

## Photolatent bases: new catalysts for UV-curing of coatings

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### ABSTRACT

A new approach for the cure-on-demand of coatings involves the photo-generation of a base catalyst, which then causes resins to crosslink and cure *via* a base-catalysed mechanism. The advantage of using a photolatent base catalyst is to be able to cure a wide range of conventional coatings at low temperatures. The influence of different parameters on the photolysis of two latent catalysts in a number of resin systems was investigated by infrared (IR) spectroscopy. The mechanical properties of the cured coatings were characterized by hardness measurements and then correlated to the degree of conversion and the photoefficiency of the photolatent base catalysts.

### INTRODUCTION

The technology of light-induced curing of coatings is widely recognized as being able to offer several unique advantages, which includes fast production of highly crosslinked polymer networks occurring at ambient temperature in the absence of solvent [1]. Such UV-cured coatings are usually based on resins containing multifunctional acrylate monomers and oligomers, and small amounts of a free-radical photoinitiator. Upon light exposure short-lived free radicals are produced that lead to the formation of highly crosslinked polymers by a radical polymerization (Scheme 1). This technology is now commonly used in various industrial applications to achieve a rapid hardening (curing within seconds) of protective coatings, printing inks, adhesives, varnishes and composites. However, the development of this UV-technology has encountered two major problems:

- Shadow cure limitation for coatings over three-dimensional objects of complex shapes, like a car body [2]
- Surface cure inhibition due to oxygen, which remains a crucial issue that needs to be managed in any successful free-radical photocuring application to give high performance materials [3].

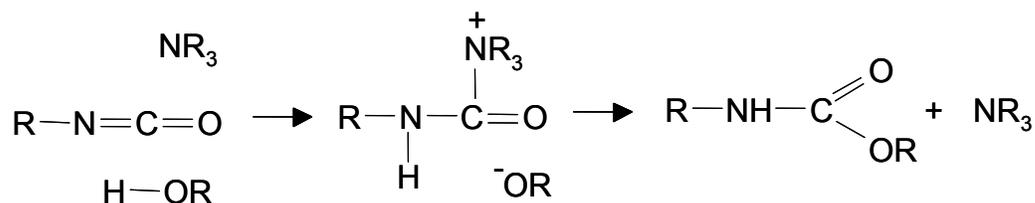
The practical aspects regarding the design of the UV equipment to be used for achieving a uniform illumination of large 3D objects have already been addressed [4], but there is still an important issue which arises from shadow areas which cannot be reached by UV-radiation and will therefore remain uncured. Similar developments were realized to overcome oxygen inhibition; however investment in new equipment is necessary.

UV-plasma curing now successfully allows one to overcome both issues simultaneously. The coated substrate is introduced in a closed chamber filled by a certain gas, usually a mixture made of nitrogen and helium. A microwave excitation produces plasma from this gas, thus emitting UV-light in the whole volume surrounding the 3D object. This promising technology is still in its infancy and requires capital investment in new equipment.

In the absence of any immediate practical solution to those two problems, the coating industry still employs existing 2-pack systems, which can be cured by a thermal process, such as 2-pack polyurethanes [5]. As represented in Scheme 2, some other 2-pack coating

