

NANO ADDITIVES FOR RAPID DRYING OF WATER-BASED, INKJET INKS

Dieter Guhl, Managing Director of Keeling & Walker Ltd, discusses the interaction of light with NIR-absorbing components and its relevance for ink design, formulation, manufacturing, stability and colour impression

The sunlight spectrum roughly covers a wavelength of 220–2,500 nm. It mostly consists of UV light (ranging from 250–400 nm), visible light (between 400–750 nm) and near infrared light (NIR) with a range of 750–2,500 nm.

Most important for daily life is visible light, because its interaction with matter allows the human eye to perceive text, image and colour. UV light makes a valuable contribution to the performance of inks when applied for curing UV inks. Until now NIR light has not yet caught any major attention. NIR light is invisible to the human eye and is only detectable as heat, which is increasing the temperature especially of darker objects. Little is known about the technical application of NIR light in particular in combination with NIR Absorber in ink formulations, here especially for water based inkjet inks.

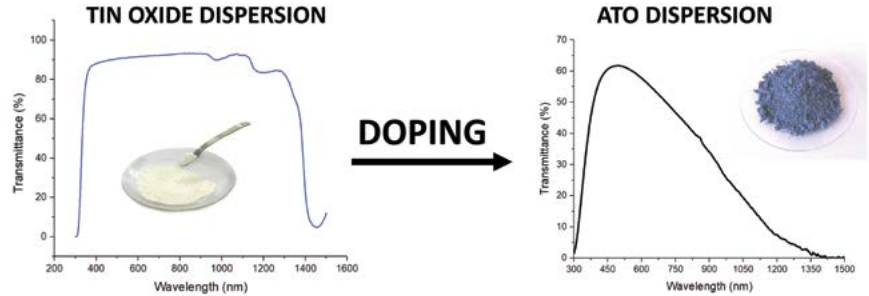
NIR-absorbing materials cover a wide range of chemistries, with inorganic pigments – mainly based on metal-oxide compounds – being the most interesting for inks (see Table 1).

METAL OXIDES

A common feature of metal oxides is that their crystal structure is modified with dopants to enable interaction with NIR wavelengths. This is achieved by the introduction of dopants or defects into the crystal lattice of the oxide. This generates free electrons or charge carriers, whose presence is responsible for the shift of absorption frequencies into the NIR-wavelength range. A typical example is displayed in Graph 1 which shows the changes of tin oxide (SnO₂) properties prior to and after doping with antimony (Sb). The formerly colourless oxide changes to blue and shows NIR-absorbing properties. Exposing those particles to NIR light leads to a rapid heating of the individual particles and an increase of their surface temperature. Due to relaxation processes, the absorbed heat is then dissipated into the surrounding environment. This process – namely the conversion of light into heat – is known as the 'photo-thermal effect' (see Graph 2).

PHOTO-THERMAL EFFECT FOR INKJET INKS

The photo-thermal effect proves to be particularly useful for aqueous, inkjet-ink formulations. Aqueous inks have become a popular solution to reduce the solvent usage.



Insulator, colourless no NIR absorption

Semiconductor, blue NIR absorptive

Graph 1: Changes of tin oxide (SnO₂) properties prior to and after doping with antimony (Sb)

NIR Absorber	Typical formula	Details	Colour
Doped Tin Oxides (ATO)	Sb _x SnO ₂	x=0.01–0.14	Grey-blue
Indium Tin Oxides (ITO)	In ₂ O ₃ *SnO ₂	85:15 – 95:5 ratio	Blue
Tungsten Oxides (CTO)	M _x M _y WO _{3-z}	M _x = Cs _{0,32} ; M _y = div. Metals; z=0,04–0,4	Dark-blue

Table 1: Technically important inorganic NIR absorbers

However, the drying process of these inks remains a challenge. Energy intensive force drying is required to achieve reasonable printing speeds, especially on non-porous substrates. Hot air drying systems have a high energy consumption and are often replaced by the more efficient NIR driers, whose latest technology works with emitters at 800–1,200 nm. NIR dryers work well on black inks, because black pigments – particularly carbon black – have a high NIR absorption and a great photo-thermal effect for the evaporation of water.

