A NANOINK PROJECT

Network nanoInk (organised by Nanoinitiative Bayern) brought together the combined knowledge of industry experts to correlate essential information for the safe development of low migration, UV-inkjet ink formulations

Dr Justus Hermannsdörfer is Project Manager at Network nanoInk/Nanoinitiative Bayern GmbH

The primary aim of the networks' project was to develop a structure-reactivity correlation of pigment-based ink formulations for the UV-curing process. Based on this knowledge, the project partners – GSB Wahl GmbH, European Center for Dispersion Technologies (EZD) and Karlsruhe Institute of Technology (KIT) – developed low-migration, UV-inkjet inks.

Ink formulation is already a demanding process and in the case of UV-inkjet inks, with low-migration properties, becomes a matter for interdisciplinary experts. The aim being firstly, to improve the overall understanding of structure-reactivity interactions of photo-initiators in low-migration, UV-inkjet inks and, secondly, to jointly develop new universally applicable, UV-inkjet inks with low-migration properties.

USE IN PRINTED FOOD PACKAGING

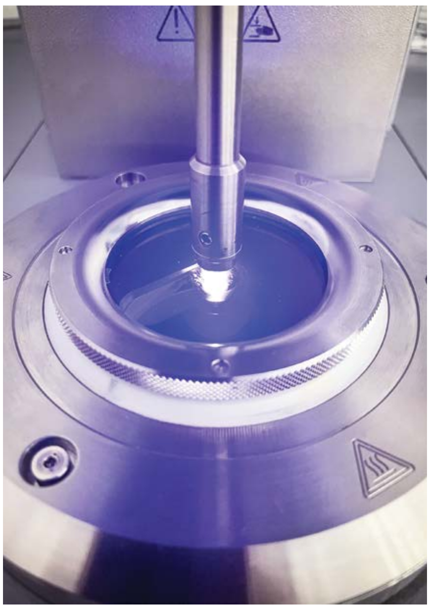
The numerous advantages of UV-curing inkjet inks, include fast curing, a wide range of application possibilities, high production numbers and small lot sizes. These factors are also of great interest in the food sector. However, conventional UV inks contain raw materials such as pigments, binders, photoinitiators and other additives that, due to their chemical structure, must not be used in this sensitive area. This is due to the risk that individual ink components may migrate into the food due to insufficient cross linking. While this is not critical for some components, others must be properly fixed or entirely avoided.

Migratory substance capacity is determined, among other factors, by the substance's molecular size, structural composition and proportion, as well as the type of functional groups. For example, large and branched molecules tend not to penetrate the layers of the substrate as easily as unbranched and small molecules. Furthermore, a high number of functional groups ensure sufficient component cross linking in the ink and can prevent the migration of individual constituents.

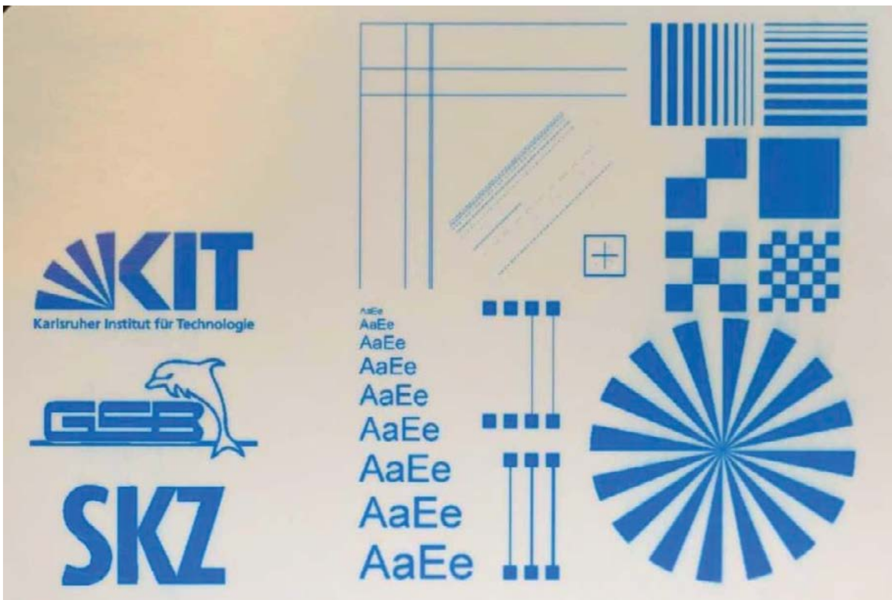
Such functional groups include double bonds. These ensure that the molecules are co-cross linked during radical polymerisation and are thus bound in the polymer film. Yet, conventional UV inks primarily use low-molecular initiators, binders and reactive diluents – usually with a single function – in order to ensure a low viscosity before curing, playing a decisive role for an optimal printing result. Nevertheless, this also results in a low degree of cross linking and individual initiator and binder molecules that are not cross linked, or insufficiently so, do migrate through the cured ink into the surrounding medium.