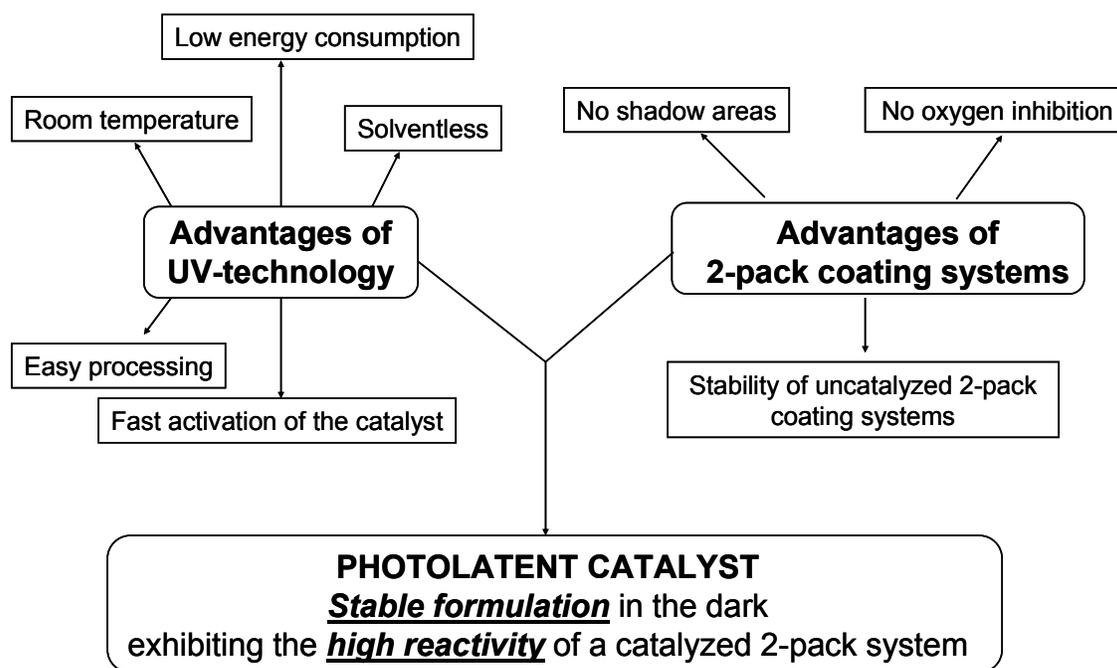


coating industry is the use of thermally latent catalysts: the blocked catalyst releases the active species under the action of heat. Here again, such systems are not adapted for applications involving heat sensitive substrates. Both possibilities, i. e. a high bake temperature or the use of catalysts, are key issues regarding the economical aspects of such coating systems. Quickly overcoming these limitations has turned into a major challenge. It has become necessary to develop a new technology providing a stable system which could rapidly cure at room temperature and could be employed in existing coating systems.



**Scheme 3: catalysis of an addition between isocyanates and alcohols to give a polyurethane network**

A logical extension to these ideas is to develop stable, low color photolatent base catalysts. In essence they represent an attractive solution by combining the advantages of the UV-technology to the stability of 2-pack coating systems (Scheme 4). These compounds are blocked catalysts, stable in the dark and provide a stable 2-pack formulation. These novel materials release the catalyst upon light exposure.



**Scheme 4: beneficial aspects of the photolatent catalyst technology**

Two types of photolatent bases were developed and tested in various coating systems: the first one is a photolatent tertiary amine, the second one being a photolatent amidine. This article gives an overview of both photolatent catalysts and shows how efficient they are in existing coating systems.

## EXPERIMENTAL

The  $pK_A$  values of the amines were calculated using Advanced Chemistry Development (ACD) Software Solaris V4.67.

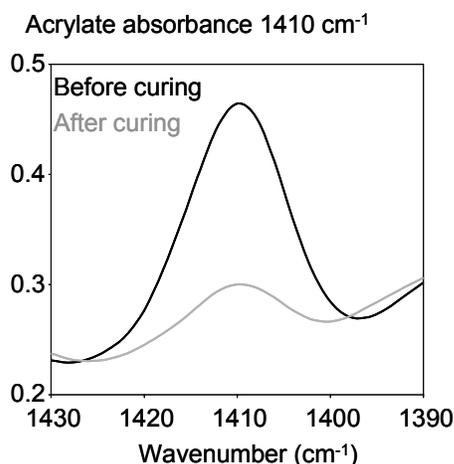
Formulations were mixed in stoichiometric proportions. All percents given in the following paper are weight percent.

The UV irradiation was performed on an IST UV belt line equipped with two medium pressure mercury lamps (electric power of  $80 \text{ W}\cdot\text{cm}^{-1}$ ). At the belt speed used, 5 m/min, the UV dose received by the sample at each pass under the lamp was measured to be approximately  $0.9 \text{ J}\cdot\text{cm}^{-2}$ . Philips lamps (TL40W/05) were employed as a UVA source (emitting from 320 to 440 nm, maximum by 380 nm). Artificial daylight lamps were employed to simulate constant natural light conditions.

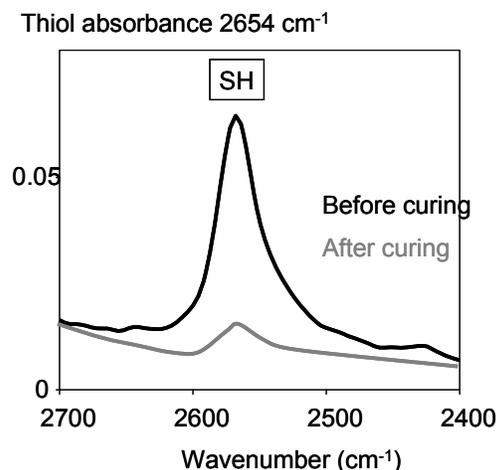
The viscosity increase of the ready-to-spray mixtures were measured with DIN Cup #4 (according DIN 53211,  $23^\circ\text{C}$ ).

The drying time of the samples was monitored using a drying recorder from Byk-Gardner, where a needle is moving during 24 hours with constant speed over the whole length of the coated substrate. For this test method, the formulation was applied with a slit coater on 30 cm long glass plates. Evaluation of the trace in the coating allows an assessment of the curing process, which can be divided into three steps: phase 1 corresponds to the evaporation of the solvent, phase 2 is a first crosslinking, and on completion of phase 3 a tack-free coating is obtained.

