New Raw Materials for UV Inkjet Inks

A. Fuchs, M. Richert, S. Biry, S. Villeneuve, and T. Bolle*
Ciba Specialty Chemicals
Basel, Switzerland

Abstract

UV-curable inkjet printing is a new technology that is expected to grow significantly in the next few years. The extremely low ink viscosities required for this application entail extensive modification of the conventional formulation equilibrium between oligomers, monomers, and photoinitiators. The impact in terms of curing efficiency then has to be balanced by modifying combinations of photoinitiators in this new binder environment. Pigment selection will be driven by more demanding requirements in terms of resistance to flocculation and gelling. This paper describes the influence of optimized additive and pigment selection on UV inkjet inks.

Introduction

UV-curable inkjet technology has developed very dynamically during recent years.[1,2] Benefits such as instant drying on UV exposure, zero VOC emission, printing on non-absorbing substrates, and high resistance of the prints to weathering and abrasion are the major driving forces for the growing acceptance of this new technology.

However, the very low ink viscosity that is required to achieve good jettability on the printer raises some technical challenges. First of all, it limits the number of raw materials that can be used for the formulation of UV-curable inkjet inks, since the viscosity of acrylate monomers and oligomers used in other radical-type UV-inks, e.g. offset or screen inks, tends to be relatively high. To avoid flocculation and sedimentation, which could lead to nozzle clogging, pigments must be carefully selected. The curing performance of UV inkjet inks is also severely impacted by oxygen inhibition; atmospheric oxygen diffuses more easily into these very low-viscosity inks, strongly inhibiting radical polymerization, especially during its initial phase[3,4]. Suitable pigments and photoinitiators are essential for the formulation of efficient UV inkjet inks.

Experimental

UV Inkjet Formulations

The UV inkjet formulations used are based on a commercially available letdown vehicle (Table 1). First, a pigment concentrate was prepared by dispersing the 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 6 or 8% photoinitiator.

Table 1. Composition of the pigment concentrate and the letdown vehicle.

Raw material	Parts
Pigment concentrate	
Letdown vehicle	65.0
N-vinylpyrrolidone	15.0
Pigment preparation	20.0
Reactive diluent	
Letdown vehicle	99.5 - x
Photoinitiator	x*
Leveling agent	0.5

*) x = 8.0 parts for 6% photoinitiator in the final ink
x = 10.7 parts for 8% photoinitiator in the final ink

Ink Viscosity

The viscosities of the final inks were measured at various shear stress levels (10-1000 s^{-1}) with a Physica US 200 rheometer (Paar Physica).

Dispersion Stability

The final inks were transferred to GC vials (2.5 ml volume) and sedimentation of the pigments was assessed visually.

Cure Speed

The inks were applied with a Citenco K Kontrol Coater to primered 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) and optionally, a nitrogen purge.

For all experiments performed under oxygen-reduced conditions a Metrotec oxygen-measuring device was used to determine the oxygen concentration of the atmosphere beneath the UV lamp.

Photoinitiators

Usually, initiators with an absorption in the UVA (315-380 nm) up to the visible range (>400 nm) are required for efficient through curing of pigmented systems. Two commercial α-aminoketones, one of them in combination with a sensitizer, and an experimental α-hydroxyketone were selected for the present assessment (Table 2).

All three initiators undergo NORRISH type I (α-cleavage)[5] photocleavage. ITX is a sensitizer that occupies an electronically excited state on UV exposure and transfers its energy to a type I photoinitiator, e.g. MMMP, provided the energy levels of the photoinitiator match the energy levels of the sensitizer.[6,7]

Table 2. Photoinitiators.

BDMB	2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone
MMMP	2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone
ITX	2-isopropylthioxanthone
DF-HK	Experimental difunctional α-hydroxyketone

Pigments

A yellow, magenta, cyan and black pigment preparation (four-color set) was selected for assessment in inkjet inks (Table 3). The preparations contain approx. 50% vinyl chloride co-polymer to ensure good dispersibility and dispersion stability, and have a small particle size with a narrow particle size distribution.

Table 3. Pigments.

Yellow pigment preparation	PY 151 / PY 110
Magenta pigment preparation	PR 202 / PR 254
Blue pigment preparation	PB 15:3
Black pigment preparation	PB 7

Results and Discussion

Ink Viscosity

The viscosity of UV inkjet inks, which ranges from 10 to 50 mPas at ambient temperature, is much lower than that other printing inks (e.g. 500-1500 mPas for UV flexo inks). Ideal inks have Newtonian rheology, i.e. their viscosity remains constant at varying shear stress.

Figure 1 shows that the determined viscosities of the four-color set range from 20 to 33 mPas (T = 23°C), with an Newtonian rheology of the inks. The presence of photoinitiators – 8% BDMB and 8% MMMP/ITX (4:1) – can influence ink rheology, e.g. black ink: 28 mPas for BDMB (1) vs. 20 mPas for initiator combination (2). The viscosities of the cyan and yellow inks, however, are comparable for both initiators. This leads to the conclusion that no major influence on ink rheology is to be expected from the photoinitiator system.

