

High performance cationic photoinitiators with low emission properties

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Abstract

A new, high molecular weight triaryl sulfonium photoinitiator is described. The structure has been optimized in order to reach the lowest migration levels, both for the photoinitiator and for its photocleavage products. The photoinitiator shows a high performance in cationic overprint varnishes (OPV), pigmented inks, and adhesives. The suitability of the product for sensitive applications, such as flexible food packaging is supported by set-off migration tests.

1. Introduction

In 1999, traces of benzene were discovered in printed yoghurt lids in Europe. Benzene had been released as a by-product from the most commonly used triaryl sulfonium salt photoinitiators. This was a major setback for cationic UV curing technology. As a result, the growing market of mid and wide web flexo printing onto plastic substrates was badly hit¹.

Since then, emission and migration of the photoinitiators and their by-products has been recognized as a challenge for UV curing in general, both radical and cationic². The availability of analytical tests capable of detecting chemicals at extremely low concentrations has raised awareness of potential exposure to chemicals among consumers³. At the same time, regulations become increasingly stringent and guidelines calling for specific maximum concentrations of by-products are being issued⁴.

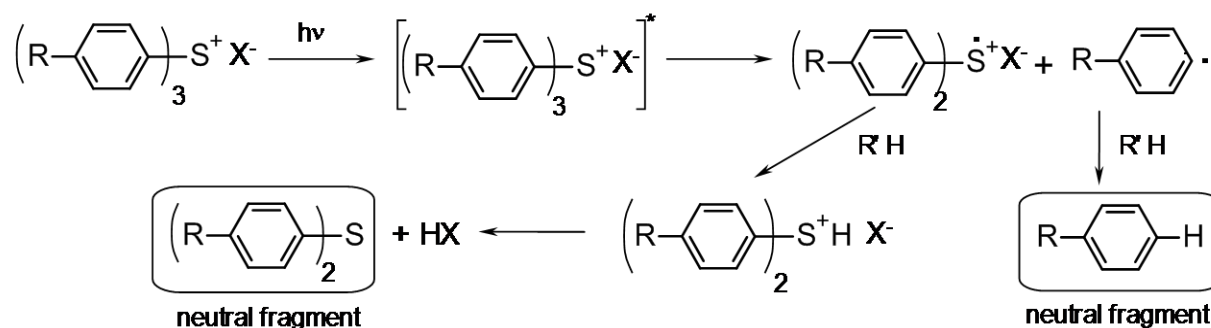
Cationic UV curing is still a niche application in graphic arts compared with the radical technology based on acrylate chemistry. On the other hand, the well-known advantages of cationic formulations (low shrinkage, good adhesion, and superior chemical resistance) would certainly help them gain market shares if efficient photoinitiators with a better emission and migration profile were available. Attractive applications exist if the legitimate concerns of converters, food companies, and consumers are properly addressed.

The dilemma is to reconcile high technical performance and low emissions because photoinitiators with the lowest migration, which are typically high molecular weight compounds, usually give slower cure speeds than small, mobile photoinitiators⁵.

2. Design of photoinitiator

With cationic photoinitiators, e.g., triaryl sulfonium salts, the polymerization starter (**HX** in scheme 1) is not produced by the primary photochemical reaction, but at the end of a series of reactions⁶. The chromophore of the photoinitiator is not chemically bound to the polymer chain but is

decomposed into neutral fragment of lower molecular weight. Therefore, the properties of those photocleavage products must be considered in the design of low emission cationic photoinitiators. From the simplified initiation mechanism of scheme 1, it is clear that sulfonium salts with unsubstituted phenyl groups ($R = H$) at the central sulfur atom will inevitably produce benzene as a breakdown product. Of course, introducing substituents on all three aryl groups ($R \neq H$) will increase the overall molecular weight, which is expected to lower emissions and migration. At the same time, increasing the molecular weight will translate into a lower number of sulfonium sites per gram. This, however, can lead to a loss of performance unless molar extinction coefficients are improved⁷.



Scheme 1: Simplified photolysis mechanism for a triaryl sulfonium salt. The heterolytic pathway and in-cage reactions are omitted. Adapted from Dektar and Hacker, ref 6.

One possible approach to “benzene-free” sulfonium salts is to incorporate phenyl rings into cyclic structures, such as thianthrenium⁸ or thioxanthonium^{1,9} salts (**A**, fig. 1). In this case, only one substituent $R \neq H$ has to be introduced. Compounds with $R' = H$ will not lead to photorelease of benzene. However, the heterocycle itself may be a problem. When $Y = (C=O)$ and $R' =$ isopropyl, ITX will be formed as a by-product and it may not be acceptable.

