

Reduction of photoinitiator migration through control and optimization of the UV-curing process

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Abstract

A number of parameters are expected to affect photoinitiator migration after a UV-curing process. The influence of curing conditions on the extent of photoinitiator migration was investigated with special focus on UV dose and photoinitiator structure. The amount of migrating species was evaluated by a specially designed analytical method. UV-dose-indicating formulations were used to allow rapid optimization of the UV-curing process with the objective of minimizing photoinitiator migration.

Introduction

A “green” technology, UV-curing continuously finds new applications in different industrial sectors but concomitantly also faces new issues, in particular in printing ink applications, where migration of photoinitiators from the packaging into food made headlines in newspapers a few years ago.

This phenomenon is essentially due to unreacted photoinitiator but also to by-products formed by photoinitiator photolysis and not involved in a polymerization reaction. Figure 1 shows typical by-products formed during photocleavage of α -hydroxyketone HK-1: they are generated by cage reactions, rearrangements or recombinations¹. Volatile by-products release the film during or just after exposure to UV-light and in some cases engender a strong odor, while molecules with a higher molecular weight remain trapped in the cured ink but can be extracted when entering into contact with an organic or aqueous phase.

Until recently, non-cleavable photoinitiators undergoing bi-molecular initiation in the presence of hydrogen donors (amines, amino-acrylates, ethoxylated monomers, etc.) were considered viable alternatives for low-emission coatings. Typically benzophenone or thioxanthone derivatives, they were unfortunately found to migrate significantly, as for instance publicly reported at the end of 2005². While these small additives do not generate secondary breakdown products, they have the disadvantage of not participating in the polymer initiation process and are therefore not grafted or attached in the final network. As a result, they are fully “available” to migrate from the film.

Increasing the molecular weight of the photoinitiator is an alternative way of reducing its mobility and consequently its ability to migrate, but this is achieved at the expense of reactivity: so far no adapted product, i.e. a photoinitiator with good reactivity and low/no emission is available on the

market. This is to some extent due to the lack of expertise in the area of migration analyses, a procedure that is crucial to all stages of development in the design of photoinitiators.

This paper describes new approaches at Ciba designed over the last few months to develop low emission photoinitiators: an analytical method was especially devised to monitor photoinitiator migration in a worst-case scenario in order to understand the phenomenon, differentiate photoinitiators and optimize this development work. The influence of the following parameters on migration was investigated:

- structure of the photoinitiator
- light dose.

The last part of this paper describes the use of UV-dose-indicating inks to monitor risk of migration on-line.

