near-UV irradiation with very low yellowing after cure in the structure designated PLA-2 (Figure 3).

Factors controlling cure speed are identified

Both the latent amine (PLA-2) and its active form (A-2) are tertiary amines and thus catalysts for the crosslinking reaction. The catalytic efficiency of the two compounds is, however, different and modulated by the steric and electronic environment of the nitrogen atom. This effect is illustrated by potlife studies on ready-to-use polythiol/polyisocyanate formulations containing either the latent or the active catalyst (Table 1). Potlife is defined as the time to doubling of the initial viscosity.

The stability in the absence of a catalyst of 36 hours at room temperature is reduced by a factor of two upon addition of 0.33% PLA-2. Increasing its concentration to 1% further decreases potlife to four hours. This shows that the latent amine has a weak but measurable catalytic activity.

To confirm the nature of the photocatalytic activation process, the active catalyst A-2 was synthesised independently. If only 0.15% of this compound is added to the formulation, shelf life is drastically reduced to less than 2 minutes. This change closely resembles the light-triggered activation of the catalyst.

Under irradiation conditions, conversion of the latent into the active form is not complete. When 0.33% catalyst is used and undergoes photoactivation with 50% efficiency, the concentration of the active catalyst after irradiation would be in the range of 0.15%. The accompanying change from 18 hours to less than 2 minutes potlife corresponds to an increase of catalytic efficiency by a factor of more than 500.

This is in good agreement with experimental data, where a cure time of three minutes was determined for a formulation containing 0.8% latent catalyst under a Philips “TL 40W/03” fluorescent lamp emitting UV-A light. An optimum balance of shelf life, dark cure and cure speed can thus be achieved by optimising the initiator concentration.

Amine properties must be matched to curing reaction

To provide a better understanding of the catalytic efficiency, basicity (pKa) values of the amine in its latent and active forms were calculated [23] (Table 2). The difference in basicity of A-2 vs. A-1 indicates that absorption by thiol functionalities in the resin.

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New chemistry has clear advantages in refinishing

A new photolatent catalyst has been developed, whose efficiency can be switched from a low to a highly reactive state under the influence of light. A two-pack formulation can be produced with extended pot life, very fast cure upon irradiation, and ultimately full cure even in shadowed areas.

The sensitivity of the photolatent catalyst to UV-A light and the absence of oxygen inhibition allows curing to be carried out by low intensity lamps that do not emit harmful radiation and can be easily used in a bodyshop environment.

REFERENCES

Results at a glance
- A new type of photolatent amine catalyst has been developed, whose efficiency can be switched from a low to a highly reactive state under the influence of UV-A light.
- This catalyst can be used in a two-pack thiol/isocyanate radiation curable formulation, which does not suffer from the ‘oxygen inhibition’ found in free-radical type coatings.
- A formulation can be produced with extended pot life, low yellowing, very fast cure upon irradiation, and ultimately full cure even in shadowed areas.
- These features allow refinish clearcoats to be formulated which cure under low intensity lamps that do not emit harmful radiation and can be easily used in a bodyshop environment.

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This paper is one of two on a novel UV-A curable car refinish clearcoat. Part II will be published in the November 2005 issue of European Coatings Journal.
Figure 1: Modification of a tertiary amine by a photoremovable group.

Figure 2: Photoinduced steric release provides latency in PLA-1.

Figure 3: Development of the new photolatent amine PLA-2.
Table 1: Shelf-life stability of a polythiol/polyisocyanate formulation in the presence of amine catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Potlife</th>
<th>Comment</th>
</tr>
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<tbody>
<tr>
<td>none</td>
<td>36 hours</td>
<td>doubled viscosity</td>
</tr>
<tr>
<td>0.33% PLA-2 (latent)</td>
<td>18 hours</td>
<td>doubled viscosity</td>
</tr>
<tr>
<td>1.0% PLA-2 (latent)</td>
<td>4 hours</td>
<td>doubled viscosity</td>
</tr>
<tr>
<td>0.15% A-2 (active)</td>
<td>&lt;2 minutes</td>
<td>gelled *</td>
</tr>
<tr>
<td>0.5% DBN (active)</td>
<td>&lt;5 minutes</td>
<td>gelled *</td>
</tr>
</tbody>
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* Time to double viscosity could not be determined due to very fast gelling
Table 2: Calculated basicities (pKa) of photolatent and active tertiary amines [23]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>pKa</th>
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<tbody>
<tr>
<td>PLA-2, latent amine</td>
<td>7.02±0.20</td>
</tr>
<tr>
<td>A-2, active amine</td>
<td>9.83±0.20</td>
</tr>
<tr>
<td>PLA-1, latent amine</td>
<td>5.76±0.20</td>
</tr>
<tr>
<td>A-1, active amine</td>
<td>8.11±0.20</td>
</tr>
<tr>
<td>DBN, active amine</td>
<td>13.10±0.20</td>
</tr>
<tr>
<td>DBN, active amine</td>
<td>12.7*</td>
</tr>
</tbody>
</table>

* Experimental pKa value [24]