READY-TO-USE PHOTOINITIATOR FORMULATIONS FOR WATER-BORNE UV CURABLE SYSTEMS

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INTRODUCTION

Use of water-borne formulations is increasing in importance not only to comply with environmental constrains, but also to satisfy the requests of new applications in which the achievement of low viscosity is a must, such as in UV ink-jet inks. Photoinitiators must satisfy more restrictive performance conditions when used in water-borne systems, mainly related with the compatibility with hydrophilic formulations and with its possible release during the flash of water before curing.
Recently, we developed ready-to-use water emulsions both of the oligomeric, polyfunctional α-hydroxyalkylphenylketone Esacure KIP 150, and of a combination of Esacure KIP 150 and acylphosphine oxide. The first emulsion is mainly used in clear coatings while the second one is suitably employed in pigmented systems.

CHARACTERISTICS OF PHOTOINITIATORS

Esacure KIP 150 is an oligomeric α-hydroxyketone with relatively high molecular weight: M.W. 409.4 for the dimeric isomers and M.W. 614.1 for the trimeric ones. The combination of polyfunctionality and molecular weight give to this photoinitiator high efficiency in polymerization of acrylated systems[1], in which it displays non-yellowing properties, low migratability and volatility (vapor pressure at 25°C = 0.002 Pa)[2]. Demonstration of the limited tendency to be released by thermal treatment is the experiment reported in figure 1.

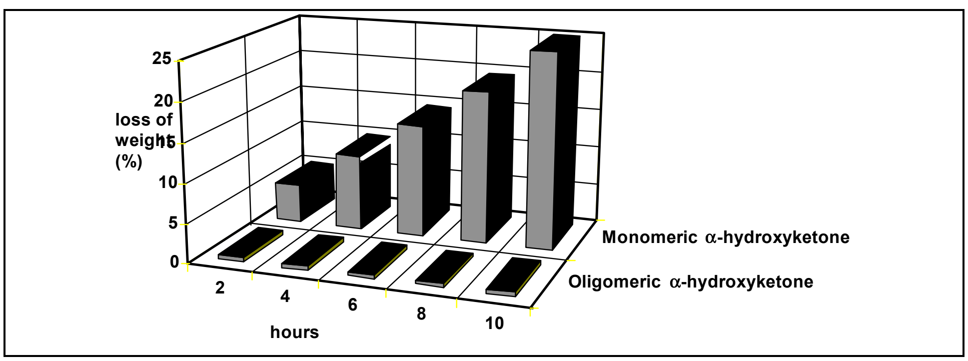

Figure 1. Release of photoinitiators after storage at 60°C: oligomeric α-hydroxyketone (Esacure KIP 150), monomeric α-hydroxyketone (2-hydroxy-2-methyl-1-phenylpropan-1-one).

After storage for 10 hours at 60°C Esacure KIP 150 is practically not released, while the monomeric α-hydroxyketone (2-hydroxy-2-methyl-1-phenylpropan-1-one) loses about 25% of its weight.
Acylphosphine oxide (2,4,6-trimethylbenzoyldiphenylphosphine oxide TPO) is a photoinitiator with an absorption band in the near UV-vis region with high thermal stability up to 180°C and resistance to the nucleophilic attack[3]. The red shifted absorption spectrum successfully competes with pigments allowing deep cure of pigmented

formulations.

CHARACTERISTICS OF PHOTOINITIATORS EMULSION

We developed oil-in-water emulsions containing 30% of photoinitiators. One formulation is based on Esacure KIP 150, commercialized with the brand name of Esacure KIP EM, and it has been designed for clear coatings. The other one is based on a combination of Esacure KIP 150 and TPO, commercialized with the brand name of Esacure DP 250, and it has been designed for pigmented applications. The two formulations do not contain alkylphenol derivatives to comply with the most advanced recommendations for environmental protection[4]; moreover they are very stable and easily incorporated into the water-borne coating formulations.

Stability

The stability of the emulsions were evaluated measuring viscosity, particle size and appearance both after storage in normal condition at room temperature and in accelerated condition (40°C).