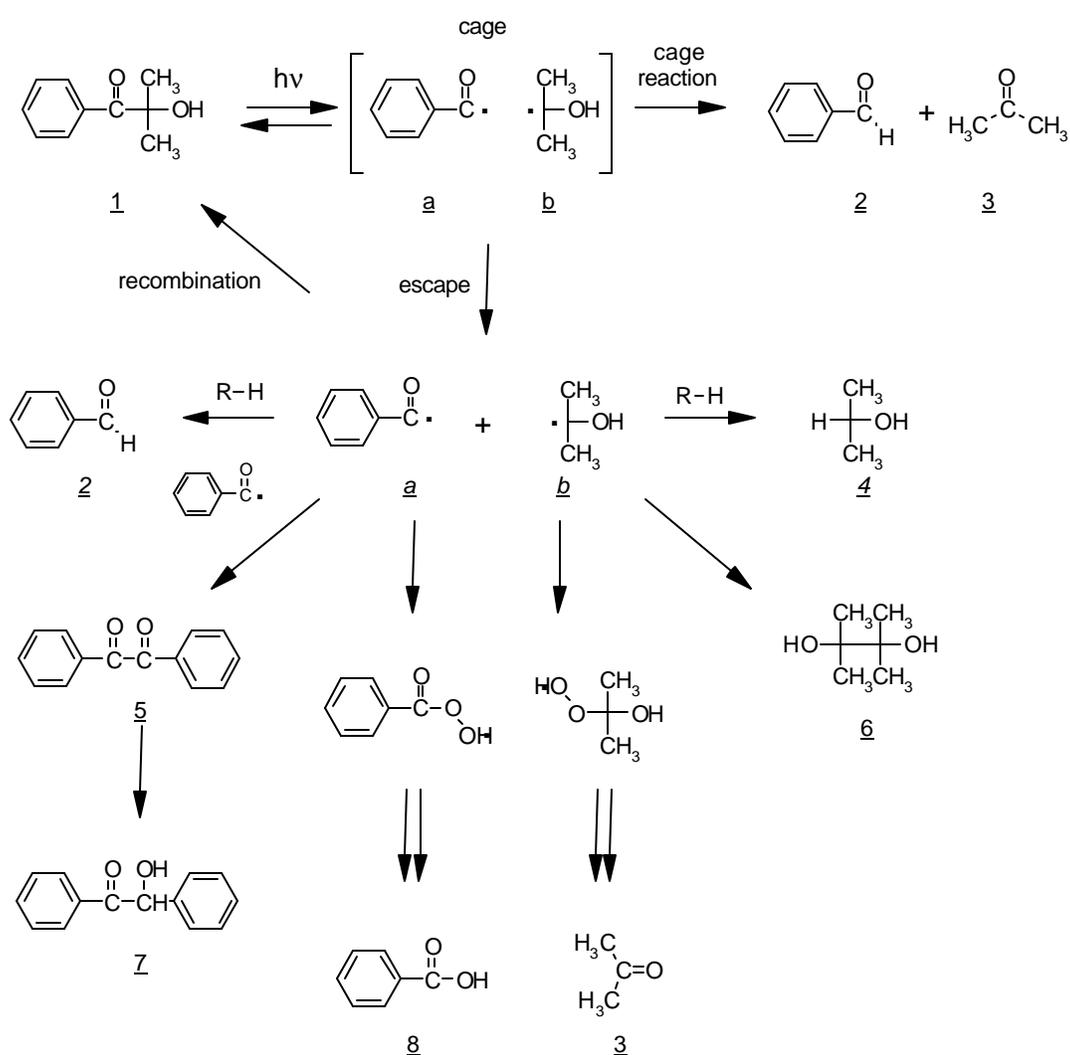


Figure 1: By-products generated during photolysis of HK-1¹

Experimentals

Formulation

For migration tests, radical photoinitiators were incorporated in a radically curable blue flexo UV ink at a concentration of 3 wt%. The flexo UV-curable ink was applied on aluminum foil using a Prüfbau printing machine.

With cationic systems, 2.5% cationic photoinitiator was incorporated in a cycloaliphatic epoxide and 12 μm thick films were applied on PET film. ANTHRACURETM UVS-1331(9,10-dibutoxyanthracene), further called DBA, was kindly supplied by Kawasaki Kasei Chemicals Ltd.

UV irradiation

UV exposure was performed on an IST UV belt line equipped with a medium pressure mercury lamp (from 80 to 200 W/cm) at different belt speeds and under different atmospheres.

Migration

Test samples were immersed in ethanol 95%, placed in a pre-heated oven and left there for 2 hours at 70°C. HPLC-UV was used to quantify extracted photoinitiator and by-products. These conditions correspond to the extraction of the photoinitiator from the printed ink placed in direct contact with the food simulate, which does not give the real levels of migration but provides a worst-case scenario, allowing differentiation between several photoinitiators.

Curing efficiency

Cure speeds were measured by determining dry rub resistance (DRR) and performing the KMnO₄ test (optical density measured after 1 min contact).

Chemical modifications resulting from acrylate crosslinking were monitored by IR spectroscopy with an ATR unit for surface measurements (Digital FTIR Excalibur Spectrometer FTS 3000 MX). The reaction of the acrylate double bonds was determined quantitatively by monitoring the disappearance of the IR band at 810 cm⁻¹ characteristic of the acrylate double bond³.

Results and discussion

The influence of photoinitiator structure on migration was investigated for the first time. Please note that migration results presented thereafter correspond to a worst case scenario (direct extraction from the ink by the solvent) and levels of migrants given here are much higher than those encountered in reality: these results should, however, allow us to observe the behavior of different types of photoinitiator.