"The numerous advantages of UV-curing inkjet inks, include fast curing, a wide range of application possibilities, high production numbers and small lot sizes"

The legalities for the use of inks in the food sector are specified by different regulations, such as the Swiss Consumer Goods Ordinance and the Nestlé Guidance Note on Packaging Inks. These positive lists are the basis for all inks, paints and varnishes for the food, pharmaceutical and cosmetics sectors. However, the already complex design of inkjet inks is made even more difficult by



UV glass peltier unit of the rheometer



Test print with developed cyan ink

CMYK print of the low-migration ink

the limited choice of components in these lists. In addition, due to technical challenges involved in synthesising such inks, hardly any low-migration, inkjet inks have been available on the market to date.

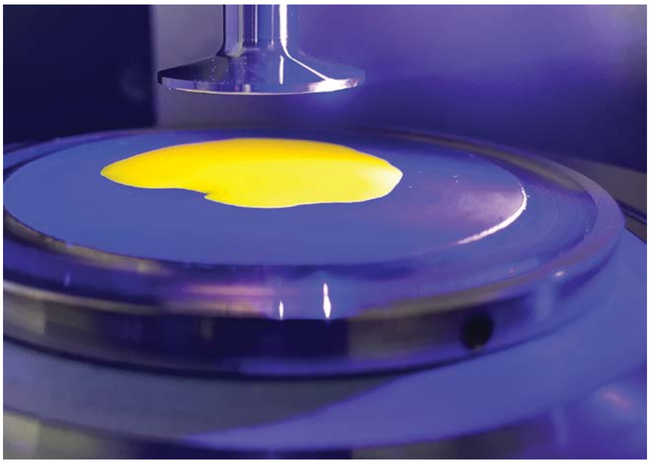
In particular, inkjet inks must contain smaller pigments (to prevent clogging of the inkjet printhead) and stabilisation methods are necessary to prevent re-agglomeration. However, these stabilisation methods can have a direct influence on the reactivity of the initiator. Furthermore, increased molecular masses of the ink components can negatively influence the rheological properties and change the Newtonian behaviour of an inkjet ink. Additionally, stability, processability and storability of the inkjet-printing inks must be checked.

PROJECT GUIDELINES

The Swiss Commodities Ordinance with Annex 6 of the Federal Department of Home Affairs (EDI) is used throughout Europe as a general guideline for the use of materials and objects intended to come into contact with food. This is not an official regulation with legal status, but is used as a reference for European ink manufacturers. On the other hand, the European counterpart – (EG) No. 2023/2006 – does not contain any explicit lists of substances that can be used. It gives only a rough guideline, "about good manufacturing practice for materials and objects that are intended to come into contact with food". As an additional selection criterion, the developed inks also meet the Swiss Consumer Goods Ordinance and European Printing Ink Association (EuPIA) recommendations.