The results of the stability evaluations are summarized in table I. In particular particle size distributions are expressed as mode of distribution and limit of particle size diameter below which 90% of the distribution is enclosed ($D_{90\%}$).

Table I. Stability of Esacure KIP/EM and Esacure DP 250 in closed dark containers.

Emulsion	Time (months)	Temp. (°C)	Appearance	Particle size distribution		Viscosity (cps)
				Mode (μm)	$D_{90\%}$ (μm)	
Esacure KIP EM	0	r.t.	White homogeneous liquid	1.60	2.82	2000
	1	r.t.	complies	1.76	3.18	-
	2	r.t.	complies	1.76	3.78	1880
	2	40	complies	2.11	3.73	1910
	0	r.t.	White homogeneous liquid	1.93	3.18	1800
	3	r.t.	complies	2.53	3.99	-
	4	r.t.	complies	2.31	3.82	1640
Esacure DP 250	0	r.t.	White homogeneous liquid	17.14	22.53	1840
	3	r.t.	complies	21.52	28.30	1860

An example of particle size distribution at the moment of preparation and after 4 months storage at room temperature for Esacure KIP EM are reported in figure 2.

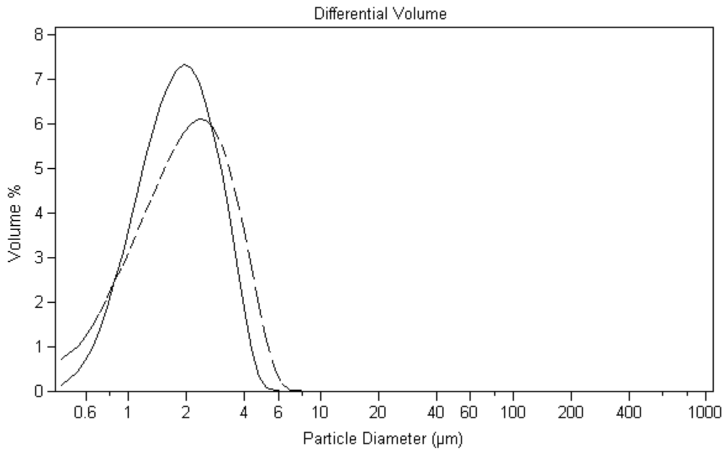

Figure 2. Particle size distribution of Esacure KIP EM at the moment of preparation (——) and after storage of 4 months at room temperature (– – –).

The stability data are in agreement with stable emulsions both after storage at room temperature and at 40°C. The distribution of particle size is still unimodal after storage supporting the stability of the emulsions. Similar results were obtained after 3 cycles of freezing and thawing

Incorporation

The ability of photoinitiator emulsions to be incorporated into water-borne systems was evaluated measuring the characteristics of cured formulations. The incorporation of each emulsion into the formulation was carried out by magnetic stirring each sample for different times.
An example of evaluation of incorporability is reported below for Esacure KIP EM.
We used an industrial varnish based on acrylated polyester with an active content of about 41%. The dosage of photoinitiator was 4% calculated as active substance on the solid resin content. The layer thickness was 75 µm wet and the formulation was dried for 5 min. at 70°C. The irradiation was carried out using a Giardina IST apparatus equipped with a medium pressure mercury lamp of 80 W/cm; the line speed was 7 m/min.
We considered the following characteristics of the cured formulation to evaluate the efficiency of the incorporation: hardness (Konig pendulum – DIN 53157) and solvent resistance (double rubs using methylethylketone-MEK).
The results are reported in figures 3. Less than 3-min. of mild stirring of the formulation are more than enough to completely incorporate the emulsion, as demonstrated by the solvent resistance test, that is the most significant for the evaluation of the photoinitiator incorporation into the formulation.
Similar results have been obtained for Esacure DP 250.

