A novel initiator for curing pigmented coatings

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Introduction

The curing of pigmented coatings has been a challenge in the field of ultraviolet (UV) curing. As pigments absorb as well as scatter light, they compete effectively with photoinitiators (PI) for the light available during the curing process. It has been reported that pigments effectively compete for light up to 370 nm. Therefore, in order for a PI to be efficient in curing pigmented coatings, it is essential that the PI has a considerable UV absorbance beyond 370 nm. Such an absorption was possessed by 2-isopropyl thioxanthone (ITX). The UV absorption characteristic of ITX coupled with its ability to abstract H – atoms from amine synergists, enabled its use for curing pigmented coatings. As a result, ITX and other thioxanthone initiators have been the most popular PIs for curing pigmented coatings.

Subsequent developments in the field of PIs resulted in the commercialisation of phosphine oxide type and α – amino ketone type initiators. The major drawback of these initiators has been their cost, and, in the case of some of the α – amino ketones, the odour too. During the early stages of radiation curing, another PI used widely for curing pigmented coatings was Michler’s Ketone (MK). A lot of studies have been reported in the literature on the use of MK for curing pigmented coatings.

As MK contains both benzophenone (BP) and tertiary amine groups in its structure, it was thought originally that it could function as an abstraction type initiator that did not require an amine synergist. However, it was found that in the absence of an amine synergist, the self abstraction by Michler’s Ketone subsequently results in the formation of the dimer and, as a result, renders the MK molecule inefficient for curing monomers. Interestingly, it was found that a mixture of BP and MK was synergistic and was very useful in curing formulations. It was reported that the mixture was 14 times more efficient than BP alone and about five times more efficient than a BP – amine system. In fact, when MK is used together with BP, mechanistically an interesting phenomenon takes place. In such systems, MK acts as the amine synergist. But, unlike in the case of BP – amine systems, where BP absorbs light, forms the triplet and subsequently abstracts H from the amine, in the MK – BP system, MK predominantly absorbs light and forms an exciplex with the ground state BP (BP can also absorb light and form the same exciplex by reacting with a ground state MK, but, owing to the stronger absorption of MK, it absorbs light predominantly). This is followed by an electron transfer from MK, and a subsequent proton transfer from BP to finally form the initiating radical. Even though MK was a popular PI for curing pigmented coatings, the use of MK as a PI was subsequently discontinued owing to its identification as a carcinogenic material.

Research in the authors’ laboratories on MK analogues resulted in the development of a new compound, viz, 4,4’bis(N-methylthyl)diaminobenzene (MEAB), which showed PI activity comparable to MK but was not toxic. The structure is shown below.

Focus:

A novel initiator for curing pigmented coatings

Summaries

A novel initiator for curing pigmented coatings

Research in the authors’ laboratories resulted in the development of a new photoinitiator for curing pigmented coatings. The new initiator is the N-methyl-N-ethyl analogue of Michler’s Ketone. Toxicity testing on this compound (MEAB) showed that it was Ames negative. Photo-differential scanning calorimetric data show that the inherent efficiency of MEAB is higher than that of the thioxanthone analogue and is comparable to that of Michler’s Ketone. Cure speed measurements revealed that its efficiency is comparable with that of Michler’s Ketone. The studies showed that MEAB can be used in formulations where Michler’s Ketone was used traditionally before being abandoned due to toxicity reasons.

Ein neuer Initiator für die Aushärtung pigmentierter Beschichtungsstoffe


Un nouveau initiator pour effectuer la réticulation des produits de peinture pigmentées

Les recherches effectuées aux laboratoires des auteurs ont abouti au développement d’un nouveau photoinitiateur pour effectuer la réticulation des produits de peinture pigmentées. Le nouveau initiator est le N-méthyl-N-éthyl analogue de la cétone de Michler. Les essais de toxicité sur ce produit indiquent qu’il est Ames-négatif. Les données fournissent par le calorimètre phorodiermatique conduisent indiquant que l’efficacité de l’initiateur de MEAB est supérieure à celle du thioxanthone analogue et comparable à celle de la cétone de Michler. Les mesures sur le stade de la réticulation révèlent que le MEAB peut être utilisé en produits où on utilisait la cétone de Michler eut que n’est pas abandonné en raison de sa toxicité.
Results of the studies carried out on this compound, comparing its efficiency with MK will be presented in this paper.

Experimental
Details of UV spectral measurements, photo DSC and cure speed measurements have been published elsewhere. In the present studies, the film thickness used for curing the clear coat formulations was 1mm.

Results and discussion

UV spectrum
The UV spectrum of MEAB is shown in Figure 1 and is characterised by a strong band with a peak maximum at 358nm and an extinction coefficient of 38,000 l/mole/cm. As discussed in the 'Introduction', the strong absorption beyond 370nm helps MEAB compete effectively with pigments for absorption of light and renders it useful for curing pigmented coatings. The UV spectrum of MEAB is almost superimposable on that of MK. The UV spectrum of MK is shown in Figure 2.

Photo DSC
The efficiency of MEAB was assessed using photo DSC. The photo DSC exotherms for the polymerization of HDDA are shown in Figure 3 and the exotherm parameters in Table 1. The photo DSC data in Figure 3 and Table 1 reveal that the efficiency of MEAB is comparable to that of MK and is distinctly higher than that of the tetraethyl analogue of MK (TEMK). The photo DSC data are in accordance with the reported comments in the literature on the efficiencies of MK and TEMK.

Table 1: Photo DSC values for the polymerisation of HDDA

<table>
<thead>
<tr>
<th>PI</th>
<th>$H_{\text{max}}$ (W/g)</th>
<th>$t_{\text{max}}$ (s)</th>
<th>$\Delta H$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEAB</td>
<td>15.7</td>
<td>9.0</td>
<td>-486</td>
</tr>
<tr>
<td>MK</td>
<td>11.3</td>
<td>6.0</td>
<td>-499</td>
</tr>
<tr>
<td>TEMK</td>
<td>5.3</td>
<td>6.6</td>
<td>-114</td>
</tr>
</tbody>
</table>

The photo DSC data of a clear coat formulation were also recorded and are shown in Figure 4. The exotherm parameters are shown in Table 2. The PI combination used in the formulation was 4% BP + 4% EDAB + 1% ITX + 0.5% MEAB/MK/TEMK. Data in Figure 3 and Table 2 also suggest that the inherent efficiency of TEMK is less than that of MK and MEAB.

Table 2: Photo DSC values for the polymerisation of a clear coat using the 'H' lamp

<table>
<thead>
<tr>
<th>PI</th>
<th>$H_{\text{max}}$ (W/g)</th>
<th>$t_{\text{max}}$ (s)</th>
<th>$\Delta H$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEAB</td>
<td>6.3</td>
<td>6.0</td>
<td>-180</td>
</tr>
<tr>
<td>MK</td>
<td>6.9</td>
<td>6.0</td>
<td>-171</td>
</tr>
<tr>
<td>TEMK</td>
<td>4.8</td>
<td>6.0</td>
<td>-104</td>
</tr>
</tbody>
</table>

The photo DSC exotherms shown in Figure 4 were obtained using a Honle UV America 'H' lamp, which was actually a medium pressure Hg lamp. As MEAB absorbs strongly in the 350 - 400nm region, it was proposed to study the effect of the light source on the photo DSC exotherms. Therefore, photo DSCs of the same formulations were recorded using the Honle UV America 'F' lamp, whose spectral output is close to that of the Fusion 'D' bulb. The exotherms are shown in Figure 5 and the photo DSC parameters in Table 3. The data show that there is a slight improvement in the effi-