1. Structure of the photoinitiator

1.1. Radical photoinitiator

Figures 2 and 3 confirm that both α -aminoketone AAK-1 and APO-1 (bis-acyl-phosphine oxide) address the demand for low migration red-shifted photoinitiators for through cure of colored and thick films⁴. Under these drastic extraction conditions, migration levels obtained with α -aminoketone AAK-1 and acyl phosphine oxide APO-1, as well as their respective by-products, are significantly lower than

with hydroxyketone HK-2, and also tend to have low migration under realistic analytical conditions: development work will therefore focus on hydroxyketones.

The structure of HK-2 (MW ~ 350 g/mol) was modified as shown in Figure 4 to give MacroPICS-1 with:

- presence of highly volatile breakdown products to ensure no persisting odor
- on the other side (literally and figuratively), presence of heavy and/or crosslinkable breakdown products with very low migration potential
- ability to crosslink with the acrylic network to minimize migration from parent molecules and increase network density
- higher molecular weight to minimize migration from the cured film (diffusion or extraction from the film and contamination of the non-printed side – inner side – of the packaging)
- highest possible cure efficiency to maintain formulation equilibrium and overall cost structure.

As shown in Figure 3, migration of MacroPICS-1 drops by a factor of almost 2 compared to HK-2, confirming that increasing molecular weight efficiently reduces migration levels.

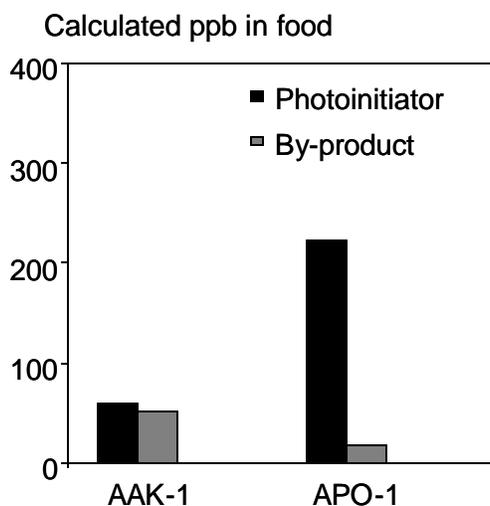


Figure 2: Migration of AAK-1 (MW ~ 370 g/mol) and APO-1 (MW ~ 420 g/mol) and their main by-product in ethanol 95% at 70°C - 2% PI in blue flexo ink, 500 ppm, lamp output=200 W/cm, belt speed=20 m/min under nitrogen – direct extraction

Molecular weight is usually increased at the expense of reactivity: Table 1 confirms that a similar cure level is obtained with MacroPICS-1 as with HK-3 after light exposure in air. Obtaining such a combination of high molecular weight and high reactivity is a major breakthrough, as several molecules had to be designed to achieve the best performance.

| Photoinitiator | Molecular weight (g/mol) | Acrylate conversion (%) after UV-exposure |
|----------------|--------------------------|---|
| MacroPICS-1 | Between 900 and 1200 | 87 |
| HK-3 | 200 | 90 |

Table 1: Comparison of cure levels achieved with MacroPICS-1 and HK-3 5 wt% photoinitiator in an overprint varnish, m. p. mercury lamp 200 W/cm at 60 m/min under air

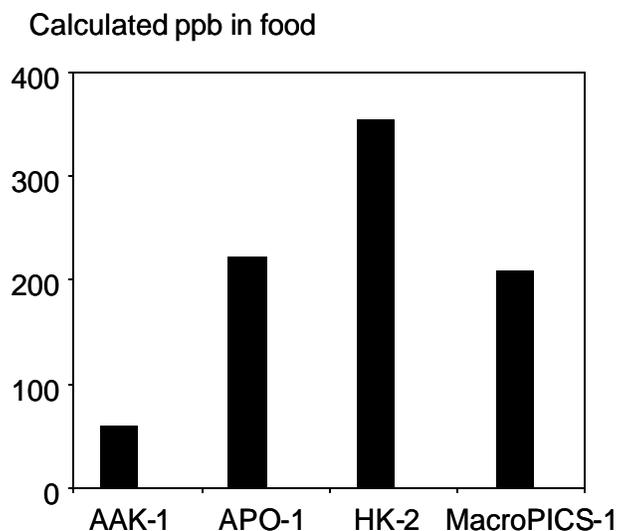


Figure 3: Migration of photoinitiator of different categories in ethanol 95% at 70°C
2% PI in blue flexo ink, 500 ppm, lamp output=200 W/cm, belt speed=20 m/min under nitrogen – direct extraction

