

## NOVEL CATIONIC PHOTOINITIATORS

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### **Introduction.**

Interest in the photoinitiated cationic polymerizations of multifunctional epoxydes and vinyl ethers has increased rapidly as this technology has found use in many industrial applications.

Coatings, printing inks and adhesives are three examples of applications in which photo initiated cationic polymerizations have experienced the most growth.

In addition to the recognized properties of cationic inks and coatings, such as excellent resistance and adhesion to difficult substrates, a further advantage that makes the cationic photoinitiators particularly indicated in food packaging applications is the post cure reaction, that minimizes the amount of free monomer<sup>1)</sup>.

These advantages have been recognized in the last years mainly for the development of flexo inks.

The discovery that benzene was generated from the most commonly used photoinitiators during the irradiation process stopped their development in food packaging<sup>2)</sup>.

Expensive iodonium salts<sup>3), 4)</sup> has been proposed in substitution of the triarylsulphonium derivatives, but the release of odour during the curing limits their use in such applications.

For these reasons a new photoinitiator characterized by a fast cure, not releasing toxic by-products during the process represents an important step in the development of cationic technology.

### **Cationic photoinitiators based on thianthrene.**

An easy way to avoid the release of benzene is to block the phenyl rings into a cyclic structure<sup>5)</sup>.

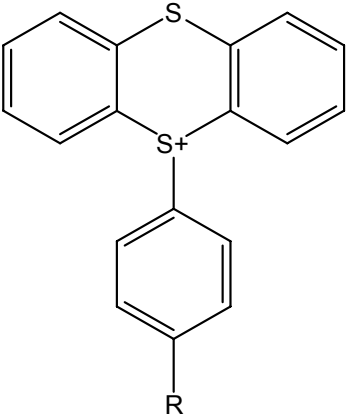
Thianthrene was selected not only for this reason but also considering that the reduction potential of the corresponding thianthrenium salts is lower than the reduction potential of triarylsulphonium salts. This difference is quite important if we consider the possibility to sensitize the photoinitiator by electron transfer from the sensitizer in its excited state to the onium salt<sup>6)</sup>.

A novel series of thianthrenium hexafluorophosphate derivatives were prepared by reaction of substituted aromatic ring with thianthrene oxide in presence of aluminum chloride as catalyst.

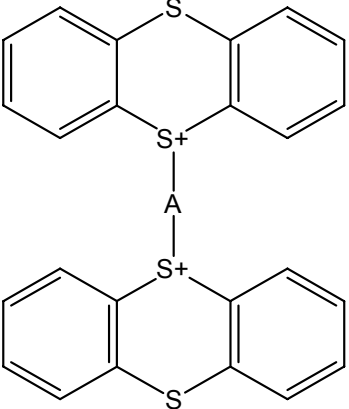
Mono and bithianthrenium chlorides were obtained according to the reagents ratio, then methathesis reaction with potassium hexafluorophosphate gave the final products<sup>6)</sup>. The structures are listed in tables 1 and 2.

To complete the study other thio-heterocycles were synthesized<sup>5)</sup>, their structures are shown in table 3.

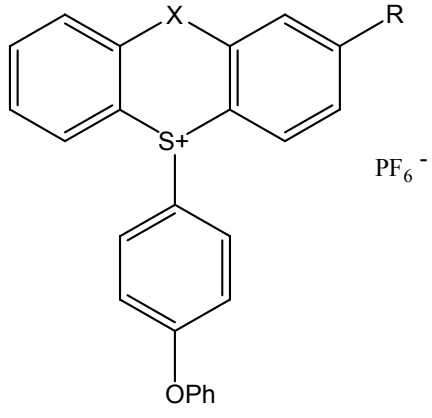
**Tab. 1: Monothianthrenium Hexafluorophosphates**

