New generation of photoinitiators for UV inks & varnishes

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Introduction

Today, UV-curable systems are well established in numerous graphic arts applications such as inks and overprint varnishes. In addition, promising new application areas, for instance UV inkjet, were developed in recent years. The availability of efficient photoinitiators is essential for the progress of UV technology, since reactivity directly influences speed and stability of the production process. High photoinitiator reactivity is vital for a high conversion degree of the binder molecules at very high cure rates; this in turn directly influences the resistance properties and the migration behavior of the cured inks and varnishes. Low volatility, low odor and migration are required to meet increasingly stringent legal restrictions, in particular for food packaging[1].

Experimental

UV absorption spectra. The UV absorption spectra of the photoinitiators were measured with a Perkin-Elmer Lambda 15, at a concentration of 0.001% in acetonitrile (path length 1 cm).

Thermogravimetric measurements. The photoinitiators were thermogravimetrically measured over a temperature range of 35 to 500 °C (heating rate 10 K/min) in a nitrogen atmosphere (20 ml/min) with a Mettler TG 50.

Solubility. 0.2 g of solid photoinitiator was stirred together with 2.5 g monomer for 15 minutes at ambient temperature. If the solid dissolved completely, solubility was given a rating of 1. If stirring for 10 minutes at higher temperatures was required, the rating was increased stepwise: 40 °C – rating 2, 50 °C – rating 3, 60 °C – rating 4, >60 °C or stirring for >10 minutes – rating 5.

Inks and overprint varnishes (OPV)

OPV. Composition of the test formulation: 30 p. epoxy acrylate, 30 p. GPTA, 24 p. TPGDA, 10 p. amine modified polyether acrylate, 5.0 p. polyether tetra-acrylate, 0.5 p. silicone hexa-acrylate, 0.5 p. leveling agent. The liquid formulations were applied on white cardboard (wire bar, layer thickness 6 µm), and cured with two medium-pressure mercury lamps (each 120 W/cm) using a lab UV curing unit (IST-Metz). The cure speed was determined with the dry rub test using a paper tissue. To investigate yellowing, the OPV was applied to white coil coat panels (wire bar, layer thickness 6 µm), and cured with two medium-pressure mercury lamps (each 120 W/cm), at a conveyor speed of 10 m/min. The b* values were measured three times with a CM-508i spectrophotometer (Minolta). The average b* values are reported here. To evaluate the odor, the varnishes were applied to aluminum foil (wire bar, layer thickness 6 µm, area approx. 450 cm^2), cured to give tack-free films, and stored for 24 hours in a closed twist-off glass at ambient temperature. The odor was assessed by three persons using the following scale: 0 = odorless, 1 = very weak, 2 = weak, 3 = moderate, 4 = strong, 5 = very strong odor. The odor of the aluminum foil was rated 1.

Offset ink. Composition of the offset ink: 42.0 p. epoxy acrylate (diluted with GPTA), 22.0 p. polyester tetra-acrylate, 3.0 p. GPTA, 7.0 p. China Clay, 1.0 p. in-can stabilizer, 17.0 p. blue Cu-phthalocyanine pigment (β-form), 6.0-10.0 p. photoinitiator. The inks were printed (optical density 1.5, approx. 1.4 g/m^2), with a Prüfbau multipurpose printability tester, on white Lumiart paper, and were cured with one medium-pressure mercury lamp (120 W/cm). After UV exposure, surface cure (ink transfer, y/n) and through cure (REL test, in m/min conveyor speed) were tested.

Flexo ink. Composition of the flexo ink: 25.3 p. flexo base resin, 17.9 p. GPTA, 16.9 p. modified epoxy acrylate (diluted with 25% TPGDA), 12.2 p. HDDA, 9.4 p. hexafunctional aromatic urethane acrylate, 1.2 p. acidic methycrylate, 0.7 p. leveling agent, 10.4 p. Cu-phthalocyanine pigment, 6.0 p. photoinitiator. The inks were printed (optical density 1.5, approx. 1.4 g/m^2) with a Prüfbau multipurpose printability tester, on white PE film (corona pre-treatment), and were cured with one medium-pressure mercury lamp (120 W/cm). After UV exposure, surface cure (ink transfer, y/n) and through cure (REL test, in m/min conveyor speed) were tested.