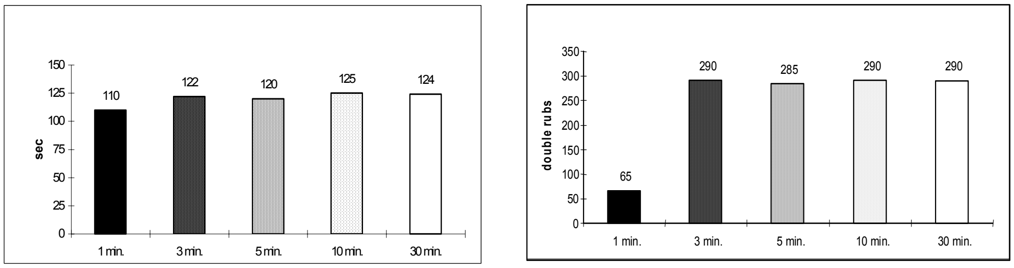

Figure 3. Hardness (Koning pendulum – DIN 53167-left) and solvent resistance (MEK-right) evaluated on the cured formulation after stirring for 1, 3, 5, 10 and 30 min from the incorporation of the emulsion.

PERFORMANCE EVALUATION

We tested the possible effects of the components of the emulsions on the performance. For this purpose we evaluated the photoinitiator emulsions freshly prepared in comparison with the photoinitiator itself added as an isopropyl alcohol (1:3) solution. The experimental conditions were the same reported in the incorporation studies except for the addition of the water resistance test (double rubs using distilled water) and color stability after conditioning (ASTM D-1925). The results are reported in figures 4 and 5.

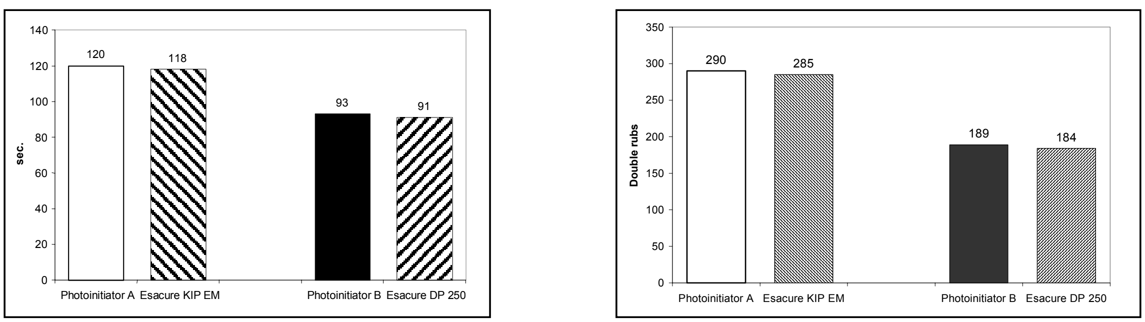

Figure 4. Hardness (Koning pendulum – DIN 53167 -left) and solvent resistance (MEK–right) evaluated on cured acrylated polyester formulation containing the emulsions Esacure KIP EM or Esacure DP 250 and the corresponding photoinitiators.

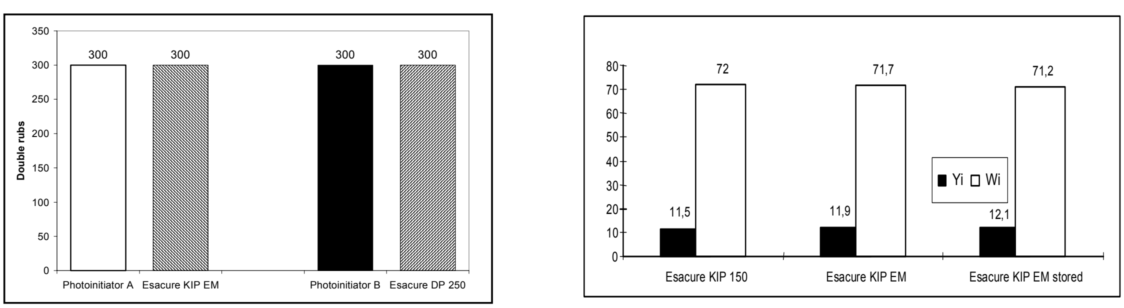

Figure 5. Water resistance (left) and color stability after conditioning (ASTM D-1925 - right) evaluated on cured acrylated polyester formulation containing the emulsions Esacure KIP EM or Esacure DP 250 and the corresponding photoinitiators.