	Sample	R
	1	CH <sub>3</sub>
	2	CH <sub>2</sub> CH <sub>2</sub> OH
	3	Ph
	4	OC <sub>2</sub> H <sub>5</sub>
	5	OCH <sub>2</sub> CH <sub>2</sub> OH
	6	OPh
	7	SCH <sub>2</sub> CH <sub>2</sub> OH
	8	SPh
	9	F

**Tab. 2: Bisthianthrenium Hexafluorophosphates**

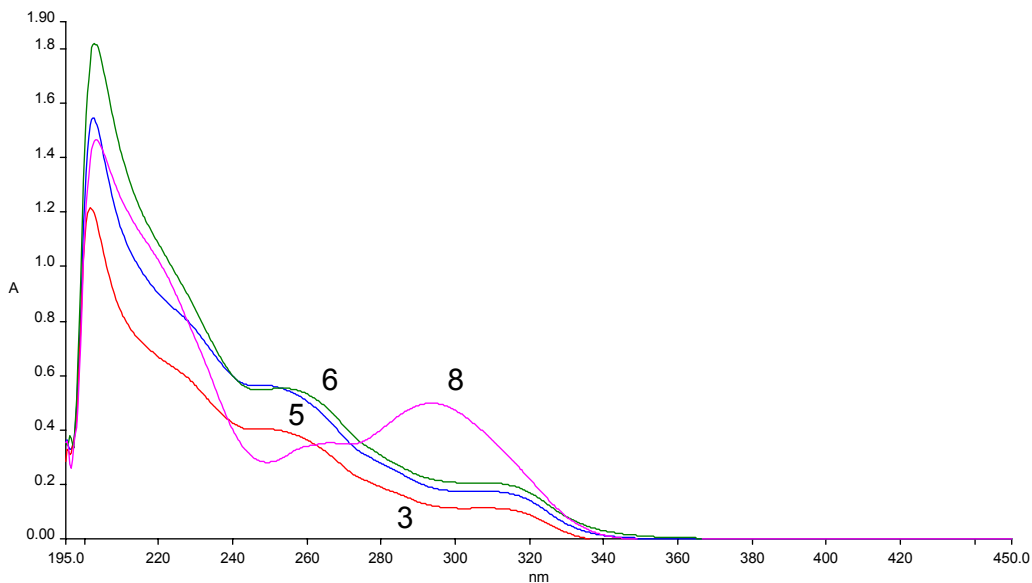
	Sample	A
	10	4,4'- biphenylether
	11	4,4' - biphenylsulphide
12	4,4' - biphenyl	

**Tab. 3: thio-heterocycles derivatives.**

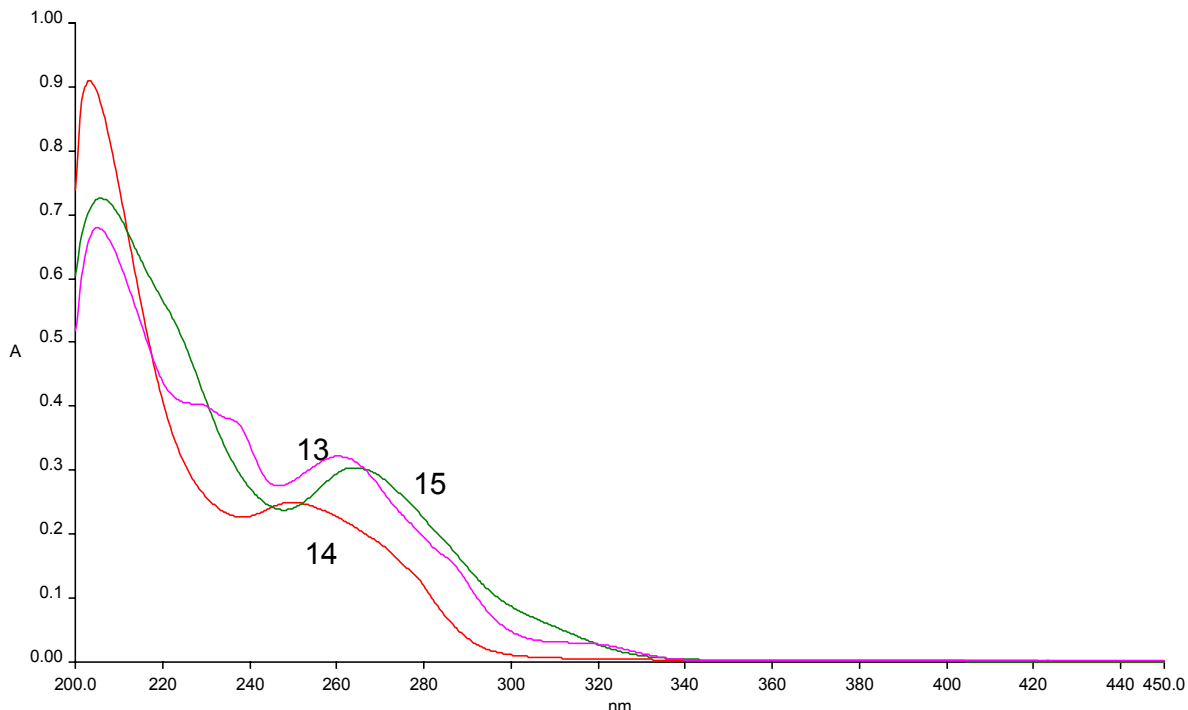
	Sample	X	R
	13	single bond	H
	14	CH <sub>2</sub>	H
15	CO	i-Pr	