Screen ink. Composition of the screen ink: 14.0 p. amine modified polyester tetra-acrylate, 24.4 p. epoxy acrylate (diluted with 20% HDDA), 7.0 p. acrylic resin (diluted with 40% TPGDA), 23.6 p. TMPTA, 14.8 p. HDDA, 0.9 p. leveling agent, 1.8 p. fumed silica, 0.9 p. defoamer, 4.6 p. Cu-phthalocyanine pigment, photoinitiator 8.0 p. The inks were printed (optical density 2.8, 8-10 g/m^2) with a 140 T screen on aluminum foil, and cured with two medium-pressure mercury lamps (120 W/cm, dichroic reflector). After UV exposure, surface cure (dry rub test, in m/min) and through cure (thumb test, y/n) were tested.

Inkjet ink. The UV inkjet formulation used is based on a commercially available letdown vehicle. First, a pigment concentrate was prepared by dispersing a pigment preparation for 15 min with a dispermat at 15 m/s in the letdown vehicle.The concentrate was then mixed with the reactive diluent at a ratio of 25:75 with a magnetic stirrer to give the final ink containing 2.0-2.5% pigment and 8% photoinitiator. Composition of the pigment concentrate: 65.0 p. letdown vehicle, 15.0 p. *N*-vinylpyrrolidone, 20.0 p. pigment preparation Composition of the reactive diluent: 88.8 p. letdown vehicle, 10.7 p. photoinitiator, 0.5 p. leveling agent. The ink was applied with a Citenco K Control Coater to primed aluminum foil, at a layer thickness of 12 µm. They were cured to the tack-free state (dry rub test) on an IST UV lab curing unit equipped with two medium-pressure mercury lamps (120 W/cm each).

Photoinitiators

Figure 1 shows photoinitiators that are commonly used in graphic arts applications today: the α-hydroxyketones HMPP, HCPK, HE-HMPP and oligo-HMPP, the α-aminoketones MMMP and BDMB and the bisacylphosphine oxide, BAPO. All initiators are type I, i.e. on UV excitation they undergo a scission of the bond next to the carbonyl group ($R_2C=O$). Depending on their absoption characteristics and other physical and chemical properties, they can be used as photoinitiators for clear varnishes or inks, or as coinitiators. Only selected products are suitable for odor- and migration-sensitive applications, e.g. food packaging.

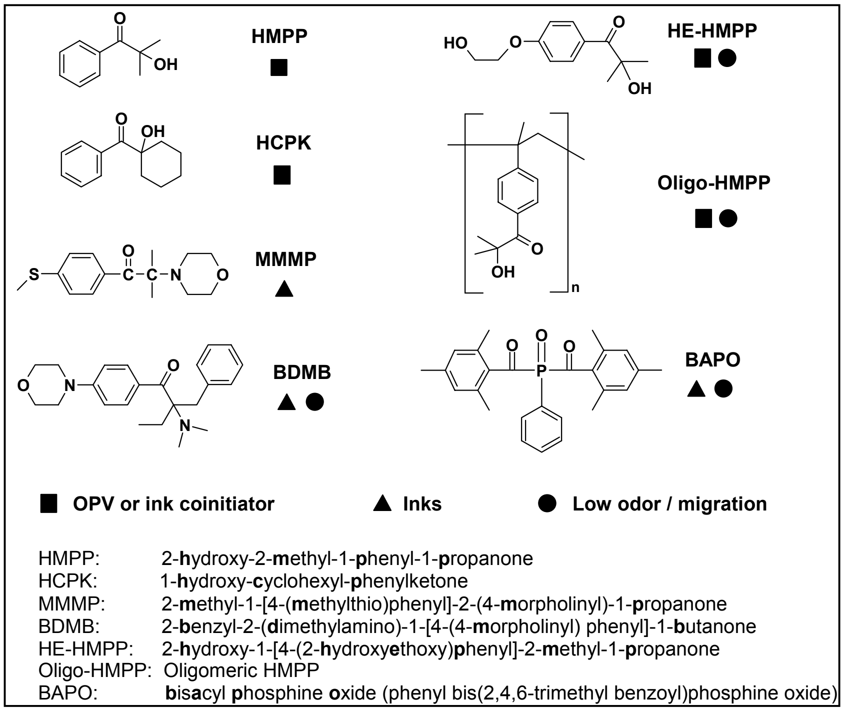

Figure 1. Commercial photoinitiators for graphic arts applications.