The chemical modifications due to the crosslinking were monitored by IR spectroscopy (FTIR spectrophotometer Perkin-Elmer 1600): therefore, the formulation was coated onto a  $\text{BaF}_2$  crystal. The reaction of the acrylate double bonds in a Michael system (acrylate / acetoacetate) was followed quantitatively by monitoring the disappearance of the IR band of the acrylate double bond at  $1410 \text{ cm}^{-1}$ , as shown in Figure 1. The reaction of the thiol groups with epoxies was followed quantitatively by monitoring the disappearance of the IR band at  $2654 \text{ cm}^{-1}$ . Figure 2 shows some typical IR spectra recorded for a stoichiometric mixture of thiol and epoxy components before and after hardening.



**Figure 1: IR absorption peak of acrylates functions before and after curing with acetoacetate**



**Figure 2: IR absorption peak of thiol functions before and after reaction with epoxies**

The degree of conversion (x) is directly related to the decay of the IR absorbance, and was calculated from the equation: Conversion(%):  $x = 100 * (A_0 - A_t) / A_0$ , where  $A_0$  and  $A_t$  represent the area of the IR band centered at  $1410 \text{ cm}^{-1}$  or  $2654 \text{ cm}^{-1}$ , before and after curing respectively.

## RESULTS

### 1. Concept – State of the art

Only a few examples of photolabile bases are reported in the literature so far, the first type of photolabile catalysts being basically latent primary and secondary amines [11]. Indeed, some carbamate derivatives and cobalt amine complexes generate primary amines such as alkyl mono- or di-amines upon UV-exposure [12-14]. These materials have been used mainly in photoresist applications, where the amine functioned as a Brønsted base for improving resolution in acid curable formulations. Since the amine is consumed during curing,

Latent amine class	Blocked amine	Photogenerated base	Ref
Ammonium salts of phenylglyoxylates			15
Benzhydryl ammonium salts			16
N-benzophenone methyl-tri-N-alkylammonium borates			17
$\alpha$ -ammonium acetophenone salts			19
Amineimide derivatives			20
N-methylnifedipine			21

**Table 1 : example of photolabile tertiary amines reported in the literature**

stoichiometric amounts of photons are required with respect to the number of reactions taking place. This means that such compounds are limited to applications requiring very low amounts of amine. These compounds are not readily adapted for coating applications, where

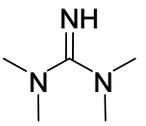
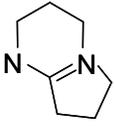
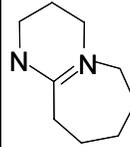
a high crosslink density is needed and therefore large amounts of photolabile primary or secondary amine would be required.

Tertiary amines can overcome the problems seen with primary or secondary amines. Namely, tertiary amines can act catalytically whereas the primary or secondary amines do not, thereby permitting chemical amplification during photocuring. The problem now is to render tertiary amines into a photolabile form.

The synthesis of a photolabile tertiary amine is actually more complicated than that of a photolabile primary amine. Indeed, the first types of photolabile tertiary amines reported in the literature are mostly based on salts, as shown in Table 1. These compounds are efficient photolabile tertiary amines, however because they are polar ionic salts, they have poor solubility in the common non aqueous coating resins.

It was therefore mandatory to design photolabile tertiary amines having a neutral structure both before and after UV-activation, and containing a nitrogen atom having no significant catalytic activity towards the coating system. It proved out that steric hindrance and basicity are the key parameters controlling the catalyst activity in a 2-pack PUR resin; the latter requirement can be achieved by increasing the steric shielding around the nitrogen atom and by minimizing the electronic interactions of its electron lone pair in the latent form.

Some of the more widely known active catalysts are tertiary amines and amidine compounds (Table 2). Our main goal was to develop photolabile forms of those two structures with the right balance of basicity and steric hindrance.

Trialkylamines	Guanidines	Amidines	
 Trimethylamine pKa=9.8	 1,1,3,3-Tetramethylguanidine TMG pKa=13.6	 1,5-diazabicyclo- [4.3.0]non-5-ene DBN pKa=12.7	 1,8-diazabicyclo- [5.4.0]undec-5-ene DBU pKa=12.5

**Table 2 : amine catalysts used for curing of coatings**

## 2. Photolabile tertiary amines

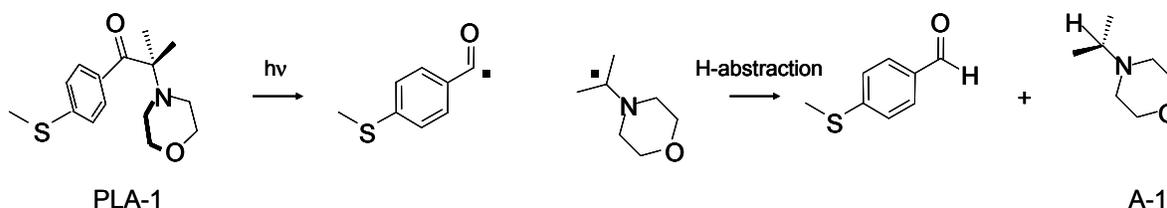
One kind of coating system used for clear coats is based on a polythiourethane network resulting from the addition between isocyanates and thiols as hydrogen donors (Scheme 2). The reaction proceeds quite slowly at room temperature in the absence of catalysts, but rapidly in the presence of a tertiary amine. The concept of a photolabile tertiary amine was of high interest for this application, for providing a stable formulation in the dark while showing a high reactivity at room temperature after UV-activation of the catalyst.