### UV spectra of cationic photoinitiators.

The influence of the chemical structure on UV absorption was investigated by the introduction of substituents on the phenyl of monothianthrenium salts (Fig. 1). Other thio-heterocycles were also compared to thianthrene as shown in fig. 2.



**Fig.1:** UV spectra: sample 5 (1.5 mg/100cc, MeOH); sample 3 (1.0 mg/100cc, MeOH); sample 6 (1.5 mg/100cc, MeOH); sample 8 (1.5 mg/100cc, MeOH).



**Fig. 2:** UV spectra: sample 14 (0.61 mg/100cc, MeOH); sample 15 (0.62 mg/100cc, MeOH); sample 13 (0.57 mg/100cc, MeOH).

As shown in fig. 1 the thio-phenyl derivative shows a more intense peak at 280 nm, while the other compounds show a less intense red shifted absorption at about 315 nm. Regarding the thio-heterocycles (fig. 2), the dibenzothiophene derivative 13 shows a reasonable absorption over 320nm comparable to the thianthrenium salt 6.

### **Reactivity of thianthrenium hexafluorophosphates.**

The performances of the thianthrenium hexafluorophosphates were evaluated by scratch test and cure speed for clear and pigmented formulations. The sensitization and the effect of the thianthrenium salt concentration were also investigated.

Esacure 1064, a triphenylsulphonium hexafluorophosphate, and ditolyliodonium hexafluorophosphate (ditolyl-I<sup>+</sup>) were used as reference compounds. All experiments were carried out under controlled conditions of relative humidity.

#### Scratch test.

The influence of some substituents on the phenyl ring was evaluated by the scratch test (ASTM D5178, D2197) on 12  $\mu$ m clear formulations (Sarcacat K126, 83 parts, Rapicure DVE 3, 15.5 parts, Fluorad FC 430, 1.5 parts) containing 4% of photoinitiator dissolved in the same amount of propylene carbonate, exposed under medium pressure Hg lamp at 700 mJ.

The number of passages of 100g pendulum necessary to completely remove the coating were referred to Esacure 1064, the results are listed in table 4.

Samples carrying oxygen, sulfur and fluorine on the phenyl ring were compared. The best performances were observed for samples 5 and 10, both were oxygen substituted. Sulfur and fluorine strongly reduce the activity of the photoinitiators, for this reason these derivatives were not developed.