Three new photoinitiators, LE-HK, LE-AK and LE-PG, were developed to meet the growing demand for low emission products. The α-hydroxyketone LE-HK and the α-aminoketone LE-AK are typical type-I initiators, whereas for the liquid phenylglyoxylate LE-PG, a type II mechanism can be assumed[2,3]. Since LE-HK and LE-PG are difunctional photo-initiators, they can form radicals at both functional groups of the molecule. In addition, LE-HK bears two radicals after photocleavage and can work as a crosslinker between the C=C double bonds of the acrylate oligomers and monomers.

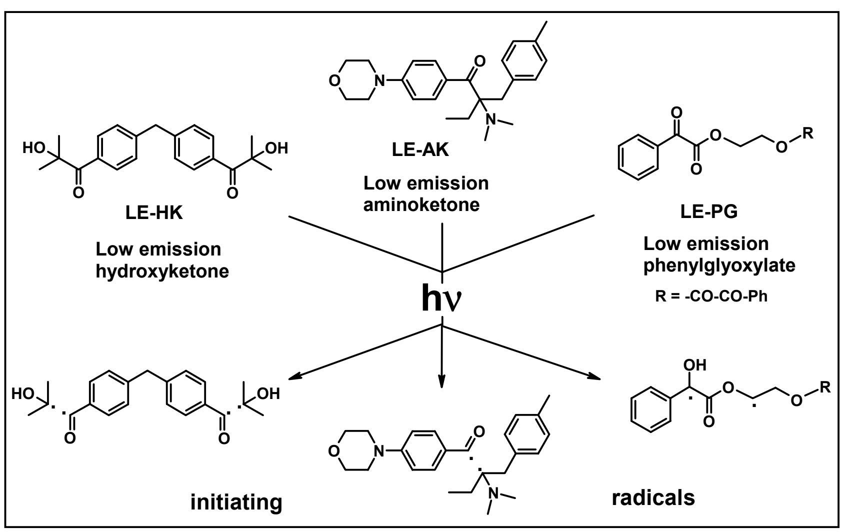

Figure 2. Bond scission of the photoinitiators LE-HK, LE-AK and LE-PG on UV exposure.

The UV absorption characteristics strongly influence the efficiency of a photoinitiator and is one key property for the effective cure of inks, where pigments compete with initiators for the light of the radiation source. Figure 3 shows the UV absorption spectra of the new initiators: LE-HK and LE-PG absorb mainly short wavelengths in the UVC range, with a slight red shift, compared to HCPK. The absorption maximum of LE-AK is in the UVA range and almost identical to that of BDMB.

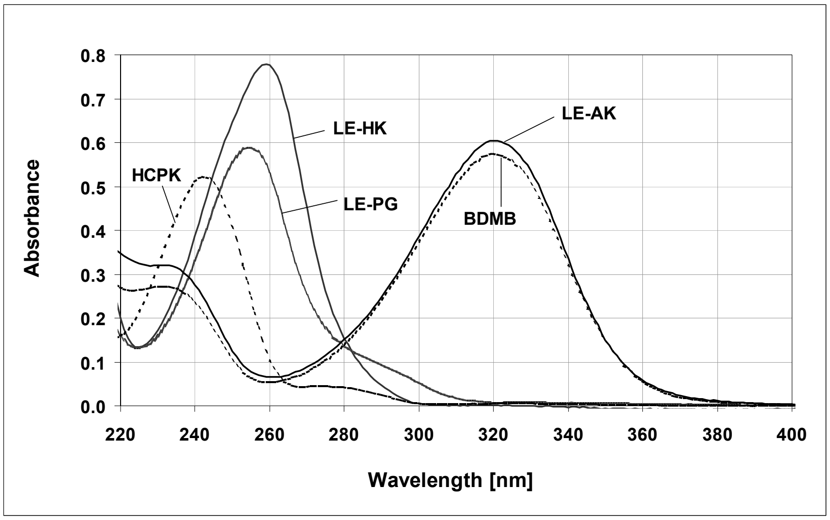

Figure 3. UV absorption spectra of LE-HK, LE-AK and LE-PG versus selected commercial initiators (concentration 0.001 wt-%, acetonitrile, path length 1 cm).