### 2.1. First generation

Some  $\alpha$ -amino acetophenones (e.g., PLA-1) are already commercially available as efficient radical photoinitiators (Scheme 5), and may also be used as photolabile bases. These compounds meet the two requirements a photolabile base must obey:

- first, the highly crowded substituents close to the nitrogen atom shield these tertiary amines, thereby minimizing unwanted nucleophilic reactions

- electronic interactions between the nitrogen electron lone pair and the substituted aromatic ring further reduce the basicity of the amine, thereby minimizing premature advancement (curing) of the resin.



**Scheme 5 : photoinduced steric release as latency concept for PLA-1**

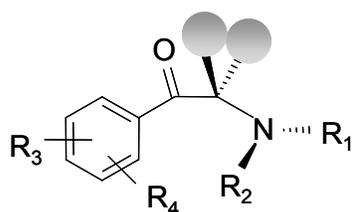
The UV-exposure activates the  $\alpha$ -cleavage to give benzoyl and amine radicals which are not active in an isocyanate/thiol formulation. The amine radicals can then undergo an H-abstraction reaction, leading to the formation of the amine catalyst A-1.

A-1 has shown to be an efficient catalyst for the curing of epoxy/carboxylic acid systems, however, the use of PLA-1 as photolabile amine showed only a slight beneficial effect on the cure speed of an isocyanate/thiol 2-pack coating. This result proves that the efficiency of the photolabile amine strongly depends on the structure and the basicity of the released amine, and that it is necessary to define a “universal” photolabile tertiary amine. Within this context, a new generation of photolabile tertiary amines was developed.

## 2.2. New generation

### 2.2.1. Release of the catalyst

Another kind of  $\alpha$ -amino acetophenone that has exhibited a better efficiency of catalyzing the coupling of isocyanates and thiols is shown in Scheme 6 (structure PLA-2 given in Scheme 6, photolysis shown in Scheme 7). The PLA-2 has good latency in the dark and exhibits high photoactivity under UVA light sources.

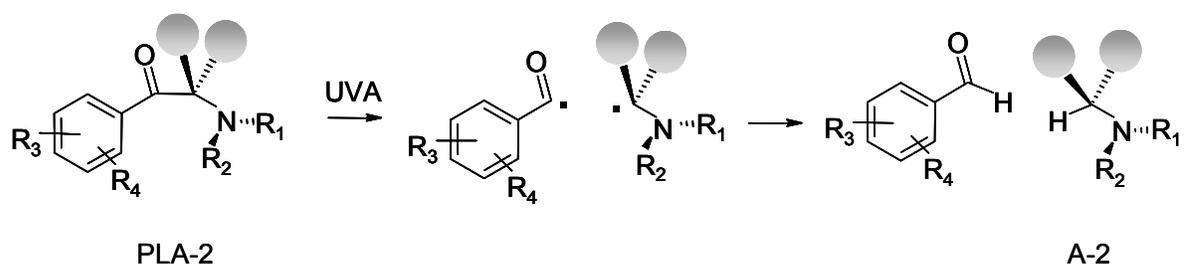


**Scheme 6: structure of the new generation of photolabile tertiary amine PLA-2**

A common feature of  $\alpha$ -amino acetophenones is their yellow coloration before and after UV-exposure, requiring the use of low amounts so as to minimize the yellowing in the final material. In the specific case of PLA-2, the nature of the substituents was optimized to obey the two following requirements:

- the film shows little or no yellowing after activation, and
- the latent catalyst can be activated by a UVA-light, which is an important requirement for car refinishing to ensure safe irradiation conditions to the user.

A further interest for such systems lies in their low sensitivity to oxygen inhibition. As no radicals are involved during the polymerization, oxygen can only interfere with the reaction by quenching the triplet excited state of PLA-2: short lifetimes of excited states do not allow such deactivation.



### Scheme 7: activation of tertiary amine PLA-2 through UVA-exposure

To characterize the efficiency of the photolabile base, pKa values were calculated for the latent and the active compound, not taking into account the steric effect. The results are reported in Table 3.  $\Delta pK_a$  is of 2.8 for the tertiary amines PLA-2/A-2: this significant value, caused by the electronic changes close to the nitrogen, should provide a stable formulation while having an active released base (pKa=9.8). Even if the basicity difference is similar for the pair PLA-1/A-1 ( $\Delta pK_a=2.3$ ), the amine A-1 is not basic enough (pKa=8.1) to be an efficient catalyst for isocyanate/thiol curing.