**Tab. 4: Scratch test.**

Sample	N° of passages referred to Esacure 1064
Esacure 1064	1.00
5	2.35
6	1.00
7	0.74
8	0.81
9	0.89
10	1.42

Cure speed

Formulation based on cycloaliphatic epoxide ( UVR 6105, 86 %) and oxetane derivative (UVR 6000, 10 %) containing 2 % photoinitiator dissolved in the same amount of propylene carbonate were printed onto a substrate to obtain a 4  $\mu$ m film, then cured with a 120 W/cm medium pressure Hg lamp, the cure speed has been set to obtain tack free immediately post curing.

The pigmented formulations, based on cycloaliphatic epoxide ( UVR 6105, 71 %) and oxetane derivative (UVR 6000, 9.5 %) containing cyan pigment (Irgalite blue NGA, 11.5 %) and 4 % photoinitiator dissolved in the same amount of propylene carbonate were tested as for as the clear formulations. The results are shown in fig. 3 and 4.

**Fig. 3: cure speed in clear formulations.**

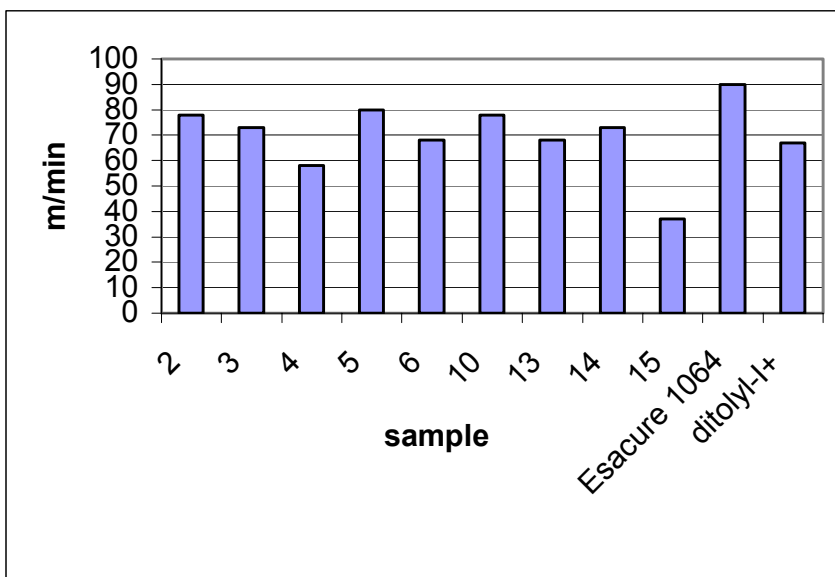
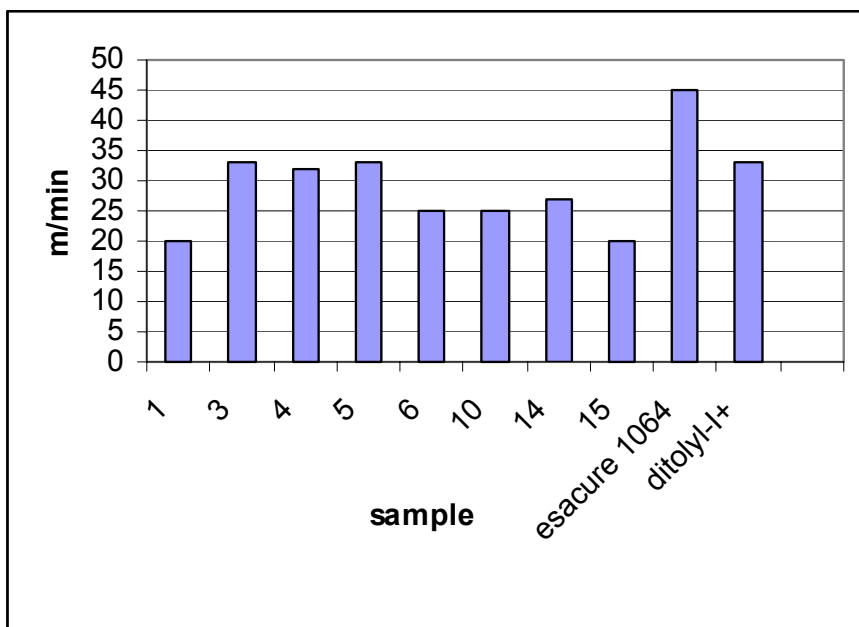


Fig. 4: cure speed in pigmented formulations.



