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3. Adjustment of New Hindered Amine Light Stabilizers (HALS) to Future Technologies

HALS compounds have been known for more than 30 years. Commercially available HALS are based on 2,2,6,6-tetramethylpiperidine (3, R = H, R' = H).

HALS 3 (R = H, CH3) as well as its nitroxyl radical 4 and the N-alkoxyamine 5, both produced from 3 during photo-oxidative degradation of polymers, are all extremely effective free-radical scavengers [5] and stabilizers for plastics and coatings. Compatibility and long-term retention are obtained by adjustment of R".

Migration of post-added traditional HALS 3 and attachment of functionalized new HALS (e.g. R, R' = unsaturated groups) to the polymer are both subjects of current investigations. In the latter case copolymerization or grafting techniques are applied, e.g. grafting during extrusion ('reactive processing'). Polymer-bound photo-stabilizers outperform traditional products in special new applications such as polymer blends or systems in extractive environments.

4. Conclusion

Polymers and coatings of extended lifetime require light stabilizers of increased performance. New products offer better protection due to their superior efficiency and their ability to remain in the substrate.

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1. Introduction

Light-induced polymerization is the basis of important advanced technologies, since it is among the most efficient methods capable to achieve fast and extensive curing of multifunctional oligomers and monomers. Highly reactive systems are cured within a fraction of a second upon exposure to intense UV radiation or laser beams, transforming the liquid resin into a strongly cross-linked solid polymer without the need of additional heat [1].

These features translate into technical advantages which made radiation curable coatings one of the most rapidly develop-

Recent Developments in Radical Photoinitiator Chemistry

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Fig. 1. Photoinitiators for clear coatings, printing plates, and water-borne systems. The dotted lines indicate the site of photoinduced cleavage.

Fig. 2. Photoinitiators for pigmented systems and resist applications. The dotted lines indicate the site of photoinduced cleavage.
3. Development of New Photoinitiators for White-Pigmented Systems and Thick Layers

Rutile-type titanium dioxide, preferentially used as a pigment in white coatings due to its high hiding power, acts as an efficient screen for the light of all wavelengths below 380 nm. A photoinitiator, efficient in the presence of this pigment, has, therefore, to absorb sufficient light of wavelengths longer than 380 nm, while its photoproducts must not absorb light in the same region. Accordingly, the design of a new photoinitiator which can fulfill both requirements was necessary.

The principle of photobleaching is known for a variety of compounds. Photoinitiators using a dye as chromophor often undergo a change in color during the irradiation, and titanocenes are another example of visible photoinitiators showing this effect [7]. The bleaching does, however, usually not result in colorless products, which is of little concern in application areas for these initiators, such as the fabrication of printing plates or resists.

A photoinitiator useful in white pigmented system must, however, undergo complete bleaching of the absorption at the blue end of the visible spectrum, resulting in colorless products. A first class of photoinitiators which fulfills these requirements are monoacylphosphine oxides (MAPO) [8], which were introduced some years ago. The increasing demand
for better hiding power of the coating required, however, the development of a new and more efficient photoinitiator, which allows the curing of formulations containing a higher pigment loading and higher film thicknesses. Research following these lines resulted in the recent introduction of new bisacylphosphine oxide (BAPO) photoinitiators. The structure of the compound 7, which has been commercialized this year as part of an optimized blend with the α-hydroxy ketone 3, is shown in Fig. 4.

The photochemistry of these compounds has been studied using CIDNP-NMR spectroscopy, preparative irradiation, and trapping techniques [9]. It was unequivocally shown that the photoinitiator undergoes cleavage of the C–P bond from a triplet state to give a benzoyl and a phosphino radical. Both radicals efficiently initiate the polymerization reaction (Scheme). The phosphinoyl radical is converted into a polymer-bound monoaerylphosphine oxide (MAPO) group, which, in turn, is a photoinitiating moiety and undergoes a second photoinduced cleavage reaction. A second pair of initiating radicals is thereby formed which also contribute to the initiation of polymerization. The BAPO photoinitiator, therefore, produces four initiating radicals in a stepwise process, twice as much as other α-cleavage photoinitiators which can only undergo one cleavage reaction. This high radical yield explains the high reactivity of this photoinitiator found in various applications.

Bisacylphosphine oxides have low energy absorption bands in the range of 380–420 nm (ε = 600 l/mol·em), which are attributed to interactions between orbitals on the carbonyl and the phosphino groups. The absorption of compound 7 in the range of 350–450 nm is shown in Fig. 5 (curve 1). Since the C–P bond is cleaved in the photochemical reaction (Scheme), the chromophore responsible for the long-wavelength absorption is destroyed. This results in the photobleaching shown in Fig. 5. Most important for applications in white pigmented systems is the fact that no new photoproducts absorbing in the visible are formed.

The high performance of this photoinitiator was shown in different applications [9], where coatings with higher pigment loadings or higher film thickness could be cured than with the hitherto available photoinitiators.

An additional advantage of the photobleaching is the fact that the optical density of the formulation in the range where the bleaching occurs diminishes during the curing process. The thickness of the resin layer that can be cured by irradiation is usually limited by the fact that light can only penetrate into the formulation to a depth determined by the photoinitiator absorption. The diminishing optical density of formulations containing the photobleaching initiator 7 allows the light to penetrate continuously into deeper layers. Formulations of several cm thickness can thus be completely cured with the new BAPO photoinitiator.

4. Conclusions

The continuous demand for photoinitiators which can meet the requirements of new applications in the coating and imaging technology has provided a major stimulus for the development of new photoinitiators over the past years. As a consequence, radiation curing became an established technique in applications which were regarded as not being feasible for this technology some years ago. An example is the curing of highly pigmented white coatings, which has become an industrially useful process with the introduction of suitable photoinitiators.

This development will continue in the future. On the one hand, the technical and economical advantages of radiation curing, as well as the increasing limitations of allowed amounts of volatile organic compounds, will initiate a change from other curing methods using solvent-based systems to this technology. On the other hand, new applications requiring photoinitiators with new properties are steadily emerging, and the demand for more efficient photoinitiators for existing markets will continue. The design and development of new tailor-made compounds, which can cope with both the technical and ecological demands, is, therefore, a continuing challenge for industrial research.

Fig. 5. Photo-bleaching of BAPO photoinitiator 7 during irradiation in the presence of an excess methyl tert-butyldelinate

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