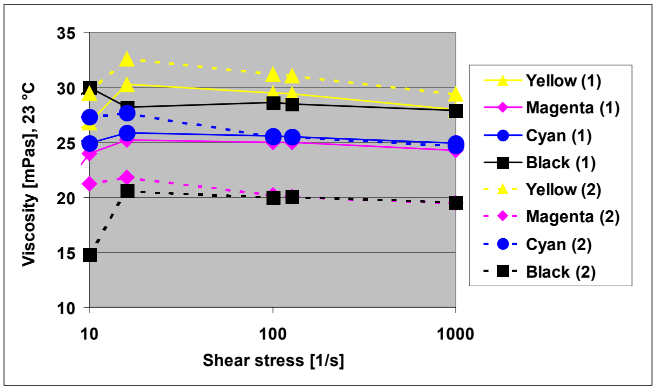

Figure 1. Rheology of yellow, magenta, cyan and black inks containing 8% BDMB (1: solid lines) and 8% MMMP / ITX (2: dashed lines) at 23°C.

Dispersion Stability

The stability of the pigment dispersion is important for storage of very low-viscosity systems such as UV inkjet inks. In the visual assessment of pigment sedimentation, the dispersions have proven to be stable over a period of 21 days (Table 4). After 27 days, the yellow inks especially showed some sedimentation: the ink containing MMMP/ITX photoinitiator was subject to the strongest sedimentation and flocculation; BDMB and DF-HK were subject to less sedimentation and no flocculation.

Table 4. Sedimentation and flocculation. The figures behind each color represent the height of the transparent ink (in mm) in the vial over the dropped pigment.

	BDMB	MMMP/ITX	DF-HK
Sedimentation [mm]	Y 2; M 1 C 0; B 0	Y 10; M 1 C 0; B 0	Y 2; M 1 C 0; B 0
Flocculation	Y -; M - C -; B -	Y +; M - C -; B -	Y -; M - C -; B -

Y = yellow, M = magenta, C = cyan, B = black.

UV Absorption of Photoinitiators

Figure 2 shows the UV absorption spectra of the compounds used. DF-HK absorbs in the UVC and UVB range, whereas MMMP and BDMB show a typical red-shifted absorption in the UVB and UVA range. The sensitizer ITX absorbs up to the visible range.

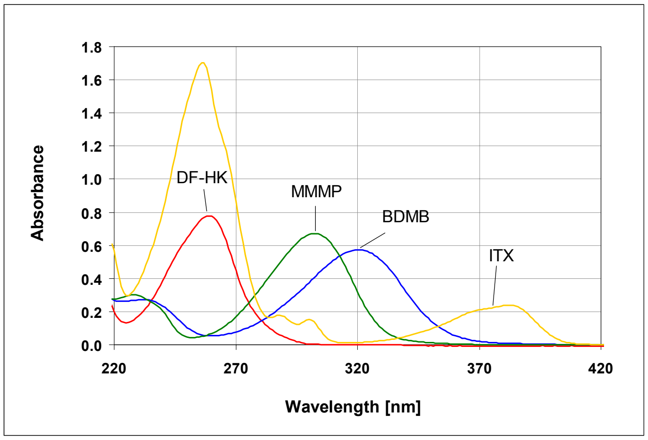

Figure 2. UV absorption spectra of photoinitiators.

Cure Speed

Figures 3 and 4 show the cure speed of the UV inkjet inks under atmospheric conditions (ca. 21% oxygen). With 8% photoinitiator, all inks cure between 2 and 3 times faster than with 6% initiator. As usual, the black ink shows the lowest cure speed within the four-color set. At a concentration of 6%, only minor differences between the selected initiators were observed. At 8%, however, DF-HK showed the best curing performance in all four colors, with surprisingly high efficiency in the black ink: 80 m/min were achieved with DF-HK, compared to 50 m/min with BDMB and the MMMP/ITX combination. These results indicate that DF-HK is the most reactive initiator under atmospheric conditions, since it allows oxygen inhibition to be overcome very efficiently.

To gain more insight into the influence of oxygen on the inhibition of the radical polymerization, the curing performance of the inks was evaluated under oxygen-reduced conditions. Figure 5 shows the cure speed of the black ink with 6% initiator at three different oxygen concentrations. At 15% residual oxygen concentration, the cure speed of the black ink was double that at normal atmospheric conditions (21% oxygen) for all initiators. At 9% residual oxygen cure speed increased dramatically, i.e. by 80-100 m/min. This reflects the strong influence of oxygen inhibition on the curing properties of low-viscosity systems. Under oxygen-reduced conditions the α-aminoketones show the same (MMMP/ITX) or even higher efficiency (BDMB) than DF-HK.