This study demonstrates that the components of the emulsions do not adversely affect the performances of the photoinitiator both in the hardness and color stability tests, but also in solvent and water resistance evaluations.

The emulsions were also tested in formulations different from the acrylated polyester one. We considered two other formulations based: a) on aliphatic water-borne polyurethane and acrylic acid esters copolymer, b) on aliphatic water-borne polyurethane acrylate. Due to the higher reactivity of the formulations we used in these studies emulsions at a concentration equivalent to 1% of photoinitiator on the solid resin content. Curing was carried out at line speeds of 15 and 20 m/min. All the other experimental conditions were the same as reported in the above mentioned studies.
Examples of the results obtained using Esacure KIP EM are reported below. In the examined conditions the emulsions are very efficient in curing both formulations at 15 m/min and 20 m/min. Most of the tests give similar results at both line speed; only solvent resistance is reduced in aliphatic water-borne polyurethane and acrylic acid esters copolymer formulation when the amount of energy is reduced, as shown in figures 6 and 7. On the contrary in aliphatic water-borne polyurethane acrylate formulation only water resistance is reduced reducing the amount of energy (figures 8 and 9)

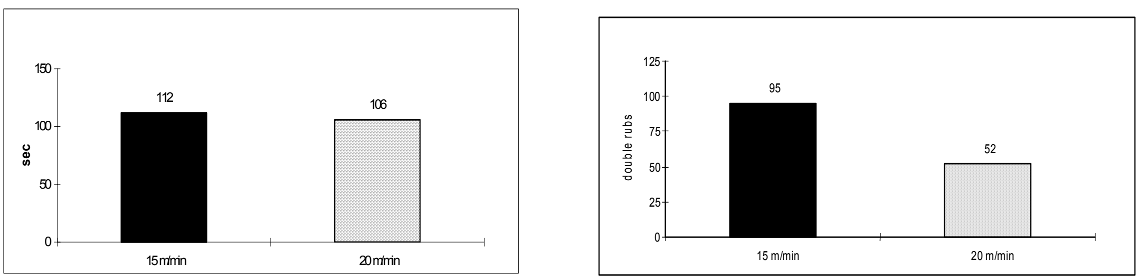

Figure 6. Hardness (Koning pendulum – DIN 53167-left) and solvent resistance (MEK-right) evaluated on the cured aliphatic water-borne polyurethane and acrylic acid esters copolymer formulation containing Esacure KIP EM cured at line speed of 15 and 20 m/min.

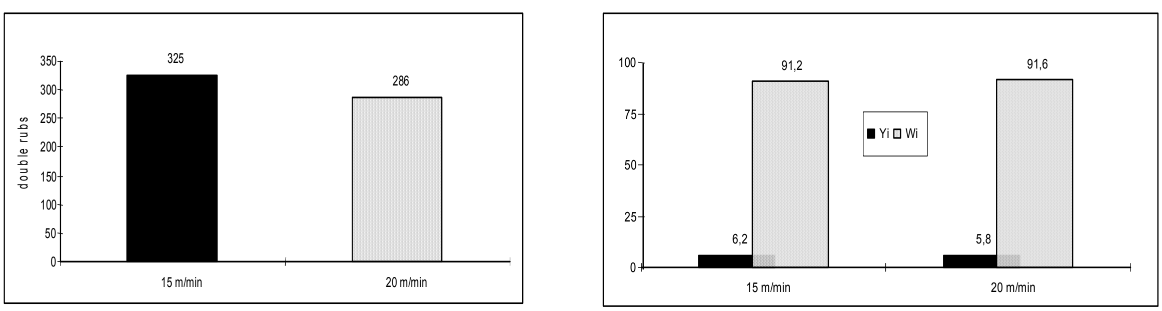

Figure 7. Water resistance (left) and color stability after conditioning (ASTM D-1925-right) evaluated on the cured aliphatic water-borne polyurethane and acrylic acid esters copolymer formulation containing Esacure KIP EM cured at line speed of 15 and 20 m/min.