The volatility of the new products – as one criterium of low odor and low emission – was tested by thermogravimetric analysis in the range of 35 to 500 °C. All new initiators show very low volatility, which is in the same range (LE-PG) or even lower (LE-HK, LE-AK) as the commercial low-odor initiators HE-HMPP and BDMB (Figure 4).

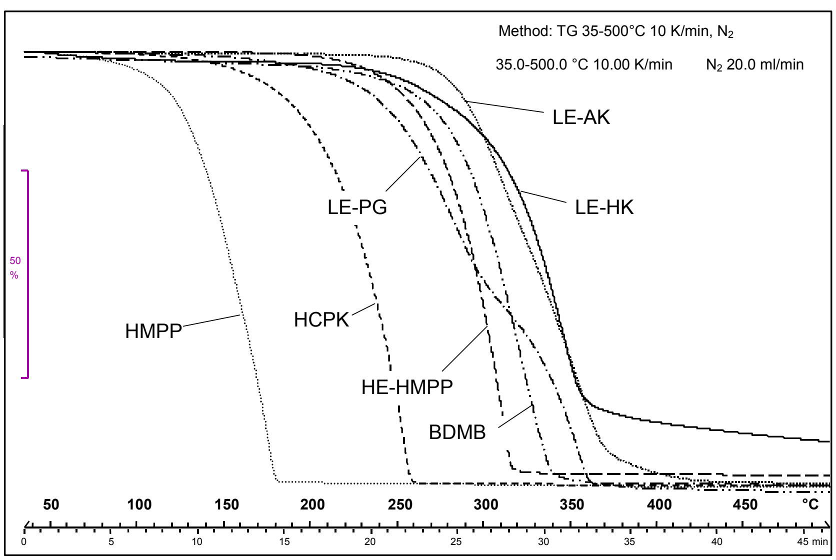

Figure 4. Thermogravimetric measurement of the new photoinitiators LE-HK, LE-AK and LE-PG versus selected commercial products.

The solubility and ease of dissolution of a photoinitiator in acrylate monomers are important properties for its handling under industrial conditions. The solubility rating of LE-AK and LE-HK in four commonly used monomers is shown in Table 1. The aminoketone LE-AK is readily soluble in all four monomers and can be compared with MMMP. LE-AK shows much better solubility than BDMB, especially in offset inks. The hydroxyketone LE-HK is readily soluble in HDDA and DPGDA at room temperature – only in TPGDA and GPTA is a slightly increased temperature of 40 °C recommended to achieve rapid dissolution.

Table 1. Solubility rating of LE-HK and LE-AK in various acrylate monomers (10 min stirring at ambient temp. – rating 1, 40 °C – rating 2, 50 °C – rating 3, 60 °C – rating 4, >60 °C or stirring > 10 minutes – rating 5).

Photoinitiator	HDDA	DPGDA	TPGDA	GPTA
LE-AK	1	1	1	1
MMMP	1	1	1	1-2
LE-HK	1	1	2	2
BDMB	1	2-3	2-3	3-4

Results and discussion

Overprint varnish (OPV)

An epoxy-acrylate-based OPV was selected to evaluate the curing efficiency of LE-HK versus commercially available, state-of-the-art α-hydroxyketone initiators. Figure 5 shows the photoinitiator concentration required to achieve a cure speed of 50, 100 and 150 m/min. At every targeted cure speed, the required LE-HK concentration was the lowest compared to all other products tested. Only 6.5 wt-% of LE-HK was necessary to cure the OPV at 150 m/min, which demonstrates the high efficiency of the new product in a typical graphic arts application. With all commercial photoinitiators, significantly higher concentrations were required: oligo-HMPP 8 wt-%, HE-HMPP 10 wt-% and HCPK 12 wt-%.

