

Beyond the usual compromises on photoinitiator performance in inks and coatings applications.

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Abstract

This paper describes new developments designed to provide formulators with materials that will enable them simultaneously to achieve high curing performance, low emission, low migration and low odor. Both free radical and cationic chemistries were investigated, as they provide potentially unique advantages that could benefit the development of radiation curing in the various graphic arts applications.

Test results demonstrate that a systemic approach (formulation composition, curing conditions and environment, targeted applications) could greatly enhance the technical and commercial chances of success, in particular by offering innovative solutions at affordable cost.

Introduction

The use of UV inks and coatings in graphic arts applications has sharply increased and this is likely to continue in the near future. Over and above the variable growth figures sometimes seen in associations' or multi-clients' reports, actors in the value chain can certainly confirm that "activity" remains high as investments done by printers and converters are driving the technology towards higher cost efficiency and superior technical performance.

One fundamental change, however, is the specialization now taking place in the different sub-segments of radiation curing technology for graphic arts applications.

Consider, for instance, raw materials for inks and coatings: until recently, so-called "work-horses" enabled sustainable development of the different formulations, but new applications require, at least partially, the introduction of new components of a significantly different nature. In the past it was conceivable to use similar raw materials and vary their ratios to formulate a UV offset system for business form printing and a UV flexo one for labels, whereas today machine performance and end application requirements call for specifically designed products. Machinery printing forms, lamps and curing equipment are apparently also developing into specialties. Overlaps are likely to decrease everywhere – from consumables to printing assets – given the difference in requirements between, say, a UV ink jet system for producing plastic cards and a UV offset system for beverage cartons.

This will lead to the co-existence of commoditized applications and more attractive and challenging applications with inherent risks as well as opportunities for business growth and financial achievement.

UV curing films with low emission characteristics

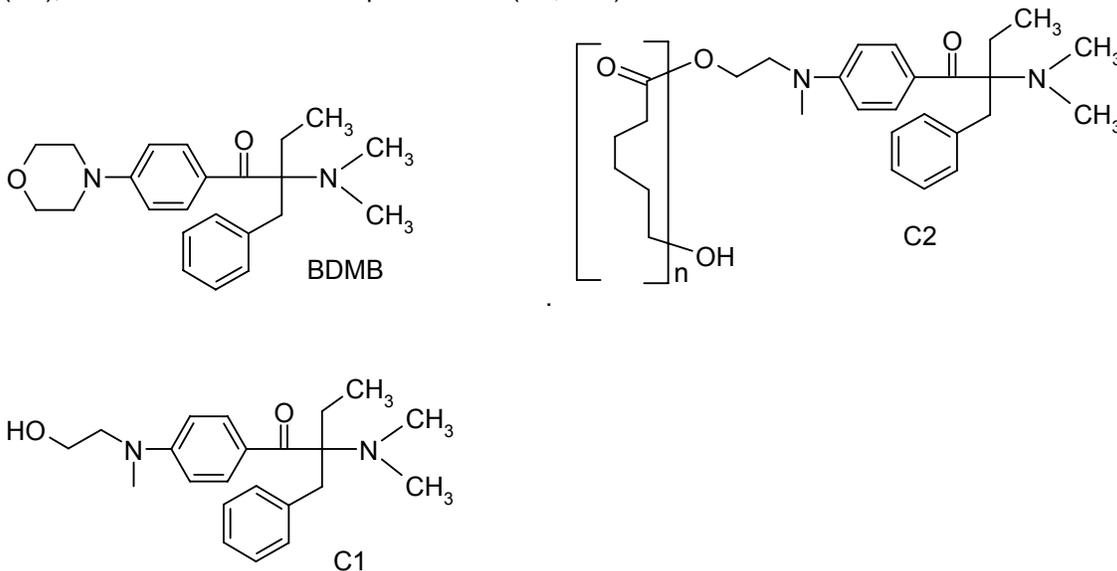
One of the challenges is the development of radiation curing technology in applications sensitive to emissions from packaging. Today, primary, and to a lesser extent secondary, food packaging is required to provide protection of the contents.