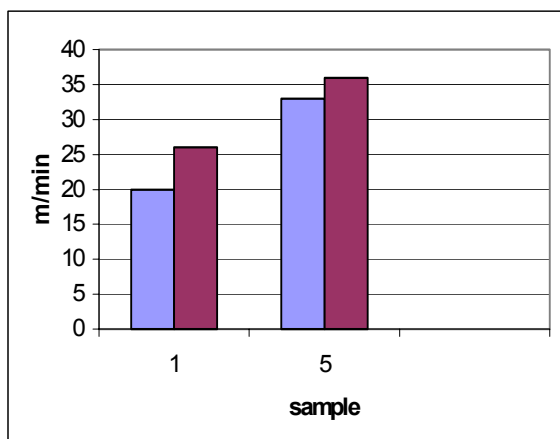
Compounds 2,3,5 and 10 were quite efficient in clear formulation, while compounds 3,4 and 5 gave the best result in the pigmented formulation.

No yellowing was observed in clear formulations . Although the reactivity for clear was quite good, in blue inks the thianthrene derivatives were about 25% less reactive than Esacure 1064 and as reactive as the ditolyliodonium hexafluorophosphate.

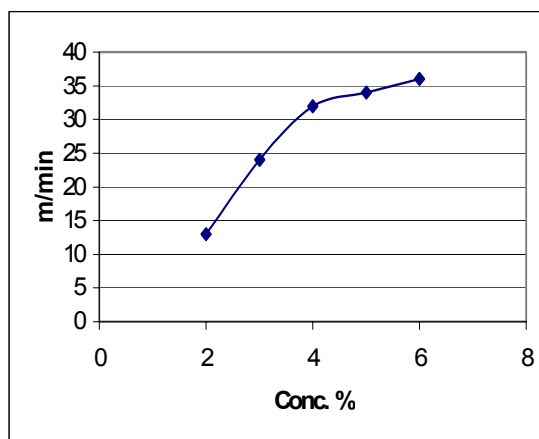
For this reason we have evaluated the reactivity of some compounds in presence of 0.5% sensitizer, the results are reported in fig. 5. The formulation and the experimental conditions were the same used for the cure speed for pigmented system.

Compounds 1 and 5 were sensitized with DBA (dibutoxyanthracene), obtaining respectively 30 % and 9 % improvement of the reactivity, no improvement of reactivity was observed for Esacure 1064.

Finally the dependence of the cure speed from the photoinitiator concentration was investigated for compound 5 in blue ink, observing a reasonable increase of reactivity from 2 to 6% as shown in fig. 6.



**Fig. 5:** Sensitization of thianthrene derivatives



**Fig. 6:** Cure speed vs Photoinitiator conc.

### Evaluation of extractables from inks.

Aim for the development of new cationic photoinitiators is the absence of volatile by-products of toxicological concern, our evaluation was focused on benzene and toluene release. The evaluation was performed pouring the cured material immediately post curing into a head-space sampling device and measuring benzene and toluene by capillary GC. Formulations containing sample 5 were analysed. Benzene and toluene concentration were under the detection limit (<2 ppm). It is also important to note that no odour was developed on cure. In addition the specific migration of compound 5 in water was lower than 0.01 mg/dm<sup>2</sup>.

### Conclusions.

Arylthianthrenium hexafluorophosphate are a class of efficient cationic photoinitiators. Due to the good performance of the monothianthrenium salts and their good solubility in the formulations, a series of 5-alkoxyphenyl-thianthrenium derivatives particularly suitable for food packaging applications has been developed.

### Acknowledgements.

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### References

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