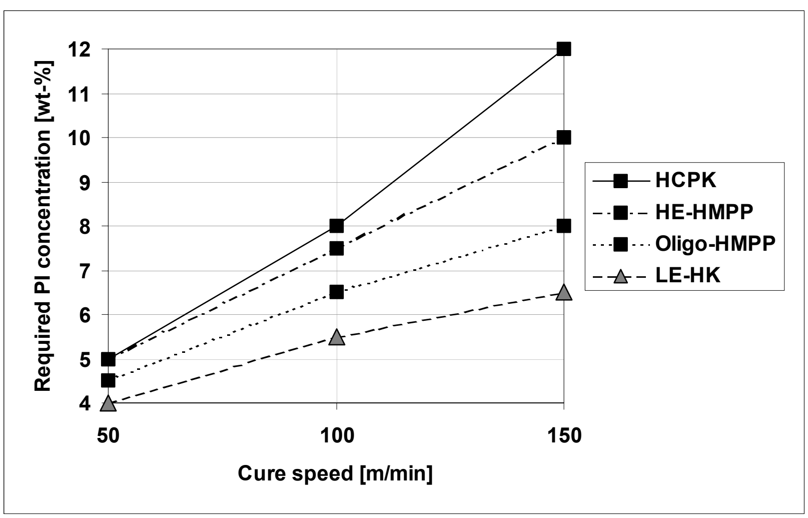

Figure 5. Photoinitiator concentration required to achieve an OPV cure speed of 50, 100 and 150 m/min (layer thickness 6 µm, 2 medium pressure mercury lamps, 120 W/cm each).

The photoinitiator should have the lowest possible impact on the yellowing of varnishes and on the odor of both varnishes and inks. The influence of LE-HK and LE-PG on yellowing (b* value) and odor was evaluated at an OPV layer thickness of 6 μm, directly after cure with two medium-pressure mercury lamps at 120 W/cm (Table 2). LE-PG showed the lowest yellowing of all products tested, followed by HCPK and HE-HMPP. For HMPP and LE-HK, slightly increased yellowing was observed, which is not an issue at typical OPV layer thicknesses, in the range of 4 to10 μm.

Further, both new photoinitiators have a negligible effect on the odor of the cured overprint varnish (see Table 2). This is one clear advantage of LE-HK and LE-PG over commercial products such as HCPK, which result in a much stronger odor.

Table 2. Yellowing (b* value, white coil coat panel) and odor (aluminum foil) of OPV after cure with LE-HK and LE-PG versus commercial photoinitiators. 0 = odorless, 1 = very weak, 2 = weak, 3 = moderate, 4 = strong, 5 = very strong odor.

Photoinitiator	b*	Odor rating
LE-HK	1.5	2-3
HMPP	1.5	3-4
HE-HMPP	1.4	3-4
HCPK	1.3	4
LE-PG	1.0	3

Offset ink

The aminoketone LE-AK can be used for efficient curing of inks, in particular offset inks, due to its improved solubility compared to BDMB. Figure 6 shows the through cure of a blue offset ink cured at three different concentrations of LE-AK and of two commonly used photoinitiator combinations, BDMB/BDK (BDK = benzil dimethyl ketal) (3:7) and ITX/EPD (2:3). BDMB alone cannot be used at the concentrations evaluated. LE-AK performs best, with 25-30% higher efficiency than the BDMB/BDK combination.

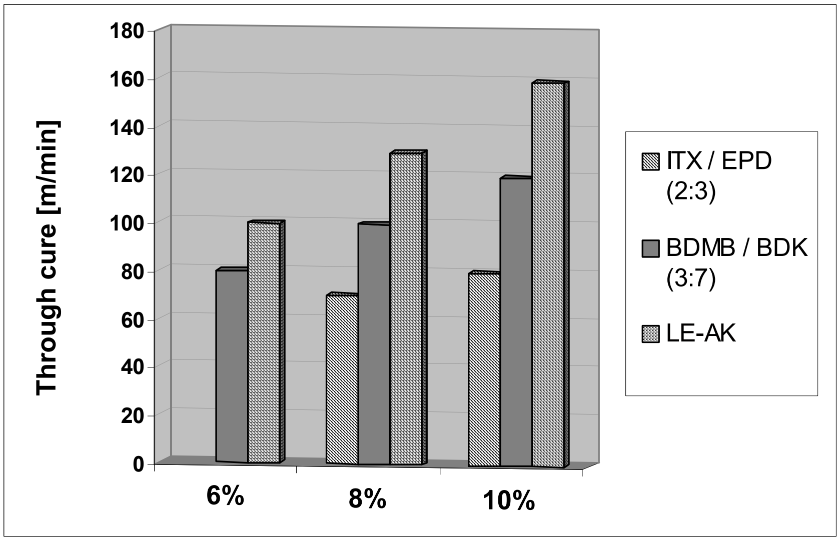

Figure 6. Through cure of a blue offset ink cured with the aminoketones LE-AK and the combinations ITX/EPD and BDMB/BDK (1 medium-pressure mercury lamp, 120 W/cm).