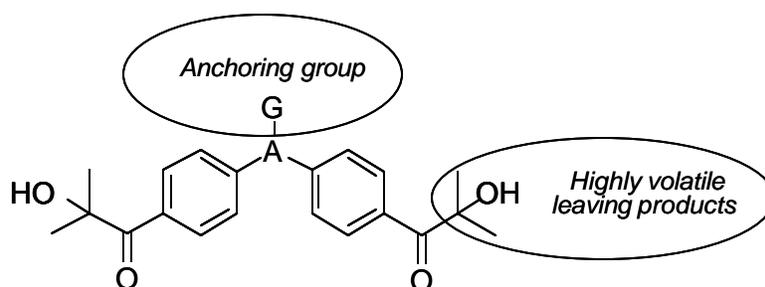


Figure 4: Structure of MacroPICS-1

| Photoinitiator concentration | HK-1 | | HK-2 | | MacroPICS-1 | |
|------------------------------|---------------------|------------------------|----------------------|------------------------|---------------------|------------------------|
| | Cure speed (m/min) | O.D. KMnO ₄ | Cure speed (m/min). | O.D. KMnO ₄ | Cure speed (m/min) | O.D. KMnO ₄ |
| 1% | 200 | 0 | 200 | 0 | 200 | 0.03 |
| 0.5% | 200 | 0.1 | 200 | 0 | 200 | 0.09 |
| 0.25% | 200 | 0.1 | 200 | 0.1 | 200 | 0.13 |
| 0.125% | 180 | 0.2 | 200 | 0.2 | 160 | 0.21 |

Table 2: Comparison of the performance of different photoinitiators under inert atmosphere
Overprint varnish, m. p. mercury lamp 200 W/cm, 500 ppm oxygen, cure speed measured by DRR and optical density O. D. after KMnO₄ test

Additional reactivity tests were conducted under inert atmosphere to avoid the detrimental effects of oxygen inhibition^{5,6} and reduce migration as well as residual odor. Lower emission is obtained because higher crosslinking density of the cured film is achieved and also fewer additives are required. The curing performance of MacroPICS-1 was therefore observed at different concentrations and compared to HK-1 and HK-2: Table 2 confirms that MacroPICS-1 has good reactivity and that working under oxygen-reduced conditions allows a significant reduction in the amount of photoinitiator required (up to 0.25%) while simultaneously ensuring the maintenance of high cure speed. As a consequence, the extent of migration (photoinitiator and by-products) is significantly reduced: results will be reported in a forthcoming paper.

1.2. Cationic photoinitiator

Emission and migration in cationic UV-curing have also been a major concern for years: the release of low amounts of benzene has been observed for non-substituted di- and tri-aryl cationic salts. Since cationic UV curing is used in food contact applications, the printing industry is seeking alternatives.

We have designed a new cationic sulfonium salt CAT-1, taking into consideration all aspects that can improve the toxicological profile of the photoinitiator and its performance. As shown in Figure 5, aromatic rings have been substituted with bulky groups to reduce its ability to migrate.