The use of radiation curing inks and coatings in the attractive flexible packaging sector depends on the ability of the industry to manage emission issues. Other ink, coating and film properties also need to be improved [1], without compromising emission performance.

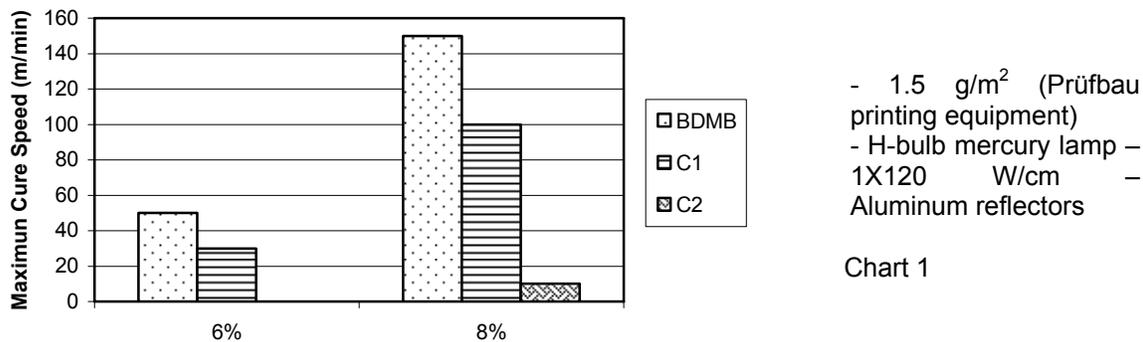
To ensure that odor, taste and composition of the packed products remain unaltered, low emission on the printed coating or ink film is essential. This means reducing odor immediately after curing, minimizing or completely eliminating odor on the formed packaging and preventing migration. Low emission levels are a top priority for the converted printing sector. They depend not only on wet formulation composition but also very strongly on curing, printing and converting conditions. Comprehensive know-how of all these is required to achieve high-quality printed packaging.

In terms of additives, and in particular photoinitiators, the profile of a low-emission product [2] or of a product that ensures low emission of the cured film is much more complex. Higher molecular-weight products are often targeted, on account of their lower volatility and bulky structure, which allow unpleasant, persistent odors and migration after curing to be avoided. One approach consists in modifying existing molecules by increasing their molecular weight by various techniques (ballast structures, oligomerization, etc.). The example below shows the potential limits of this approach.

The cure performance of an alpha-aminoketone (BDMB) is compared with an analogous product (C1), which is ballasted with caprolactones (C2; n=3).



The cure performance (chart 1) of each of the three photoinitiators has been measured at 6 and 8% (w/w) in a UV flexo formulation containing a PB15:3 pigment (circa 11%).



The results are typical of what is often observed when the process is restricted to the increase of the molecular weight of a known photoinitiator or photoinitiator class:

- First of all, the modification of the substituents to allow subsequent grafting, oligomerization, etc., can affect the photochemical performance of the photoinitiator (See C1 versus BDMD)
- Secondly, even a moderate molecular weight increase (C2) causes a major drop in reactivity (C2 versus C1).

A significant loss of reactivity is clearly a major concern, since in graphic arts applications, printing and converting speeds are very demanding criteria. Hence, a more complex approach needs to be developed in order to be able to increase the molecular weight of the photoinitiator while maintaining a very good cure performance.

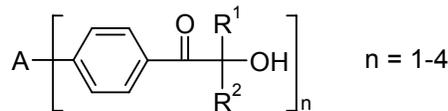
Should we then give up and simply admit that “bulky” photoinitiators are inevitably slow?

They are, however, as already discussed above, highly desirable for sensitive applications in packaging, as they would allow the use of even lower-emission raw materials, provided they don't force a compromise on printing-line productivity.