Flexo ink

To optimize the overall cure response and the ratio of surface cure to through cure of flexo inks, LE-AK can be used in combination with LE-HK, as shown in the example in Figure 7. At a ratio of 2 parts LE-HK : 3 parts LE-AK (by weight), both through cure and surface cure of the blue flexo ink are increased, compared to LE-AK alone.

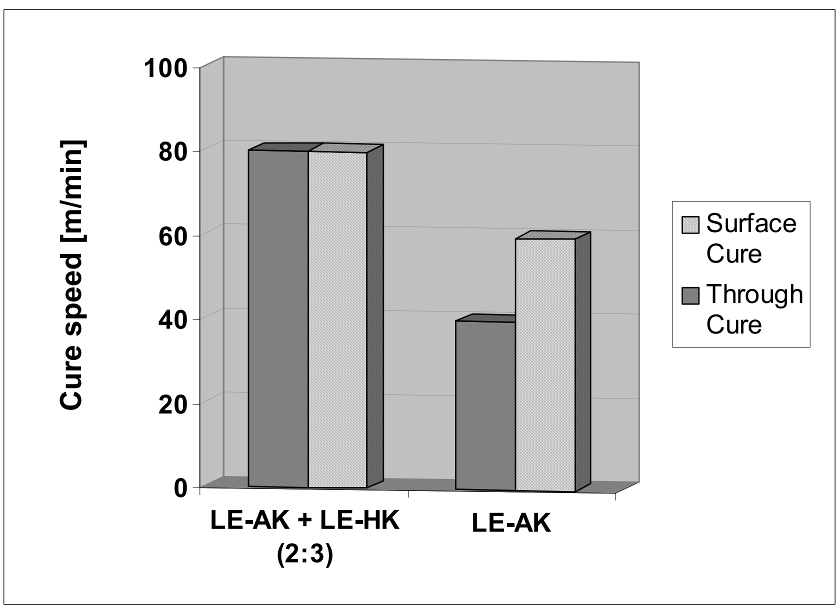

Figure 7. Cure speed of a blue flexo ink cured with 6% of the aminoketone LE-AK and 6% of the combination LE-HK + LE-AK (1 medium-pressure mercury lamp, 120 W/cm).

Screen ink

A combination of LE-HK with BAPO, at a ratio of 4:1, can be used for efficient curing of screen inks (Figure 8). A rate of 140 m/min of surface cure of the blue screen ink has been achieved with this mixture, compared to 70 m/min for both HCPK/BAPO at the same ratio and EDB/ITX (ratio 3:2), or 100 m/min with the MMMP/ITX combination (ratio 4:1).