To comply with these strict guidelines and to develop safe and sustainable inks, only components from groups 1A and B can be used for respective ink formulations. These components are toxicologically examined and have a low migration potential or a high molecular

Continued over


Shear, rate-dependent measurement of a test ink with a plate–plate geometry

weight ≥1,000 atomic mass unit (Da). These elements include, high-molecular and higher-functional acrylates as binders, higher functionality reactive diluents, branched photo-initiators, additives – with reactive double bonds that can also be cross linked – and chemically stable and durable pigments.

UNDERSTANDING AND DEVELOPMENT

Narrow choice of low-migration components, insufficient knowledge of their interdependence and impact on ink printability was a limiting factor for the development of low migration, UV-inkjet inks. The Network nanoInk therefore brought together interdisciplinary skills to improve the overall understanding and jointly develop respective UV-inkjet inks.

"A high number of functional groups ensure sufficient component cross linking in the ink"

Of vital importance was the choice of the correct photo-initiator together with its concentration, as it is essential for curing the ink, but is also the components with the highest migration potential. While a high level of initiator will ensure the ink is fully cured, it also increases the risk that the remaining initiator will not be fully cross linked and thus be able to migrate through and beyond the ink. Hence, the chemical reactivity of the initiators is an important key to control the migration ability of a UV-inkjet ink.

CORRELATION STUDY

As the reactivity is strongly influenced by the other ink components, including pigments (surface functionalisation) and binders (polymeric structure), an extensive correlation study was initially performed to better understand these dependencies. This study provided important knowledge about the structure-reactivity interactions of photo-initiators in low-migration, UV-inkjet inks. UV-supported dynamic differential calorimetry measurements were carried out to determine the individual reactivity of the components used. Both for the binder and for the reactive diluent – based on polyacrylate – it was shown that pure UV irradiation (without additional initiators) enables good cross linking. This is presumably due to the high reactivity of the acrylic groups in the used wavelength (320–500nm). A more defined dependence was observed for the examined pigments. In particular, highly absorbent (carbon black) or highly reflective (yellow, white) pigments can influence the necessary concentration of the initiator.

INFLUENCE OF PIGMENT

The influence of the pigment on the curing reaction was further investigated in-situ using UV-based, rheological measurements. A rotary MCR302 rheometer from Anton Paar GmbH with an additional glass peltier unit, together with a separate UV source (measured in oscillation mode) was used. The purpose was to calculate characteristic values, such as storage and loss modulus. Additionally, due to a data point recording speed of 100m/s, it was possible to record very fast curing reactions in detail. However, the limiting factor in the UV-assisted rheological investigations was the minimum gap distance of 50µm. Such a film thickness is significantly undercut during the printing process (typically 5–10µm).

Although no direct comparison can be made between the measured values and those obtained during a printing process, this characterisation method – currently rarely used – gives in-depth insights into the dependence of the curing reaction on the ink formulation. The investigations showed that the curing of the colour layer is slower at higher pigment proportions (associated with a strong UV absorption) and that a higher initiator concentration is necessary.

CONCLUSION

Based on the results of the correlation study, the partners jointly developed UV-inkjet inks that meet the stringent requirements for low migration and can unproblematically be used by all printhead manufacturers. Results showed viscosity in the range of 10–15mPas at 30–50°C and particle sizes of d50<100nm. The pigment-based, UV-inkjet inks have rheological and colour properties equal to conventional inkjet inks. They have also been optimised regarding the substrates to be printed (paper, PET and glass). This creates a colour system of yellow, magenta, cyan and black for graphic colour printing. The consortia is now looking for interested partners for further developments. The project was funded within the ZIM programme. ■

Dr Justus Hermannsdörfer is Project Manager at Network nanoInk/ Nanoinitiative Bayern GmbH

nanoInk NETWORK

Further information:
Network nanoInk/Nanoinitiative Bayern, Würzburg, Germany
tel: +49 931 3189377
email: info@nanoink.de
web: www.nanoink.de