DIFUNCTIONAL PHOTOINITIATORS

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INTRODUCTION

One of the critical issues in energy curing is the migration and the release of photoinitiators or their photodecomposition products from the cured formulation. This is particularly important both in UV curable inks for food packaging and in conventional coatings.
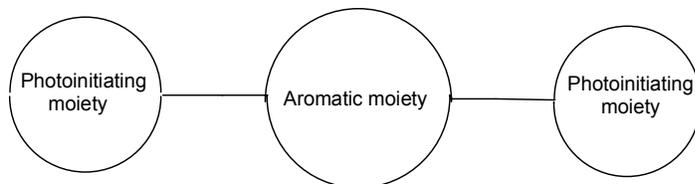Monofunctional photoinitiators suffer this problem because they are generally low molecular weight compounds. If this characteristic is an advantage in order to have more molecules suitable for generation of radicals (the dosage is made on weight percent bases and not on molar concentration in the art), it makes them very favorable for the migration from the cured surface. Moreover Type I compounds give rise to volatile photodecomposition products due to the cleavage mechanism adding to the migration the problem of release of odor. In this respect Type II photoinitiators have a more favorable profile because the ketyl radical either is oxidized back to the ketone or gives rise to recombination products with formation of higher molecular weight derivatives with a lower volatility than the parent compounds.

To overcome this limitation different approaches have been studied, such as incorporation of functionalised photoinitiators in polymeric systems[1,2,3,4,5].
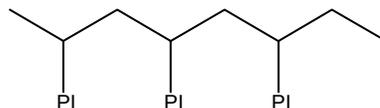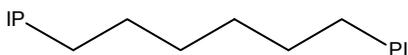
Most of them suffer for the dilution of the photoinitiating moieties in the polymeric backbone: this requires high amount of product to obtain reactivity equivalent to that of the original photoinitiators, reducing the flexibility of formulating. Moreover they can suffer from quenching effects due to the steric proximity of neighboring photoactive groups[6,7], with an intrinsic loss of reactivity.

A solution to these problems can be the use of difunctional photoinitiators. They have been developed according to the following principle: selection of a scaffold containing aromatic groups (driving the UV absorption profile) and introduction of a photoinitiating moiety on each aromatic group as substituent.

This approach allows the development of photoinitiators with a) an equivalent weight per photoinitiating moiety similar to that of the monofunctional compounds, b) a molecular weight in the range of 500 AMU, high enough to reduce the migration problems, and c) a

possibility to have in the same molecule different photoinitiating moieties, taking advantage of possible synergistic effects.

According to this basic approach we developed two difunctional photoinitiators one mainly acting by Type I mechanism, designed for clear coatings and the other acting mainly by Type II mechanism, designed for pigmented systems.

DIFUNCTIONAL PHOTOINITIATOR FOR CLEAR COATINGS

The difunctional photoinitaitor for clear coatings (LFC 1861) contains two α-hydroxyketone moieties. The product is a solid compound with a melting point in the range of 100°C. Its UV absorption is reported in figure 1.
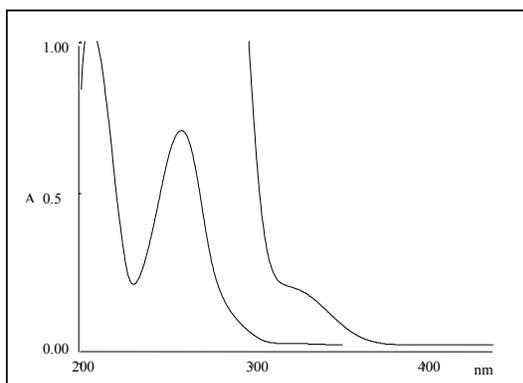

Figure 1. UV absorption profile of difunctional α-hydroxyketone LFC 1861 in methanol conc. 0.01 g/l and conc. 0.2 g/l

The mechanism of generation of radicals occurs mainly through an α-cleavage process with a small component of formation of ketyl radical as demonstrated by the time resolved EPR spectrum in ethanol.