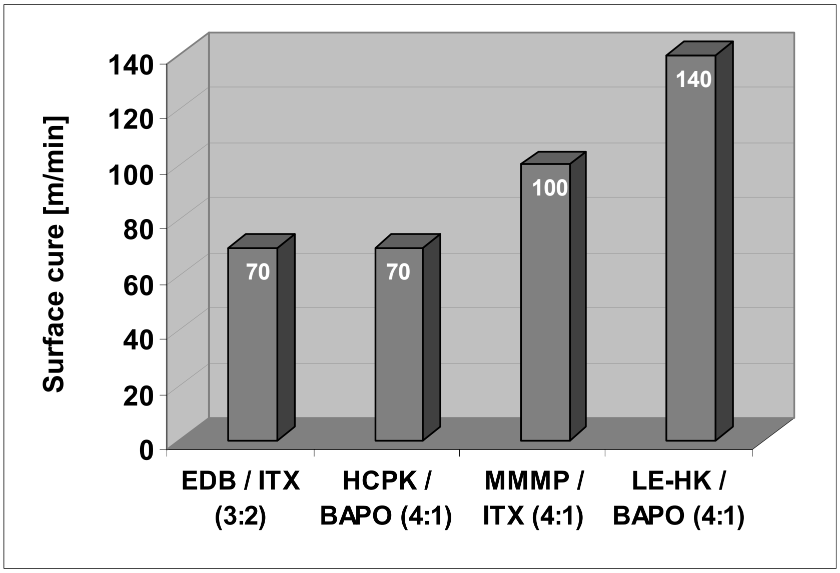

Figure 8. Surface cure of a blue screen ink cured with 8% of various photoinitiator combinations (2 medium-pressure mercury lamps, 120 W/cm each, dichroic reflector, layer thickness 8-10 μm).

Inkjet ink

High reactivity of the photoinitiator is crucial for rapid curing of UV-curable inkjet inks. This can be attributed to the low ink viscosity and the thin layers of ink that are jetted onto the substrate, which facilitate the penetration of atmospheric oxygen into the ink layer and result in marked inhibition of the photo-induced radical polymerization of the olefinic double bonds of the acrylate oligomers and monomers[4]. Figure 9 shows the cure response of yellow, magenta, cyan and black inkjet inks at an initiator concentration of 8%. LE-HK showed the best curing performance in all four colors, with surprisingly high efficiency in the black ink: a rate of 80 m/min was achieved with LE-HK, compared to 50 m/min with BDMB and the MMMP/ITX combination. These results indicate that LE-HK is the most reactive initiator under atmospheric conditions, since it allows oxygen inhibition to be overcome very efficiently.

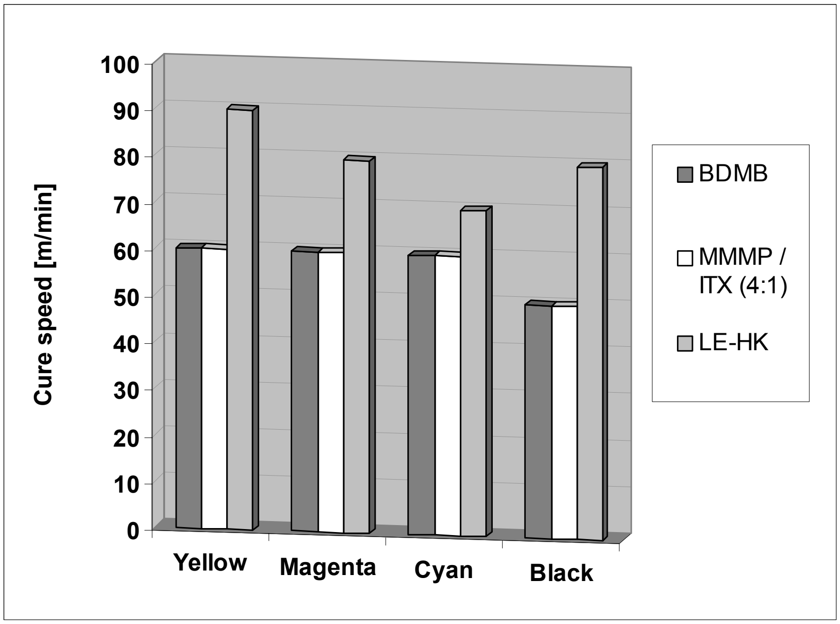

Figure 9. Cure speed of inkjet inks cured with 8% of various photoinitiator combinations (2 medium-pressure mercury lamps, 120 W/cm, layer thickness 12 µm).

Conclusions

Three new, low-emission photoinitiators, LE-HK, LE-AK and LE-PG, were tested in overprint varnish (OPV) and a number of inks. The difunctional hydroxyketone LE-HK allows curing at the highest speed, even under difficult conditions such as low layer thickness and low viscosity, and has little effect on the odor or the yellowing of the cured OPV. The aminoketone LE-AK is readily soluble in acrylate monomers and allows efficient curing of inks, e.g. offset ink, at high cure speed. The liquid LE-PG, which shows very low yellowing and causes less odor than commercial photoinitiators, can be used as co-initiator in low-odor / low-yellowing overprint varnishes.

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