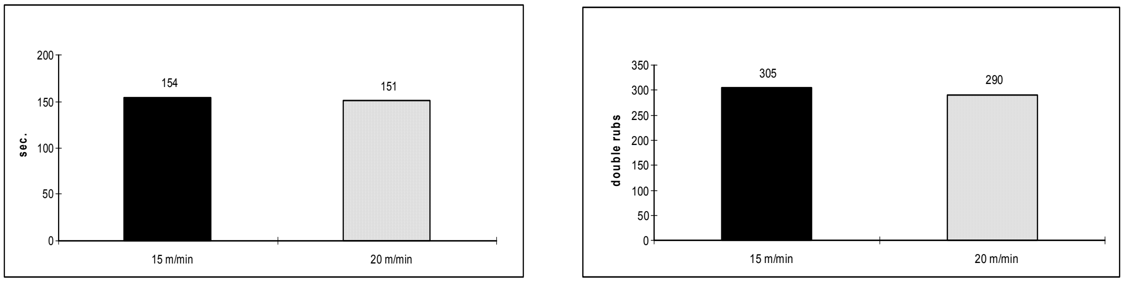

Figure 8. Hardness (Koning pendulum – DIN 53167-left) and solvent resistance (MEK-right) evaluated on the cured aliphatic water-borne polyurethane acrylate formulation containing Esacure KIP EM cured at line speed of 15 and 20 m/min.

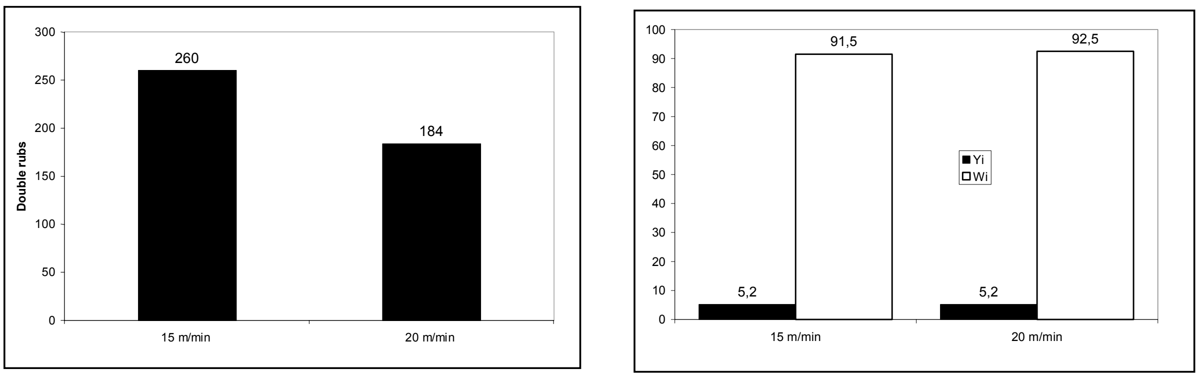

Figure 9. Water resistance (left) and color stability after conditioning (ASTM D-1925-right) evaluated on the cured aliphatic water-borne polyurethane acrylate formulation containing Esacure KIP EM cured at line speed of 15 and 20 m/min.

CONCLUSIONS

We developed stable oil-in-water emulsions containing either the oligomeric polyfunctional photoinitiator Esacure KIP 150 or a combination of Esacure KIP 150 and an acylphosphine oxide.
The first one has been developed for clear systems while the other for pigmented applications.
These emulsions are especially suitable for water-borne UV curable systems mainly because: a) they are easily incorporated into water-borne formulations; b) they give very good performances in test industrial water-borne formulations; c) the components of the emulsions do not adversely affect the performance of the photoinitiators; d) the photoinitiators included into the emulsion are particularly suitable for this purpose due to their very low vapor pressure.

ACKNOWLEDGMENTS

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