Catalyst	pKa
PLA-2	7.02
A-2	9.83
PLA-1	5.76
A-1	8.11
DBN	13.10

**Table 3: calculated pKa values of latent and active forms of the catalysts (+0.02)**

#### 2.2.2. Application results

The efficiency of PLA-2 was evaluated by measuring the pot life of an isocyanate/thiol formulation in the presence of different amounts of the latent and active catalyst. Pot life is defined here as the time needed to reach two times the initial viscosity of the formulation, which is the effective working time during which the lacquer can be applied onto the substrate. Table 4 shows that the neat (uncatalyzed) formulation has a pot life of 36 hours, while the presence of 0.33% of PLA-2 reduces this duration to 18 hours. The formulation gels within less than 2 minutes when using the active base A-2 (at 0.15%). These results show the simultaneous high efficiency of A-2 and the poor negative effect of PLA-2 on the stability of the 2-pack isocyanate/thiol system, forming thus an effective photolabile catalyst.

It should be also noted that by increasing the concentration of PLA-2 to 1%, the pot life decreases to four hours. Thus, depending on the time needed for application, it is possible to obtain a formulation which is stable during a reasonable period of time, which hardens rapidly in the exposed areas (a few minutes), but which also presents some dark-curing proceeding within a few hours (4 hours by 1% of PLA-2). Therefore, it is necessary to select the right concentration of PLA-2.

Catalyst	Pot life	Comment
None	36 hours	Doubled viscosity
0.33% PLA-2	18 hours	Doubled viscosity
1% PLA-2	4 hours	Doubled viscosity
0.15% A-2	< 2 minutes	Gelled
0.5% DBN	< 5 minutes	Gelled

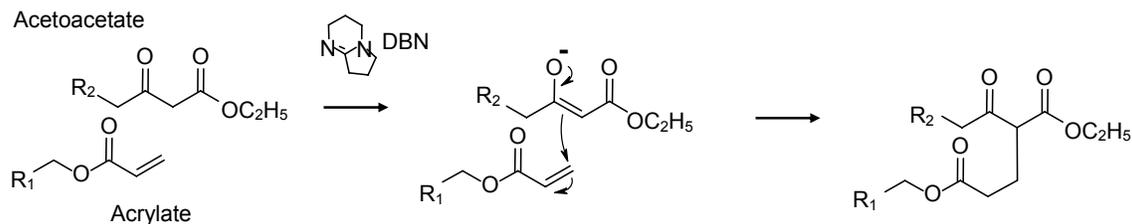
**Table 4: shelf-life stability of a polyisocyanate/polythiol formulation in the presence of amine catalysts**

Based on the data in Table 4 it is also clear that the strong non-nucleophilic base DBN shows a lower activity towards the hardening of NCO/SH systems compared to the tertiary amine A-2. It is therefore crucial to identify the optimal catalyst for each type of crosslinking mechanism.

### 3. Photolabile DBN

Strong amidines are well-known catalysts employed by the coating industry for the hardening of various types of systems, especially those based on a Michael addition between acrylates and acetoacetates (or malonates or thiols). Another possible application is epoxy/thiol systems. The high basicity of DBN, DBU or TMG is due to the conjugative interaction of two nitrogen atoms via the carbon-nitrogen double bond. The result is to make these products highly efficient ("super") Brønsted bases. Also of significance is the fact that these strong bases do not show significant nucleophilic properties.

Scheme 8 shows the Michael addition between acetoacetates and acrylates induced by DBN.

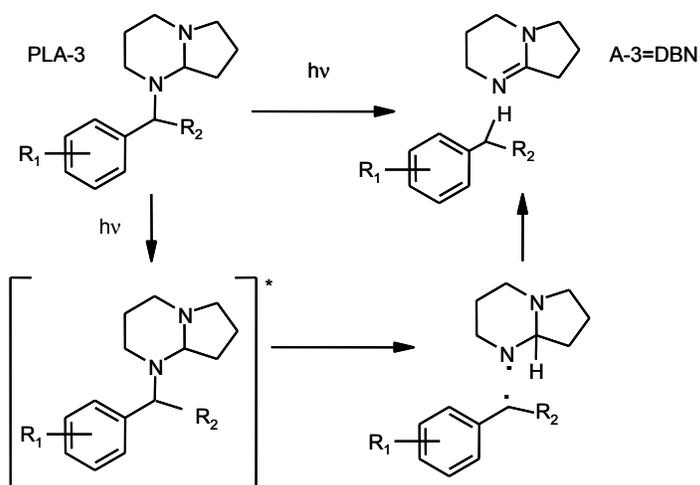


**Scheme 8: Michael addition of an acetoacetate/acrylate coating system [23]**

The objective now is to develop a photolabile amidine, and more especially a photolabile DBN.

#### 3.1. Release of the catalyst

As represented in Scheme 9, compound PLA-3 was found to generate DBN under UV-exposure.



**Scheme 9 : photolysis of PLA-3 to give DBN**

Table 5 shows that pKa values of the latent and active forms of A-3 are dramatically different ( $\Delta pK_a = 4.4$ ). A-3 is obviously a strong base, while the basicity of PLA-3 is less pronounced. It should be noted that the pKa value of this tertiary amine is quite high (pKa=8.96), hence the latent form should still exhibit some activity towards the curing of coatings which can be catalyzed by tertiary amines.