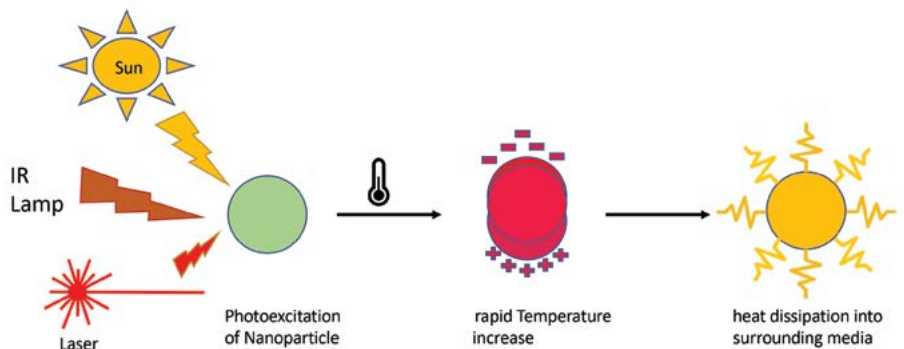
In multicolour prints, the situation varies, as each colour shows a different photo-thermal effect and hence a different drying behaviour. Typically, the ink colour with the slowest drying speed, defines the total energy input and the possible printing speed. Modifying the individual inks in a way

“NIR light is invisible to the human eye and is only detectable as heat”

that they all show the same drying speed – preferably close to the black inks – would therefore allow one to save energy and increase printing speed. It is at this point NIR absorber becomes useful. The photo-thermal effect of NIR absorber allows the adjustment of the drying speed of otherwise low-absorbing ink colours.

Some side conditions must be matched to make this approach successful. The NIR absorber dispersion needs a particle-size distribution suitable for all printheads. Additionally, the stability of the ink must not be compromised and have the lowest possible influence on the colour aspect and other properties.

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Graph 2: The 'photo-thermal effect' – the conversion of light into heat

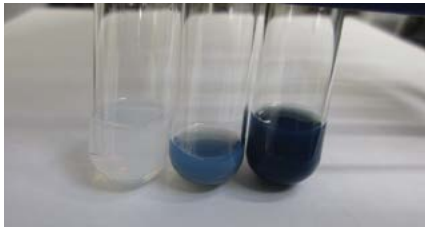


Image 1: Clear inks with 0%, 0.95% and 6.7% BITO solids (left to right)

“The NIR absorber dispersion needs a particle-size distribution suitable for all printheads”

NANO DISPERSIONS

As the pure solid inorganic NIR absorbers are not soluble in aqueous inks, their conversion into water-based nanodispersions is the first step for their incorporation into the inkjet-ink formulation. In this case, expert knowledge is needed to match the stability requirements and avoid a collapse of nano dispersions. Depending on the NIR absorber type, slight colour adjustments may also be required. However, once the formulation issues are solved, excellent results in acceleration of the NIR drying can be obtained.

COLOURLESS AND MAGENTA INKS

In a proof-of-concept formulation, a commercial colourless and a magenta aqueous inkjet ink were combined with a 20wt% indium tin oxide (ITO)-based nano dispersion with particle sizes around 100 nm. The drying behaviour was subsequently evaluated in a static drying test with a NIR lamp.

A slight colour change was observed for the clear non-pigmented ink. Image 1 shows a definite blue tint compared to the blank original

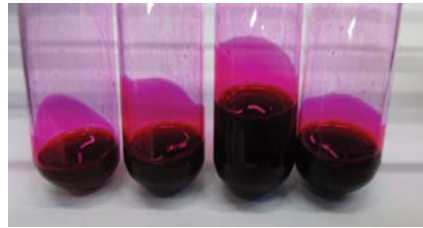


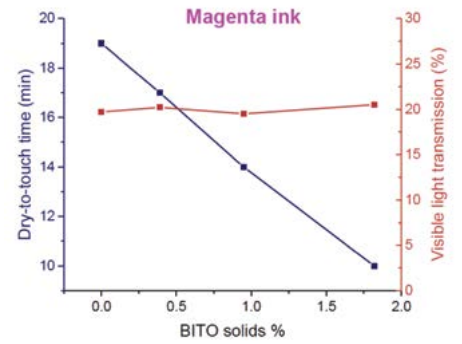
Image 2: Magenta inks with BITO solids at 0%, 0.39%, 0.95% and 1.8% (left to right)

ink, correlating with the ITO concentration. The magenta-coloured ink in Image 2 does not show any visible change of colour. In both cases, the stability of the inks is good and no sedimentation is measured over time.