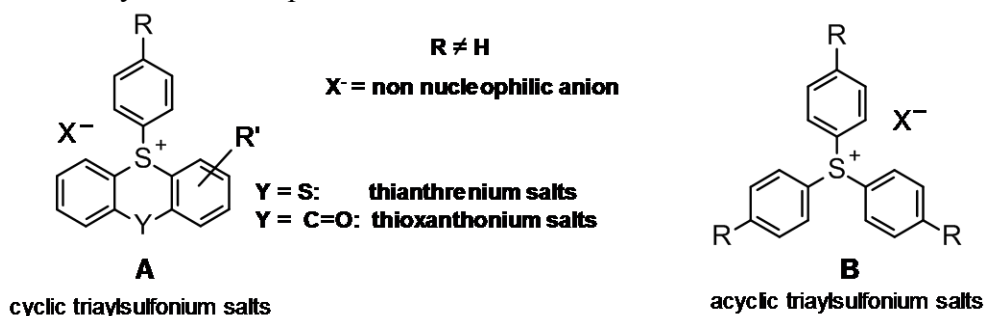


Fig. 1: “Benzene-free” triaryl sulfonium salts

In this article, we report results obtained for symmetrical acyclic compounds of type **B**. Since all three C-S⁺ bonds in **B** are equivalent by symmetry, salts of this type are expected to yield only two primary photoproducts, Phenyl-R and R-(Phenylene)-S-(Phenylene)-R.

It is important to remember that cleavage products from the chromophore are not chemically bound to the polymer network and are, therefore, available for extraction and migration. We have designed a new cationic sulfonium salt, **CatS-1**, taking into consideration all aspects that can improve the toxicological profile of the photoinitiator and its performance¹⁰. All aromatic rings of the symmetrical molecule are substituted by bulky groups in order to reduce their ability to migrate (Fig. 2).

Finally, the choice of hexafluorophosphate as anion is dictated by the need to avoid heavy metals and is a compromise between price and reactivity.

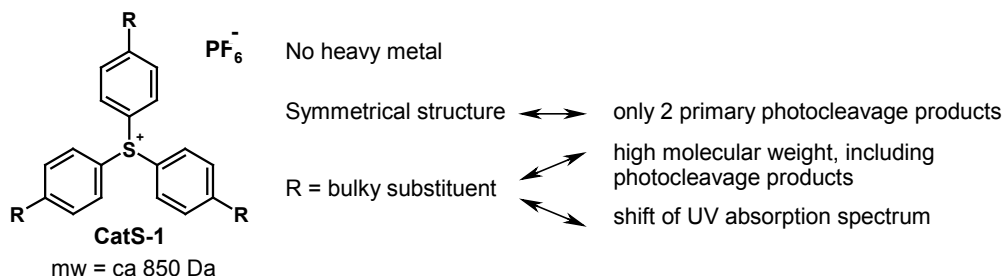


Fig. 2: Main features of of **CatS-1**

Absorption spectra of **CatS-1** and reference cationic initiator salts **CatS-2**, **CatS-3**, **Cat I-1** and sensitizer **DBA** are reported in Fig. 3. The intense band in the UVA region centered at ca. 320 nm matches well the emission spectrum of mercury lamps. As a result, **CatS-1** is expected to be a suitable photoinitiator for OPV and pigmented inks.

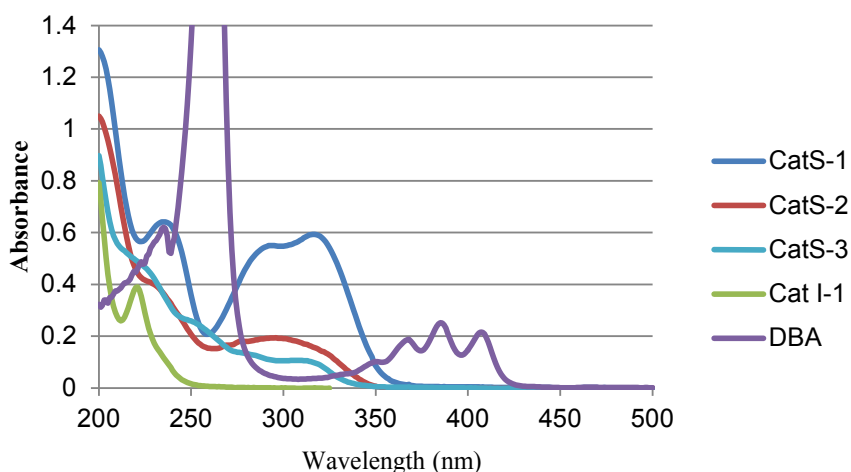


Fig.3: UV absorption spectra of selected photoinitiators. Concentration: 0.001% on solids in acetonitrile. For structures see fig. 4.