Catalyst	pKa
PLA-3	8.96
A-3 (DBN)	13.4

**Table 5: calculated pKa values of latent and active forms of DBN**

By modifying the nature of the substituents of PLA-3, it is possible to control the absorption spectrum of the molecule. Once the structure of PLA-3 had been optimized, it was found that its absorption is limited to the UV-range, as shown in Figure 3. To facilitate the photolysis of PLA-3 and to allow a UVA-activation of the system, a photosensitizer was introduced into the formulation.

The photosensitizer absorbs in the near-visible range and transfers the electronic energy to PLA-3, thus enabling the PLA-3 to use light at longer wavelengths. The major issue when employing a photosensitizer is potentially introducing slight color into the coating. Depending on the film thickness and the coloration constraints, it is necessary to adjust the sensitizer concentration. However, a large number of photosensitizers are now commercially available, which makes the selection and optimization process more feasible.

Figure 3 shows that by employing ITX as the photosensitizer, the formulation becomes photoactive up to 410 nm. In this case the system can be activated by a UVA lamps or even daylight: this type of long wavelength radiation ensures safe curing conditions and easy processing.

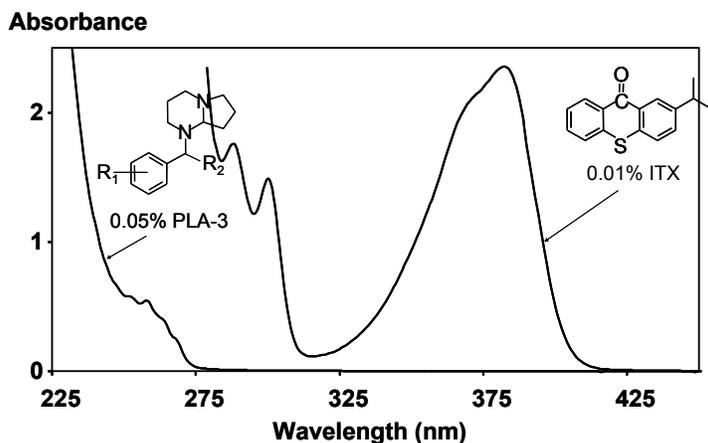


Figure 3 : UV absorption of PLA-3 with and without ITX

### 3.2. Application results

The efficiency of PLA-3 as a photolatent base was evaluated in two kinds of coating systems used by the coating industry: acetoacetate/acrylate mixture (Michael addition) and thiol/epoxy coatings.

#### Acetoacetate/acrylate coating

Promising results were obtained with PLA-3 as the photolatent catalyst for an acetoacetate/acrylate coating formulation. The results are given in Figure 4, which plots the light exposure time to achieve a tack-free surface of the coating as a function of sensitizer. As expected, no hardening took place in the absence of sensitizer, as the formulation does not absorb above 280 nm while the lamp emission starts by 380 nm. The addition of 1% of benzophenone (BP), absorbing up to 390 nm gives a tack-free film within 3 hours. A great improvement was achieved by using 0.5% 2-isopropylthioxanthone (ITX), as it was possible to handle the coating after only 30 minutes.

#### Tackfree time under daylight (h)

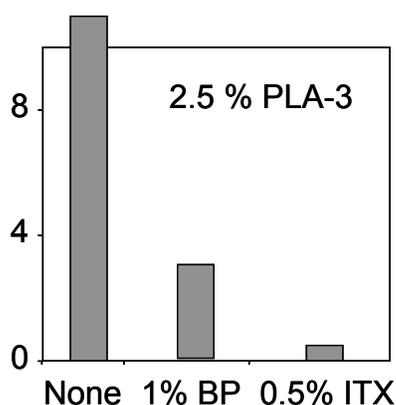


Figure 4: time (h) required to obtain a tack-free film for an acetoacetate/acrylate coating containing 2.5% of PLA-3 and various sensitizers exposed to an artificial daylight

#### Acrylate conversion (%)

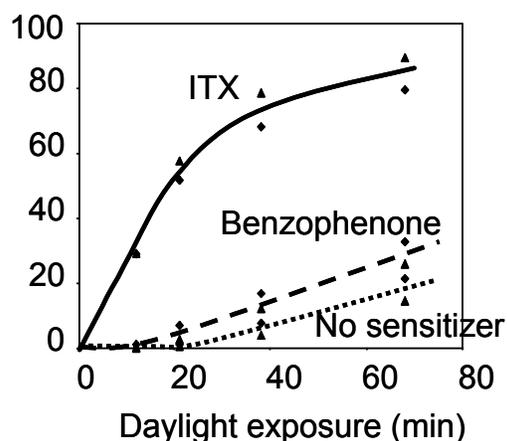
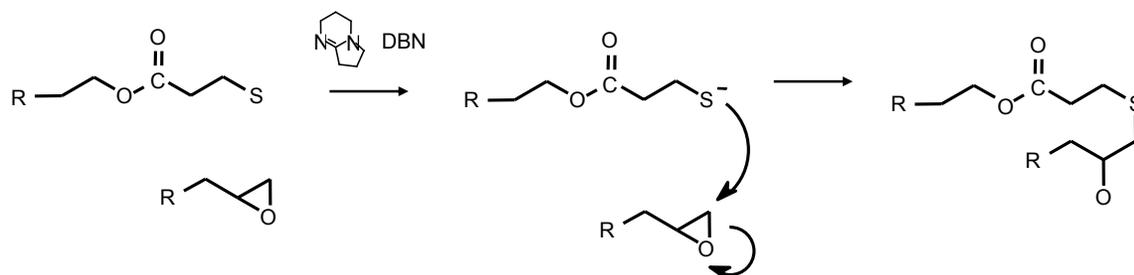