BITO CONCENTRATION LEVELS

The above inks were coated onto acetate sheets using a wire-wound rod (BYK #4104, 8µm wet-film thickness) and dried under an infrared lamp at a distance of 10cm. The temperature under the lamp was monitored throughout the drying process and the set-to-touch and dry-to-touch times were measured respectively (Table 2). Increasing the BITO concentration leads to an increased absorption of NIR light and hence, surface temperature. The result is a significant decrease in the drying time for both clear and magenta inks (Graph 3).

Transmittance spectra were recorded to further investigate the effect of BITO addition on the colour of the inks (Graph 4). For the clear-ink coatings, the transparent ink and blank acetate have identical transmission curves, while the 0.95% BITO ink coating has significantly more infrared absorption (11% more at 1,500 nm) and 1–2% lower transmission across the entire visible area. Despite the fact that the BITO dispersion is



Graph 3: Decrease in drying time for magenta inks

a blue-coloured material, the spectrum only shows a minor colour influence of the additive. This is confirmed for the magenta ink coatings, with low BITO solids content. There is little difference in the 500–600 nm region for up to 0.95% BITO. A slight colour influence only becomes visible at higher concentrations.

CONCLUSION

In the meantime, these very basic results have been confirmed by technical trials. The trials concluded that drying acceleration is significantly higher than the basic proof-of-concept study shows. As a result, the expected energy savings have been achieved. It can therefore be concluded that, once the formulation difficulties are overcome, NIR-absorber dispersions are valuable additives. They can shorten the drying time and lower the energy costs considerably without affecting the ink properties and colour aspect. Together Keeling & Walker and network nanoInk will further develop this approach and are looking for interested project partners. ■

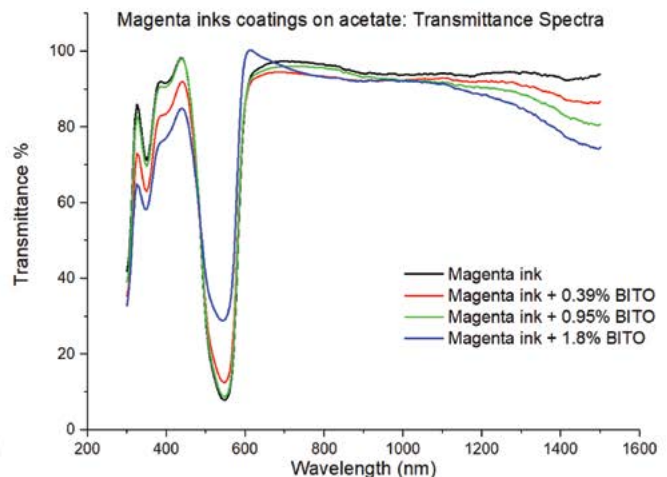
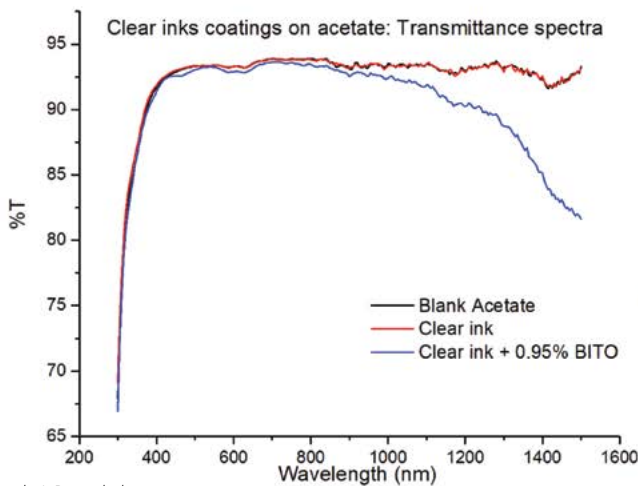
Dieter Guhl is Managing Director of Keeling & Walker Ltd

Further information:

Keeling & Walker Ltd, Stoke-on-Trent, UK
 tel: +44 178 274 4136
 email: sales@keelingwalker.co.uk
 web: www.keelingwalker.co.uk

Ink	Set-to-touch time (min)	Dry-to-touch time (min)	Temperature (°C)
Magenta ink	16	19	32–38
Magenta ink +0.39% BITO	14	17	30–35
Magenta ink + 0.95% BITO	9	14	40–43
Magenta ink + 1.8% BITO	6	10	36–41
Clear ink		47	30–45
Clear + 0.95% BITO		23	36–49

Table 2: Drying performance for inks on acetate sheets



Graph 4: Recorded transmittance spectra