3. Materials and methods

Formulations:

Table 1: Cationic clear formulation

Components	Parts (% w/w)
3,4-Epoxy cyclohexylmethyl 3,4 epoxy cyclohexane carboxylate	81.8
3-Ethyl-3-hydroxymethyl-oxetane	11.7
ε-Caprolactone triol	5.9
Silicone surface additive	0.6

The white cationic ink used for set-off migration was composed of 70% w/w of cationic clear formulation and 30% TiO₂ (rutile). 2% CatS-1 and 0.5% DBA were added. The mixture was stirred thoroughly with glass beads during one hour.

Table 2: Formulations for pigmented cationic flexo inks

Component	Yellow	Magenta	Cyan	Black
PY13 (Irgalite Yellow LBG)	13			
PR 254 (Cromophthal Red 2030)		14		
PB 15.3 (Irgalite Blue GLO)			16	2
PBl 7 (Special Black 250)				15
3,4-Epoxy cyclohexylmethyl – 3,4-Epoxy cyclohexane carboxylate	65	64,5	63,5	61,5
3-Ethyl-3-hydroxy methyl-oxetane	18	17,5	16,5	16,5
EFKA 7305	0,5	0,5	0,5	0,5
Luwax AF30	0,5	0,5	0,5	0,5
Propylene carbonate	3	3	3	4
Total	100	100	100	100

Photoinitiators

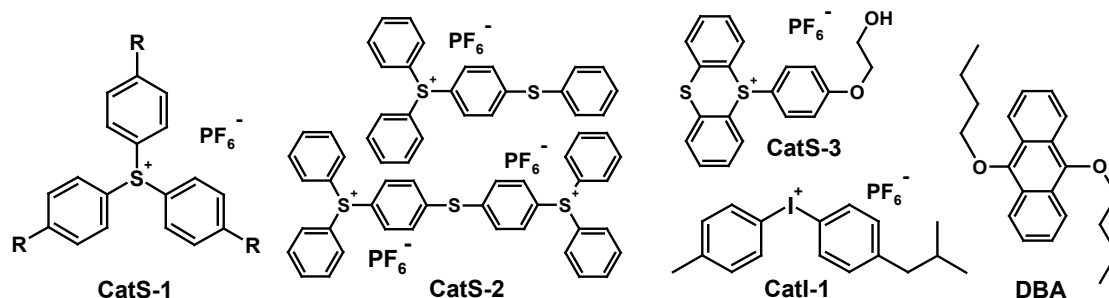


Fig. 4 Photoinitiators and sensitizer tested

Extraction and migration set-up

For set-off migration, fully cured ink samples were pressed against LDPE films sandwiched between aluminum coil coats (with uncoated Al side towards sample or LDPE contact film). The assembly (fig. 5) was placed during one week in an oven at 40°C.

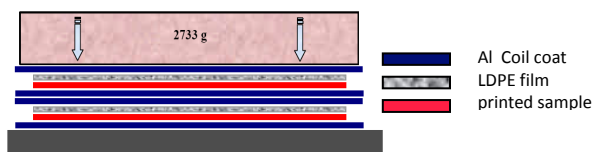


Fig. 5: Set-up used for simulated migration

Discs of 30 mm diameter were cut from the set-off LDPE samples. Each disc of 30 mm diameter was immersed in 25 ml EtOH 95 % (food simulant) in a two-side migration test during 2 h at 70°C. The total surface (two sides) of the disc being 0.141 dm², the volume to surface ratio is 176.68 mL/dm².

Using the EU calculation assuming a volume to surface ratio of 1L/ 6 dm², a concentration of 100 µg/L of a migrant in the ethanol solution corresponds to 106 ppb into food.