We tested the reactivity of LFC 1861 in different acrylic formulations in comparison with monofunctional α-hydroxyketone photoinitiators (2-hydroxy-2-methyl-1-phenyl propan-1-one (α-OH-IBP) and 1-hydroxycyclohexylphenylketone (α-OH-CPK)). The concentration of each photoinitiator was 4%, the layer thickness 50μm and curing was achieved by a Fusion apparatus equipped with a medium pressure Hg lamp at 120 W/cm (50% of max power). The formulations were based on epoxyacrylate (Laromer EA 81 + TPGDA: 70+30), polyester acrylate (Ebecryl 810 + TPGDA: 80+20), aliphatic polyurethane acrylate (Ebecryl 270 + TPGDA: 70+30) and aromatic polyurethane acrylate (Ebecryl 220 + HDDA + OTA 480: 75+12.5+12.5). The reactivity was measured as line speed to obtain tack-free and resistance to surface abrasion. The results are reported in figure 2 and 3.

The results clearly show that LFC 1861 compares very well with the monofunctional photoinitiators. In particular in both aliphatic and aromatic polyurethane acrylate the difunctional α-hydroxyketone shows better activity.
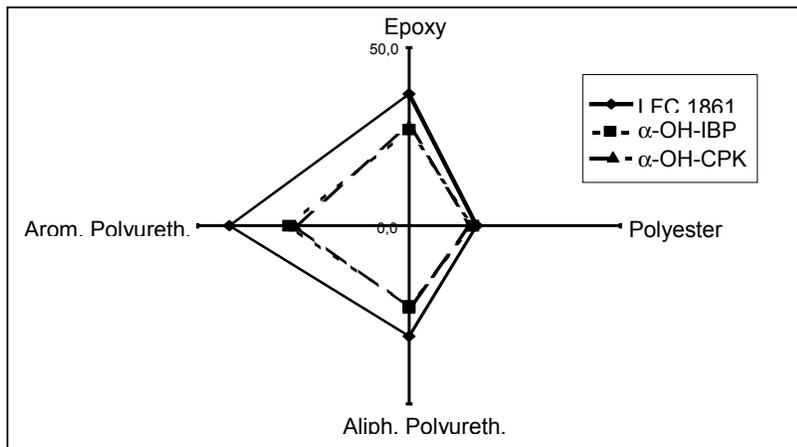
Figure 2. Reactivity (line speed to tack-free) of LFC 1861 vs α-OH-IBP, α-OH-CPK in different acrylated systems.
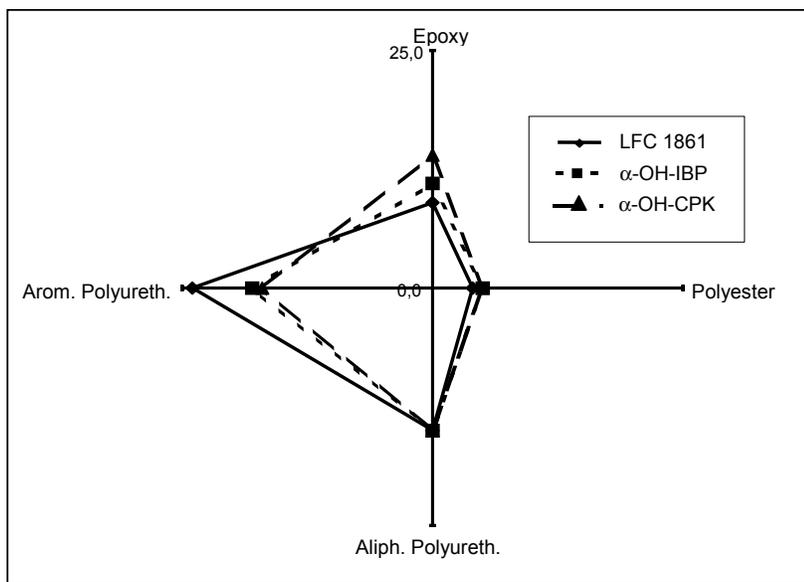

Figure 3. Reactivity (line speed to surface abrasion) of LFC 1861 vs α-OH-IBP, α-OH-CPK in different acrylated systems.

One of the most important advantages of LFC 1861 is its low migration from the cured formulation. This hold true both for the release of photoinitiator when the cured surface is in contact with simulating fluids and for the release of photodecomposition products.