Conclusion

Three photoinitiators and four pigment preparations were assessed in UV inkjet applications. Low-viscosity inks, with viscosities in the range from 20 to 33 mPas and Newtonian rheology, were prepared by mixing with the raw materials. The selected pigment preparations have two benefits: they show little tendency to flocculation and they give a stable dispersion over a period of 21 days.

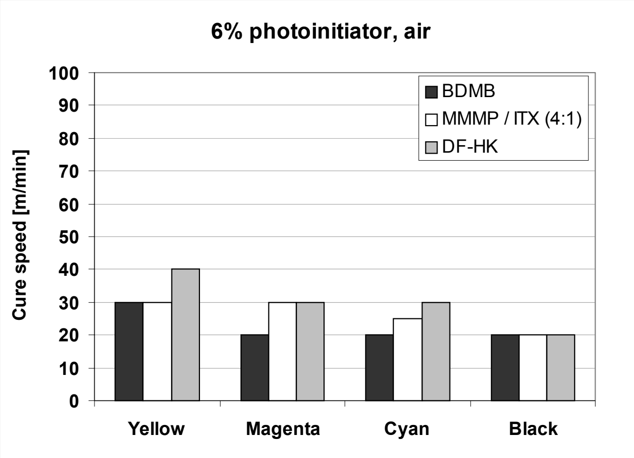

Figure 3. Cure speed of UV inkjet inks containing 6% photoinitiator, under atmospheric conditions.

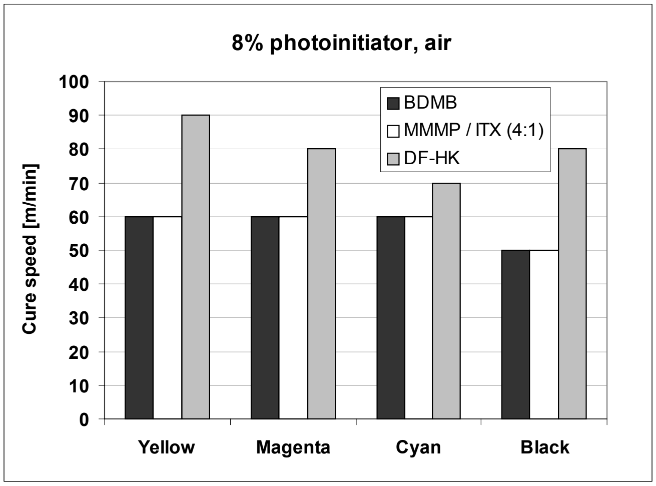

Figure 4. Cure speed of UV inkjet sinks containing 8% photoinitiator, under atmospheric conditions.

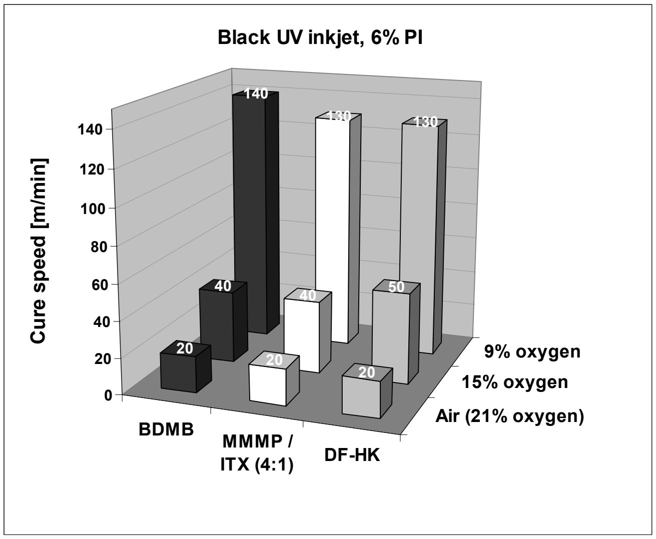

Figure 5. Cure speed of UV inkjet inks under oxygen-reduced conditions (6% initiator).

Highly efficient photoinitiators, such as the α-aminoketones BDMB or the MMMP/ITX combination, can be recommended for UV inkjet curing. The new, experimental difunctional α-hydroxyketone showed the highest curing efficiency of all tested initiators, since it overcomes the marked oxygen inhibition of the low-viscosity inks most efficiently.

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Biography

Dr. André Fuchs studied chemistry at the Technical University of Merseburg, Germany, obtaining his diploma in 1992. He holds a Ph.D. in Inorganic Chemistry from the University of Bonn.

In 1997 he joined Henkel KGaA in Düsseldorf, Germany. There he was responsible for the development of raw materials (acrylate monomers and oligomers) for radiation-curable systems.

In January 2001 he became Head of the Technical Center for Energy Curable Inks at Ciba Specialty Chemicals, Basel, Switzerland.