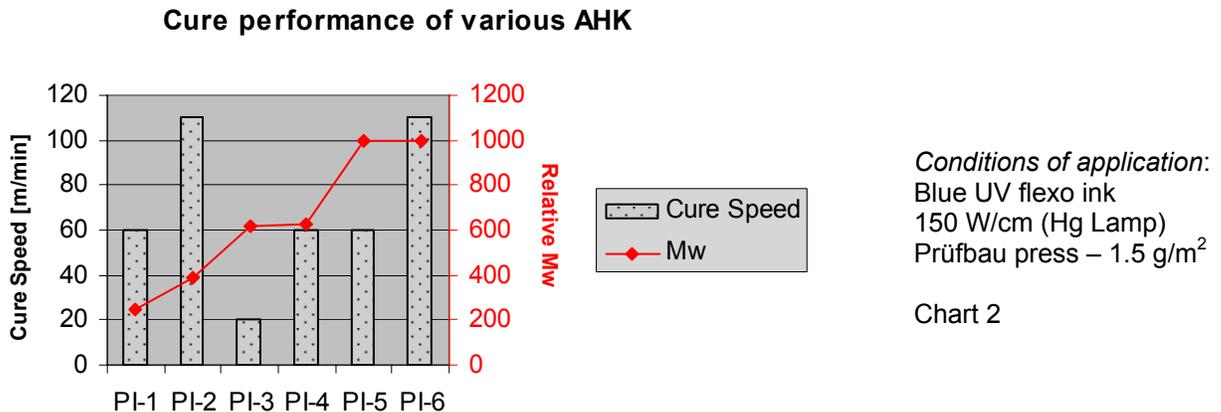
In a recent project, we were able to identify new photoinitiators whose cure performance is not so dramatically affected when their molecular weight is increased.

These photoinitiators belong to the alpha-hydroxy-ketone class (AHK). This class was an important target since there is currently a limited choice of photoinitiators designed for surface cure that exhibit satisfactory surface cure properties. Surface-cure performance is clearly crucial – due to oxygen inhibition – if high converting speed is to be maintained.

The cure speed and molecular weight of a series of AHKs are compared in chart 2. The hydroxyketone component of the initiator is identical for all compounds, while variation of A allows adjustment of the molecular weight:



A comparison of PI-1 and PI-2 shows that increasing the molecular weight does not necessarily reduce photoinitiating efficiency. PI-3, on the other hand, exhibits the typical decrease in performance usually associated with higher Mw. However, PI-4 is able to restore an intermediate cure performance at a Mw comparable to PI-3. Finally, PI-5 and particularly PI-6 demonstrate that it is possible to attain the high performance level of PI-2 despite a high Mw (ca 1000). Products with the structure and performance profile of PI-6 are currently the focus of our attention.



Structural information and concepts underlying the design of PI-6 cannot be shared at this point and precise explanations of performance variations in a relevant ink formulation are not yet available. However, kinetic measurements in a model acrylate formulation have been carried out in Prof. C. Decker's laboratory at the Ecole Nationale Supérieure de Chimie de Mulhouse [4],

Chart 3 shows the similar kinetic behavior of PI-2, PI-4, and PI-6 in terms of double bond conversion, in contrast to the results in blue flexo ink. The complex interplay of all factors involved (light, intensity, concentration, termination reactions, etc.) makes it difficult to rationalize the results with a simple explanation.