We evaluated the migratability of the difunctional photoinitiator from cured formulations, according to the EEC guidelines for plastics[8]. We considered different simulating fluids (distilled water, 3 % acetic acid in water and 10% ethanol in water) which were analyzed by HPLC after conditioning at 80°C for 2 hours and at 40°C for 10 days in direct contact with the cured formulations. The results are reported in Table 1

Table 1- Migration of LFC 1861 in different simulating fluids (2 h at 80°C + 10 d at 40°C)

| Simulating fluid	Total migration	Specific migration
Distilled water	< 8 mg/dm^2	u.d.l.
3% acetic acid	< 8 mg/dm^2	u.d.l.
10% ethanol	< 8 mg/dm^2	u.d.l.

u.d.l. = under detection limit of HPLC method (50 µg/dm^2)

In each experiment, the total migration was lower than 8 mg/dm^2 (maximum allowed: 10 mg/dm^2) and the specific migration of the photoinitiator could not be found at the detection limit of the analytical method.

The release of photodecomposition products mainly affects the odor post curing of the formulation. We tested the release of photodecomposition products of different formulations cured using LFC 1861 in comparison with α-OH-IBP and α-OH-CPK by an organoleptic test (by means of a panel of trained person) and by GC. The difunctional photoinitiator gave the lowest odor in the organoleptic test, while we could not detect any volatile photodecomposition product released by the cured formulation containing LFC 1861 by GC.

DIFUNCTIONAL PHOTOINITIATOR FOR PIGMENTED SYSTEMS

The difunctional photoinitaitor for pigmented systems is a benzophenone-ketosulphone derivative built on the diphenylsulphide structure as reported below.
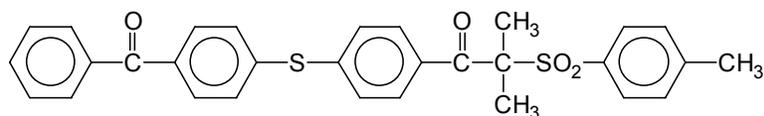
LFC 1001

The product is a solid compound with a melting point in the range of 100°C and its UV spectrum is reported in figure 4.
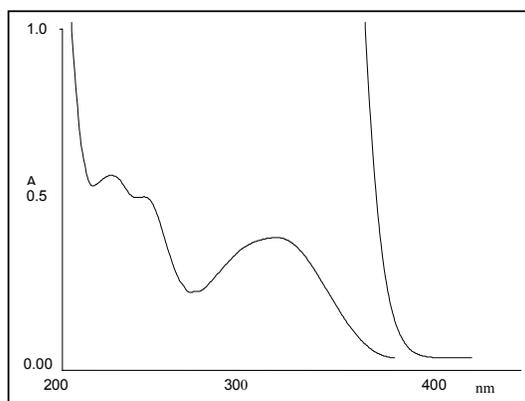

Figure 4. UV absorption profile of LFC 1001 in methanol conc. 0.01 g/l and conc. 0.2 g/l

The mechanism of generation of radicals occurs mainly by formation of ketyl radical by interaction with a hydrogen donor through a charge transfer complex (CTC). A further minor mechanism of generation of radicals is a β-cleavage process as reported in figure 5.
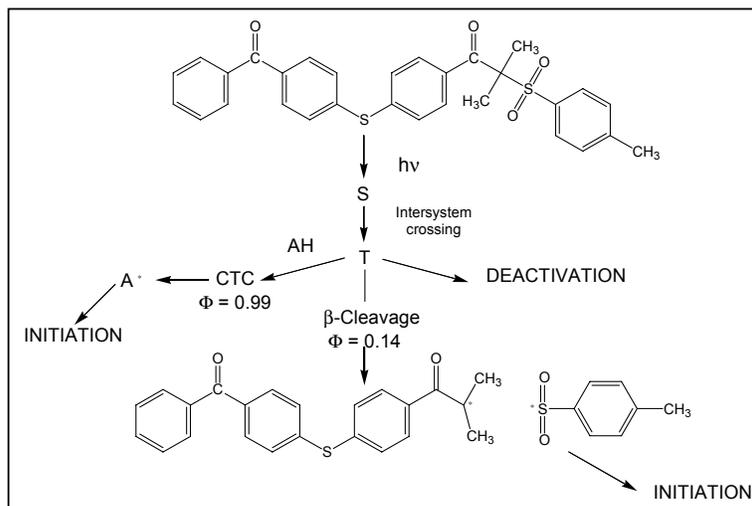

Figure 5. Mechanism of generation of radicals from LFC 1001

This behavior clearly shows that the use of a hydrogen donor co-initiator is required to better exploit the reactivity of LFC 1001 [9].