Figure 5: acrylate disappearance upon daylight exposure of an acetoacetate/acrylate coating + 2.5% PLA-3 with different sensitizers - 10  $\mu$ m thick films

These results were further confirmed by monitoring the acrylate disappearance by IR spectroscopy. Figure 5 shows the acrylate conversion of an acetoacetate/acrylate film upon daylight exposure without catalyst and in the presence of benzophenone and ITX. Using ITX as the sensitizer it was found that more than 55% of the acrylates were converted during a 20 minute light exposure, after which the polymerization rate progressively slowed down due to the gelation of the film.

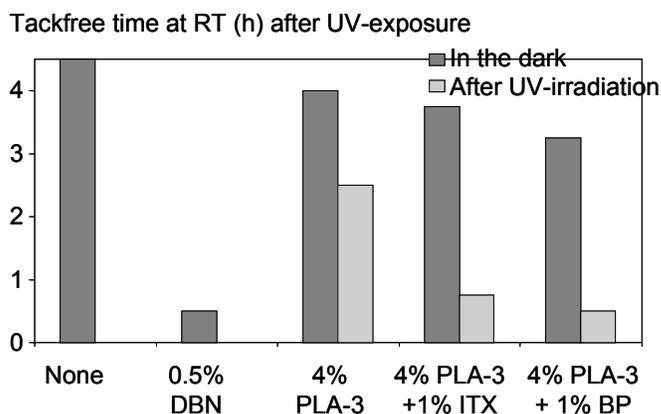
### Epoxy/thiol coating

Scheme 10 shows the mechanism of curing of a thiol/epoxy that is initiated by DBN.



**Scheme 10: curing of a thiol/epoxy coating system**

Figure 6 shows that PLA-3 is also highly efficient for the curing of thiol/epoxy mixtures after UV-activation. The results clearly reveal the problem which arises from this type of coating, which cannot harden at room temperature, but which cures rapidly in the presence of low amounts of catalyst (pot-life of 20 minutes with 0.5% DBN). The photolabile base PLA-3 is obviously a good solution in overcoming this issue, since it is possible to handle the formulation longer than 3.5 hours, while still getting efficient hardening after UV-exposure (within less than one hour). Here again, the effect of light is more pronounced in the presence of sensitizers ITX or BP.



**Figure 6: tack-free time after UV exposure (2X80 W/cm) of a thiol/epoxy film with and without catalyst and sensitizers**

IR spectroscopy allowed us to observe the formation of DBN in the film, amidines exhibiting a characteristic peak at  $1664\text{ cm}^{-1}$  (Figure 7). Therefore, it was quite easy to observe the influence of several parameters on the DBN formation, such as the curing conditions and the concentrations of the species. In such viscous coatings, the catalyst concentration is a

crucial parameter determining the cure speed of the film. Therefore, it is essential to define the best curing conditions to facilitate the application work.

### Influence of the lamp

Table 6 shows the influence of the lamp on the photolysis of PLA-3 in the presence of ITX: the higher the amount of converted PLA-3, the higher the DBN concentration released in the coating and the faster the hardening takes place. One UV-exposure using the UV belt lamp is equivalent to approximately 7 minutes irradiation by the UVA lamp (50 to 60% PLA-3 have reacted). Obviously, these UVA lamps are also adapted for the curing of 2-pack coatings containing a photolabile catalyst, the release of the catalyst is however not as fast as with mercury belt lamps, the UV-dose being lower.

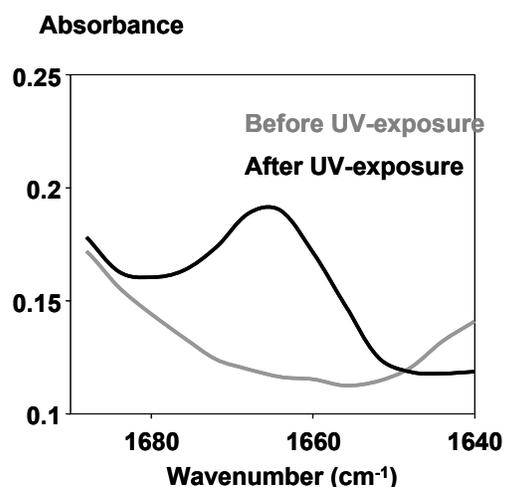


Figure 7: IR spectra of a thiol/epoxy formulation containing PLA-3 before and after UV-exposure  
10 µm thick films, 3.5% PLA-3