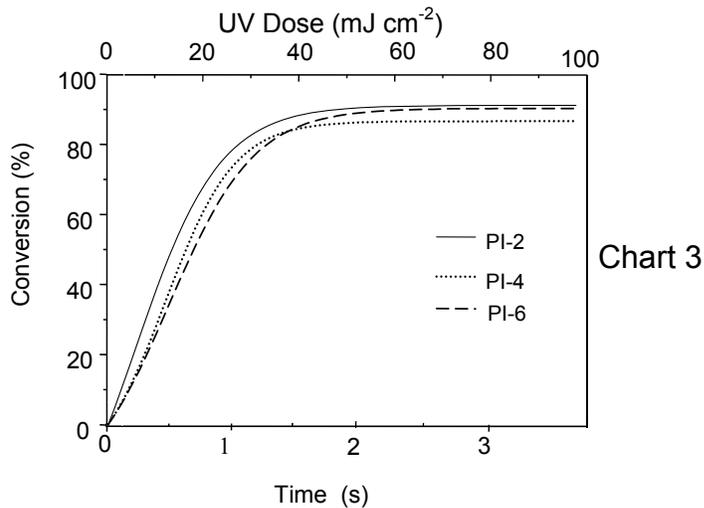


Chart 3: Double bond conversion of a model formulation (70% Ebecryl® 8402 : 30% HDDA, 12 μ m thick) in the presence of 1.5% photoinitiator. Ebecryl® is a trademark of CYTEC.

New developments in cationic curing

This section presents some perspectives based on results obtained with new sulfonium salts.

In this paper we deliberately combine results on new photoinitiators for free radical curing and cationic curing inks. The sterile dispute between supporters of free radical inks and cationic inks does not help the development of radiation curing technology. It is easy to imagine the confusing effect of two directly conflicting presentations on a doubtful converter trying to understand better the benefits of radiation-curable inks

The strengths and weaknesses of both systems are well known and they both require further optimization. It is to be hoped that they will become complementary and allow a wider range of solutions for the printing ink industry. Hopefully also the latent conflict between UV and EB will not cause a new division detrimental to the technology.

We based our research on new sulfonium salts with the following product profile (diaryl-iodonium salts were not targeted, due to their typical persistent odor after curing as well as to synthetic considerations):

- High reactivity in coatings and inks
- Low yellowing
- Low odor
- Benzene-free, harmless breakdown products, preferably free of labeling
- Solid form, good solubility and stability in cationic binders
- Excellent cost-performance ratio

It is also very important to target a compound that could be used in both clear coatings and inks. Today, cationic coatings represent the highest volume. They are technically perfectible and offer the volume and business attractiveness necessary to merit initially an ambitious, radically new development and to ensure commercial success in the longer term. Cationic technology has suffered too long from being perceived as an unaffordable niche. We strive to avoid this pitfall as the original inherent strengths of cationic-cured film deserve raw materials that will promote their development in a wider number of applications.

To develop new sulfonium salts, a cost-effective synthesis route providing compounds with excellent initiation performance is needed. On the cost-performance side, the benchmark of commercially available hexafluorophosphate triarylsulfonium salts is very challenging. Alternative products not generating benzene under UV light are only worth considering if they can match the initiation efficiency of unsubstituted arylsulfonium salts.

The application results of a very promising new class of sulfonium salts are shown below.

The clear coating formulation used for this test had the following composition:

Components	% (w/w)
3,4-epoxycyclohexylmethyl carboxylate	80-85
3-ethyl-3-hydroxymethyl-oxetane	8-12
ϵ -caprolactone triol	4-7
Silicone surface additive	0.4-0.8

The cure performance of the base coating formulation is tested at various PI concentrations (see chart 4). The application and testing conditions were as follows:

- OPV applied with a 4 μ m wire on aluminum foil (85 μ m)
- Cured under Hg-mp 1*120 W/cm with aluminum reflector
- Surface cure tested immediately after curing by rubbing the surface with a tissue. Maximum cure speed under these conditions then determined.

In chart 4, the initiation performance of three new sulfonium salts is compared with:

- TAS-1: commercially available Cyracure® UVI-6992 from The Dow Chemical Company.
- TX-based: a sulfonium salt containing a thioxanthone in its onium structure

All percentages in chart 4 refer to active substances only and not to additional diluents from the supply form.