Due to the presence of a benzophenone moiety in the structure of LFC 1001, it is interesting to compare the reactivity of the two products in a clear coatings formulation, in presence of the same amount of co-initiator. The reactivity was tested in a formulation based on Ebecryl 600-OTA 480-TMPTA (40+30+30) using an acrylated amine as co-initiator (Esacure A 144, 7%). Benzophenone (BZO) was dosed at 5% while LFC 1001 at 5 and 2.5%. The results are reported in figure 6.
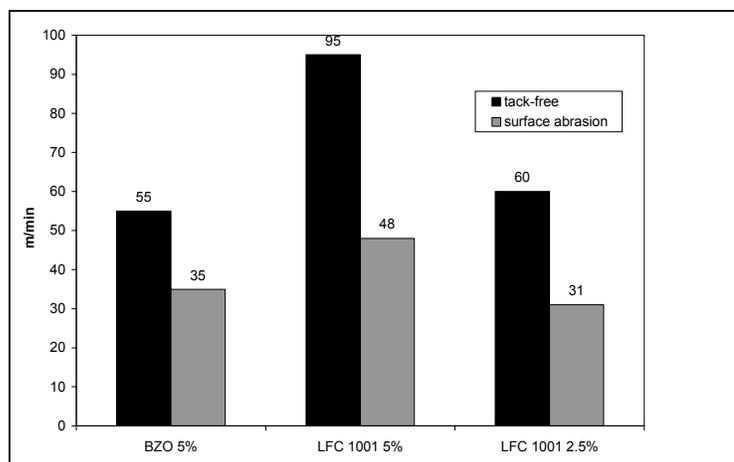

Figure 6. Comparison among the reactivity of two clear coating formulations containing BZO (5%) and LFC 1001 (5% or 2.5%) respectively. Line speed to obtain tack-free and surface abrasion.

The results of this test clearly show that LFC 1001 has a reactivity that is at least double than the reactivity of BZO in the reported conditions. This behavior can be explained by a better exploitation of the lamp emission from LFC 1001 than from BZO.

We tested the reactivity of LFC 1001 in comparison with 2-methyl-2-morfolino-1(4-methylthiophenyl)propan-1-one (MMTPP) measuring the conversion of acrylic double bond by FT-IR in pigmented formulations based on urethane acrylate and epoxyacrylate. An example is reported below: the formulation, containing 2% of photoinitiator, 18% of blue pigment and supplemented with 2% of ethyl-4-dimethylaminobenzoate (EDB) as co-initiator for LFC 1001, was cured using a Fusion apparatus equipped with a medium pressure Hg lamp set at 120 W/cm (50% of max power). The results of the conversion of double bond are reported in figure 7. In the reported conditions the two photoinitiators have very similar performances.

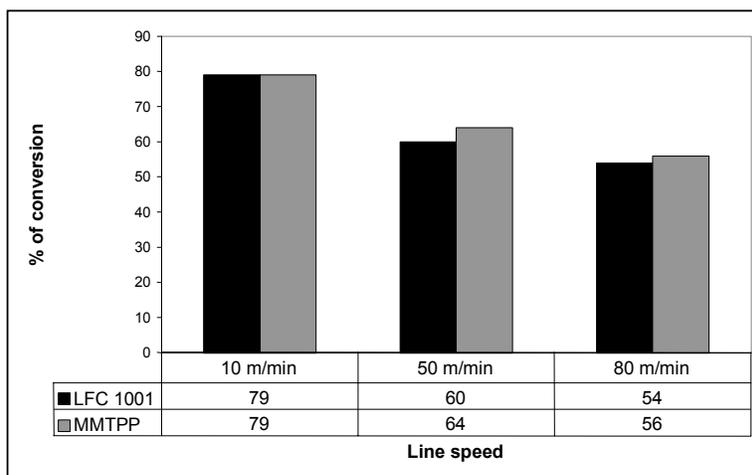|	10 m/min	50 m/min	80 m/min
■ LFC 1001	79	60	54
▨ MMTPP	79	64	56

Line speed

Figure 7. Reactivity of LFC 1001 in comparison with MMTPP in pigmented blue ink. Percentage of conversion measured by FT-IR.