The extract was carefully concentrated and analyzed by HPLC using standard solution of reference substances (photoinitiators and photocleavage products). All tests were run in triplicate from three different samples. The detection limit for migrants is < 1 ppb into food. Quantitative values can be given for concentrations > 1 ppb into food.

4. Results and discussion

4.1 Performance in overprint varnishes and pigmented inks

Fig. 5 shows the performance of **CatS-1** and reference initiators in a cationic OPV. **Cat I-1** and **CatS-2** both release volatile species — toluene and benzene respectively. **CatS-3** is an example of a commercial "benzene-free" triaryl sulfonium salt of type A.

At a concentration of 2% (on solids), **CatS-1** is significantly more reactive than **Cat I-1**. This may be due to better light absorption. On the other hand, **CatS-1** is slower than **CatS-2**; probably as a consequence of the lower molecular weight of the latter, which corresponds to a larger number of acid equivalents per weight. At 4%, **CatS-1** is found to be slightly more active than **CatS-2**, possibly due to the softening effect of the propylene carbonate contained in **CatS-2** (50% by weight).

Interestingly, in spite of its lower molecular weight, **CatS-3** is much less reactive than **CatS-1** at both concentrations. Structural differences present in **CatS-3** may affect the efficiency of acid generation.

All results were obtained with photoinitiators used alone. Higher cure speeds can be reached with iodonium and sulfonium compounds in the presence of suitable sensitizers^{11,12}. However, the sensitizers are also small molecules that can migrate, even though they are typically used at lower concentrations than the photoinitiator. This point will be addressed later.

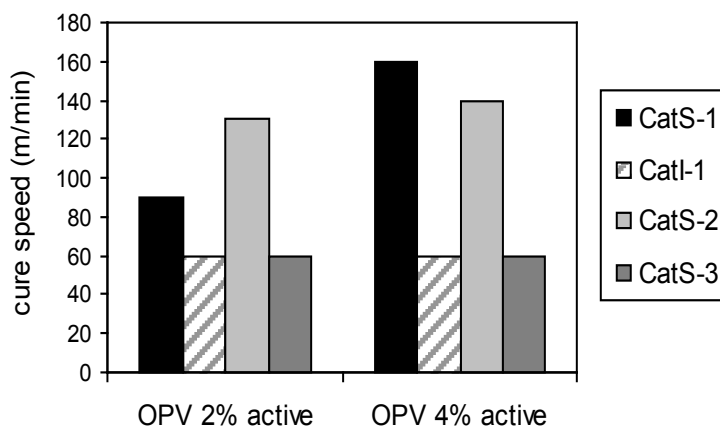


Fig. 5: Cure speed of a cationic OPV (6µm on coil coat) with selected photoinitiators. Curing conditions: 80 W/cm Hg lamp with Al reflector, 45-50% relative humidity

Tests in pigmented flexo inks are reported in Fig. 6. As expected, the reactivity sequence is Yellow > Magenta > Cyan. **CatS-1** is faster than the iodonium salt **Cat I-1** and slightly less efficient than **CatS-2** at the same concentration of active ('solid') initiator. The use of a cold mirror and the very short post-cure time were selected in order to better judge the initiation steps of the process.

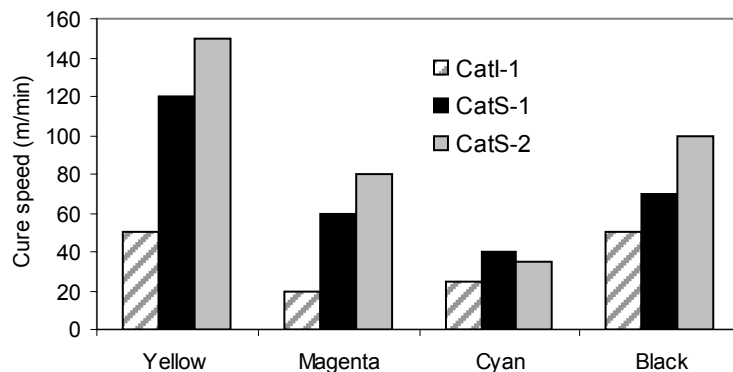


Fig.6. Performance of cationic photoinitiators in pigmented flexo inks, 1.8g/m²; 3% (solids) initiator in colors, 4% in black. Hg lamp 200W/cm with cold mirror, 1 min postcure.