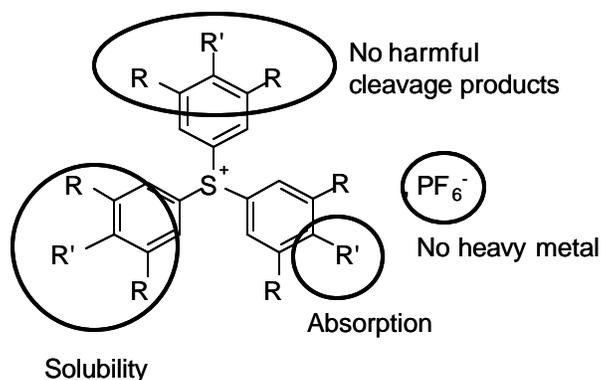


Figure 5: Structure of new cationic photoinitiator CAT-1

Table 3 summarizes the reactivity of CAT-1 and compares it to commercial sulfonium salt CAT-2: under these low-intensity curing conditions, CAT-1 has a significantly higher cure speed than CAT-2 (45 s drying time vs. 120 s in the presence of 9,10-dibutoxyanthracene DBA) in spite of its higher molecular weight. The second valuable piece of information shown in this table is the sensitizing effect of DBA, which seems to be more efficient with CAT-1 than with CAT-2.

| Sensitizer | Concentration | CAT-1 | CAT-2 |
|------------|---------------|-------|-------|
| - | - | 60 | 120 |
| DBA | 0.25 | 45 | 120 |
| | 1.5 | 30 | 55 |
| CPTX | 1.5 | 50 | 110 |

Table 3: Drying time (s) of a cationic clear formulation measured by thumb twist High pressure mercury lamp (V valve) 366 nm, light intensity: 1 mW/cm²

Migration results of CAT-1 are under investigation and will be reported in a forthcoming paper.

2. Influence of light dose

Developing HMW photoinitiators is the key to minimizing migration, but it is also essential to select the right curing conditions, such as the curing atmosphere and in general all parameters impacting the efficiency of the process, with emphasis on the light dose. Indeed, the quantity of light controls the amount of unreacted photoinitiator and the crosslinking density of the ink, which will directly impact migration ability.

The results reported thereafter focus on AAK-1, but similar behavior is expected of other types of photoinitiators. Levels of migrants (photoinitiator and by-products) were measured for three inks cured under light doses ranging from 330 to 530 $\text{mJ}\cdot\text{cm}^{-2}$ (Figure 6). As expected, the higher the light dose, the lower the AAK-1 migration, which can be explained by improved conversion of the photoinitiator. A much more interesting observation is the migration of the by-product, which remains stable irrespective of light dose: increasing the quantity of light thus improves the crosslinking density, consequently decreasing the ability of migrants to remove the film during extraction.

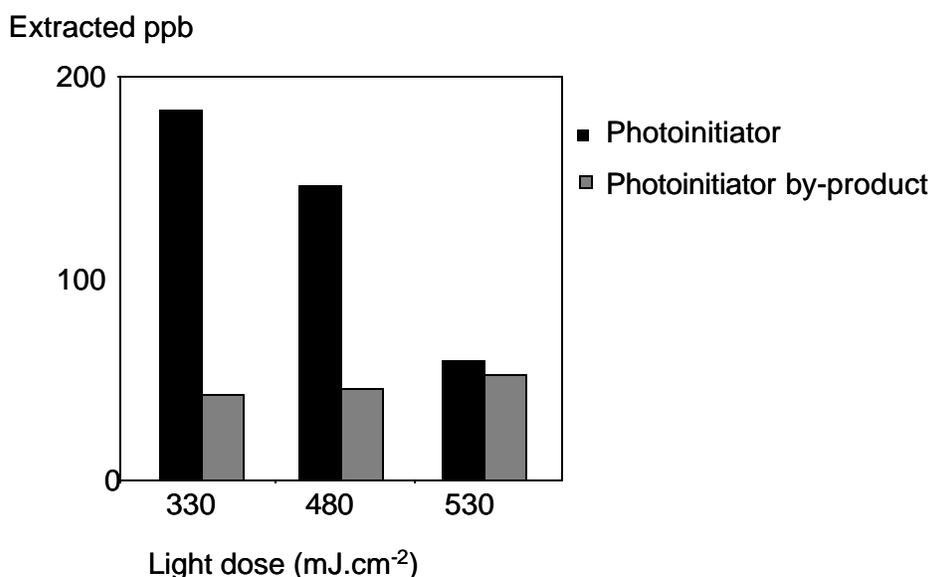


Figure 6: Migration of AAK-1 and by-product exposed at different light doses
2% PI in blue flexo ink, 500 ppm, under nitrogen – direct extraction in ethanol 95% at 70°C

3. On-line control of UV dose

Monitoring the UV dose is therefore of high interest to the printing industry: as mentioned in the previous paragraph, the quantity of light directly impacts the efficiency of the UV-curing process. This is especially true for lines running at very high speeds where minor dose changes might have dramatic consequences on film emission.