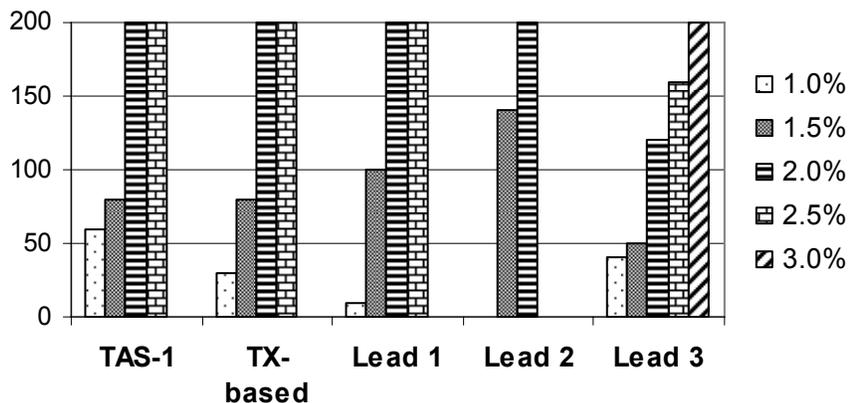


Chart 4

Curing performance results from our lead candidates are very encouraging as they match the state of the art TAS-1. The small differences in curing activity at 1% should be regarded with caution, as performance is strongly affected by the presence of water, which acts as an efficient inhibitor. At higher concentrations, the excess of active PI overcomes the influence of humidity in the curing environment.

As previously mentioned, we believe that a sulfonium salt that shows good versatility in both clear and pigmented systems will have higher value and greater potential. Hence, the yellowing performance of the products tested was also assessed (see chart 5).

Testing conditions were as follows:

- OPV were applied at 30 μm thickness on white board
- Curing was performed at 20 m/min under Hg-mp 1*200 W/cm with aluminum reflector
- Yellowing was determined by calculating the average of 2 values of b^* (CIE lab), measured with a Minolta spectrophotometer

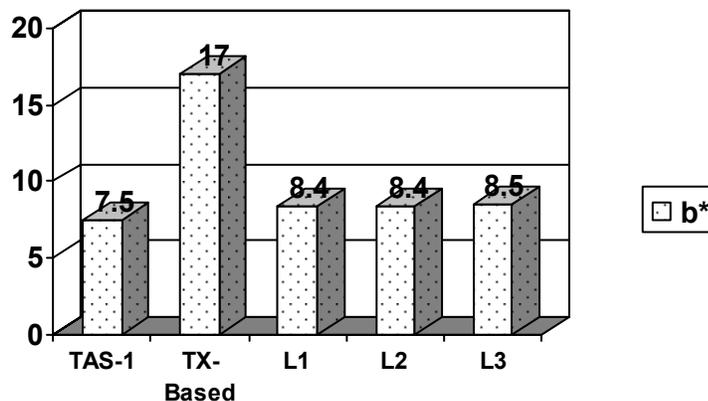


Chart 5

As far as yellowing is concerned, our lead candidates exhibit only a minor increase in yellowing compared to state of the art TAS-1 at 30 μm film thickness. They are therefore suitable for clear coatings for graphic arts applications.

Positive results were also obtained for:

- Thermal stability: stable DSC profile (pure compound) up to high temperature and good storage stability at 70°C in formulations
- Residual odor after curing: a very mild odor in simple laboratory "sniffs" tests.

Conclusion

New additives for both free-radical and cationic polymerization show very encouraging results. It is to be hoped that the new perspectives offered by these raw materials will support the development of converting strategies that will make the best use of complementary techniques such as curing under inertization [3], management of heat and UV radiation [1], substrate modification [5], etc. Economic considerations clearly play a major role in the future success of raw materials that enhance performance. Detailed processes and converting breakdown cost structures need to be thoroughly investigated as mere cost/kg calculations will not be a sufficient incentive.

References:

- [1]: S. Villeneuve et al., can UV Curing Inks and Coatings Exhibit enough Technical and Economical Advantages to penetrate into Flexible Packaging applications?, Radtech 2005, Barcelona.
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- [5]: S. Villeneuve, J.P. Wolf et al., New Priming Technology, JCT Coatings Tech, May 2004, p 46-51