4.2 Performance in film to film lamination adhesives

CatS-1 can be used in other applications: Results in cationic film to film lamination adhesives are shown in Fig. 7. In this application, photoactivation of the adhesives helps provide a long potlife on the coating station. Three formulations were tested with 2% **CatS-1** or **CatS-2**. Peel strength achieved with **CatS-1** is at least equivalent to that of **CatS-2**, and high values are already reached after relatively short postcure (15 min).

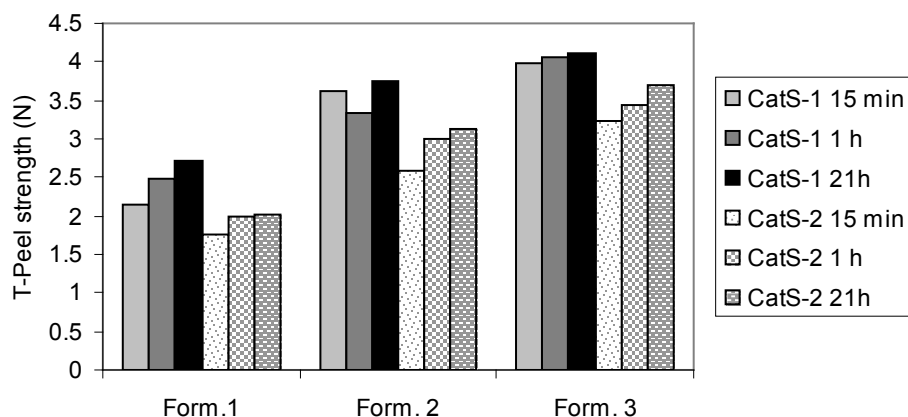


Fig 7: T-Peel strength of 3 adhesives formulations cured with **CatS-1** and **CatS-2**, measured on film to film laminates of BOPP coated with adhesive (4 g/m²). Formulations are based on bisphenol A glycidylether, cycloaliphatic epoxide and oxetane in the following ratios: Form.1: 50:40:10; Form 2: 70:20:10; Form 3: 70:25:5. Time refers to curing time after light activation. Irradiation: 2 mp-Hg lamps, 1.5 J/m²

4.3 Migration

As already mentioned, the symmetrical structure of **CatS-1** leads to the formation of only two primary photocleavage products, which are themselves low migration products. As a consequence of the symmetry, the solubility of **CatS-1** in formulations is sufficient for high performance but low enough to reach extremely low migration. Actually, **CatS-1** could not be detected in the set-off migration test (Table 3).

Table 3: Set-off migration results measured for **CatS-1** in OPV

Cure speed	CatS-1 (ppb into food)	Σ primary photocleavage products (ppb into food)
40 m/ min	<1	17.5
20 m/min	<1	7.4

Cleavage products were only found at extremely low concentrations (7-17 ppb for the sum of all cleavage products into food) and are not expected to be problematic at this level. These results give us confidence that **CatS-1** is also suitable for sensitive applications including indirect food contact.

Obviously, low-migration properties of a cationic formulation do not depend on the photoinitiator alone. One particular cause of concern may be other low-molecular weight components that must be added. In the case of white-pigmented formulations, for instance, a photosensitizer must be added in order to reach a good cure. There would be no point in designing a low-migration photoinitiator if it has to be used in combination with a high migration sensitizer. In the case of sulfonium salts, anthracene derivatives are one of the preferred classes of sensitizers. It was interesting, therefore, to check the behavior of 9,10-dibutoxy anthracene (**DBA**) in combination with **CatS-1** in a set-off migration test.

Samples of white cationic ink (30% TiO₂) coated on Al were cured at 20 m/min under a medium pressure mercury lamp (200 W/cm) and were submitted to the same set-off simulation test as described above:

Table 4: Set-off migration results measured for **CatS-1** in white flexo ink

Component	with 0.5% DBA (ppb into food)	without DBA (ppb into food)
CatS-1	not detected	not detected
Σ of primary photoproducts	<2	<2
9,10-Dibutoxyanthracene	<1	(not detected)

Data from Table 4 show undetectable levels of **CatS-1**, an extremely low migration of the photocleavage products and of **DBA**. There is no difference in the behavior of **CatS-1** and its migrants in the presence of the sensitizer. **DBA** is shown to give very low migration in the test.

5. Conclusion

Cure performance alone is no longer sufficient. Health safety and environmental considerations have become increasingly important. In fact, low emission and migration may even play a decisive role in certain applications. The new initiator presented here demonstrates that high technical performance can be reached and at the same time the most severe migration criteria can be met.

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