An important characteristic of a photoinitiator, designed for pigmented systems, is its ability to be sensitized by suitable sensitizer absorbing light of wavelengths in the range of 400 nm (in general isopropylthioxanthone (ITX)). The reason is that the photoinitiating package can better exploit the emission of the lamp and takes advantage of the transmittance window of the pigments.

To test this characteristic we measured the reactivity (deep cure and surface cure) of LFC 1001 (3%), of ITX (0.5%) and of a combination of the two in presence of 2.25% of an amine co-initiator (EDB) in a blue ink formulation. The formulations were based on Ebecryl 600, Ebecryl 220, Ebecryl 350 and TMPTA. The pigment was used at concentration of 18%. The formulations were cured using a Fusion UV system apparatus equipped with a medium pressure mercury lamp operating at 160 W/cm (66% of max power); the layer thickness was 3μm. As reported in Figure 8 a significant improvement of the performance was obtained when the combination of LFC 1001 and ITX were used in the formulation, in comparison with the sum of the reactivity of each single photoinitiator. Because this behavior cannot be explained by a direct sensitization of LFC 1001 by ITX (the triplet energy of LFC 1001 is 278 kJ/mole, higher than that of ITX, 256 kJ/mole[10,11,12]) and the potential of red-ox process doesn't allows the transition, J.P. Fouassier proposed a three component mechanism in which a regeneration of ITX occurs by LFC 1001[10].
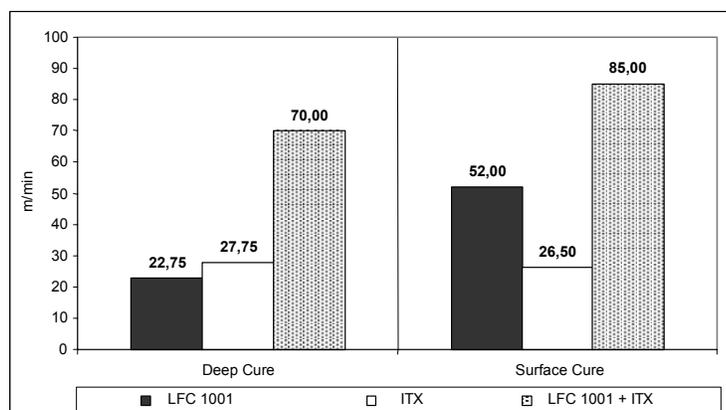
Figure 8. Reactivity (deep cure and surface cure) of LFC 1001 (3%), ITX (0.5%) and the combination of the two in blue ink formulation, in presence of 2.25% of EDB

Another important parameter in ink technology is the stability of the formulation. We tested the influence of LFC 1001 at 3% in combination with EDB in the blue ink formulation. The evaluation was carried out measuring autopolymerization and the reactivity after storage up to 180 days at 4, 20 and 45°C in comparison with a freshly prepared sample. The results are reported in table 2.

Table 2. – Stability of blue ink formulation containing 3% of LFC 1001 and 3% of EDB.

Temperature (°C)	Autopolymerization		Reactivity (m/min to obtain tack-free)	
	t = 0	t = 180 d	t = 0	t = 180 d
4	Not polymerized	Complies	36	32
20	Not polymerized	Complies	36	33
45	Not polymerized	Complies	36	32

The migratability of LFC 1001 has been tested both as migration of the product from the cured formulation, when it is in contact with food simulating fluids[8], and as release of photodecomposition products evaluated by an organoleptic test. Using distilled water and 3% acetic acid as simulating fluid the total migration was always lower than 3 mg/dm^2 (maximum allowed 10 mg/dm^2) and the specific migration of LFC 1001 was always below the detection limit of the HPLC method (4 µg/dm^2).
The odor test was carried out on a clear varnish cured using LFC 1001, containing EDB as co-initiator, in comparison with the same varnish cured with Esacure KIP 150 and MMTPP. The results are reported in table 3.

Table 3 – Evaluation of odor released from a clear formulation cured using LFC 1001, Esacure KIP 150 and MMTPP as photoinitiators

Photoinitiator in the formulation	Odor (score)
LFC 1001	0
Esacure KIP 150	0
MMTPP	5

0 = no odor, 5 = very intense odor

LFC 1001 practically does not release any odor post curing like Esacure KIP 150, a recognized low odor photoinitiator, while MMTPP develops a strong unpleasant smell. This behavior is noteworthy because the molecule contains a sulfur atom and it is due to the fact that no cleavage occurs at sulfur level [13].

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