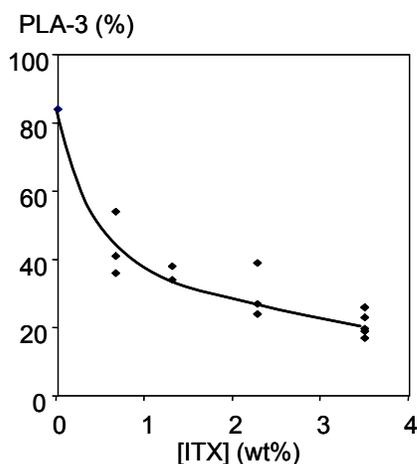
Lamp	UV-passes / Exposure time	Converted PLA-3 (%)
UV mercury lamp (2X80 W/cm)	1 pass	52
	2 passes	71
	3 passes	85
UVA Philips lamp (maximum at 380 nm)	5 minutes	40
	10 minutes	60
	15 minutes	65

Table 6: influence of the UV light on the generation of DBN in a thiol/epoxy formulation  
10 µm thick films, [PLA-3] = 3.4%, [ITX] = 1.3%

### Influence of the sensitizer concentration and type

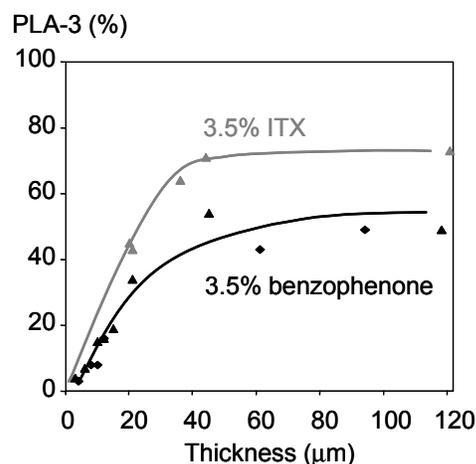
Similarly, Figure 8 shows that by increasing the concentration of ITX to 1.5%, it is possible to convert up to 60% of PLA-3 after only one UV-exposure. This value remains stable even when employing higher amounts of sensitizer. This result is explained by the fact that a higher UV-dose is required to improve the photolysis of PLA-3.

Because ITX being slightly colored an optimal concentration should be defined, subject to the coloration constraints and the expected curing duration required for the application. Benzophenone can be an alternative as shown in Figure 9, which also proves that this sensitizer is more adapted than ITX for the curing of films thicker than 40  $\mu\text{m}$ .



**Figure 8: influence of ITX concentration on the photolysis of PLA-3 in a thiol/epoxy formulation**

10  $\mu\text{m}$  thick films, [PLA-3] = 3.5%, UV-dose = 0.9  $\text{J}\cdot\text{cm}^{-2}$



**Figure 9: influence of the sensitizer and the film thickness on the photolysis of PLA-3 in a thiol/epoxy formulation**

[PLA-3] = 3.5%, UV-dose = 0.9  $\text{J}\cdot\text{cm}^{-2}$

## CONCLUSION

A major concern for 2-pack systems employed by the coating industry is to find a compromise between the lack of stability of the formulation in the presence of catalysts and their poor reactivity at room temperature in the absence of catalysts. It was basically not possible to find a satisfying balance before now, where the adopted strategy was to favor one parameter at the expense of the other one. Whatever choice the user made, the result would have had a negative impact on the economics of such systems.

A paradigm shift was required to overcome the deficiencies of the conventional technology. To this end photolabile base catalysts were developed. It was found that they can be added into the formulation without significantly affecting its stability, yet these compounds confer a high reactivity to the coating system once applied onto the substrate and exposed to a light source. These photo-generated catalysts greatly improve the cure speed of the coating and can be activated at room temperature, broadening the application field of stable 2-pack systems to heat sensitive substrates and to a wide range of new coatings.

Two photolabile base catalysts were developed and were found to be highly efficient in various kinds of coating systems, such as isocyanate/thiol, thiol/epoxy and Michael systems. The formulations examined were usually stable for several hours and had a pot life of a few minutes in the presence of active catalysts but remained stable longer than 4 hours with the photolabile catalysts. In the presence of the photolabile base catalysts the formulations could be photocured at room temperature. Photocuring was fairly efficient, based on the fact that hard films could be produced even after a few minutes of light exposure. A further beneficial effect of these compounds is that the latent form also shows some slight catalytic activity, thus improving the dark-curing (shadow curing) compared to the neat (uncatalyzed) coating mixture.

Other investigations also proved that the behavior of photolatent catalysts towards light is similar to the behavior of photoinitiators: cure parameters such as light emission, UV-dose and film thickness had the same effect on the generation of the catalyst as on the initiating efficiency of a radical polymerization in the case of photoinitiators.

## References

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