As reported in a previous paper⁷, a new tool has been developed to allow on-line monitoring of the light dose: this UV-dose-indicating ink can be applied via a printing unit or by inkjet at one place on the

packaging. Curing is initiated on submission to the UV-curing process and the ink simultaneously develops color. As shown in Figure 7, color depends on the amount of light absorbed by the film, thus allowing fast and cheap evaluation of the UV dose once the process is completed. Defined for a specific ink, a calibration curve indicating photoinitiator migration level as a function of coloration (example shown in Figure 8) allows rapid assessment of expected migration levels.

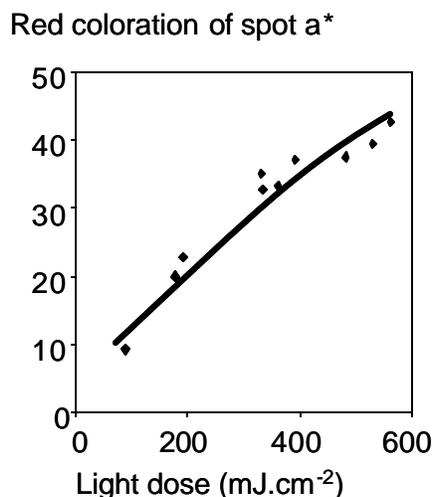


Figure 7: Coloration of the UV-dose-indicating ink as a function of the light dose

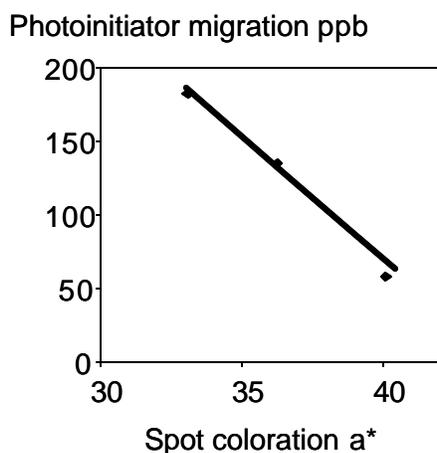


Figure 8: Migration of AAK-1 from a blue flexo ink by direct extraction in ethanol 95% at 70°C as a function of the coloration of the UV-dose-indicating ink

Conclusion

This preliminary work allowed us to design a reproducible analytical method to monitor photoinitiator migration in UV-printed inks and to differentiate photoinitiators. The extraction method presented in this paper is a worst-case scenario of direct contact solvent/ink at high temperature, and does not correspond to realistic migration levels in final packaging applications: a more realistic method is under development.

To reduce migration risks, photoinitiator structure is the first element which has to be optimized essentially through its molecular weight. Extensive work has been done to design high-molecular-weight photoinitiators with good reactivity.

The right photoinitiator also requires the right curing conditions: in the case of radical UV-curing, working under inert conditions improves the photolysis of the photoinitiator and ensures much better control of the reaction, thus reducing the amount of migrants. Simultaneously, it allows the amounts of photoinitiator required to be significantly reduced while maintaining high cure speed.

Constant control of the light dose is mandatory to ensure proper curing on UV-printing ink lines. UV-dose-indicating inks have been developed that allow on-line monitoring of the light-dose: a spot applied by inkjet on the packaging cures and at the same time develops color as a function of the dose.

From the findings described above, we conclude that suitable combination of component selection and process conditions should permit the production of high-quality packaging at viable cost.

Acknowledgments

The authors thank *Kawasaki Kasei Chemicals Ltd* and *Ciba Inc.* for permission to publish this article.

Special thanks also to A. Metzger and Dr. G. Weidenbrück for checking the article, and to G. Haller and B. Spony for the experimental work.

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