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Target screening of acrylates from radiation-curing inks

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Ultraviolet (UV) cured coatings show excellent appearance, durability and little or no volatile organic compound (VOC) emissions while enabling increased productivity and lower overall costs. A UV-curable coating is one of the best finishing methods in the paper and packaging industries to protect ink layers from physical and mechanical defects [1]. In addition to photoinitiators, which start this polymerization, the formulations of printing inks contain monofunctional acrylic esters for viscosity adjustment and as a crosslinker to ensure rapid polymerization. After curing, it is possible and likely that this reaction will not be complete and the diluents and crosslinkers used will be unbound in the polymer.
The UV-curing printing inks and coatings are widely used, even in the printing of food contact materials.
For the photoinitiator isopropylthioxanthone (ITX) a mass transition from the printed packaging material into the foodstuff was demonstrated [2]. A migration of incompletely cured acrylate monomers is also likely. For trimethylolpropane triacrylate (TMPTA) a carcinogenic effect was reported [3].

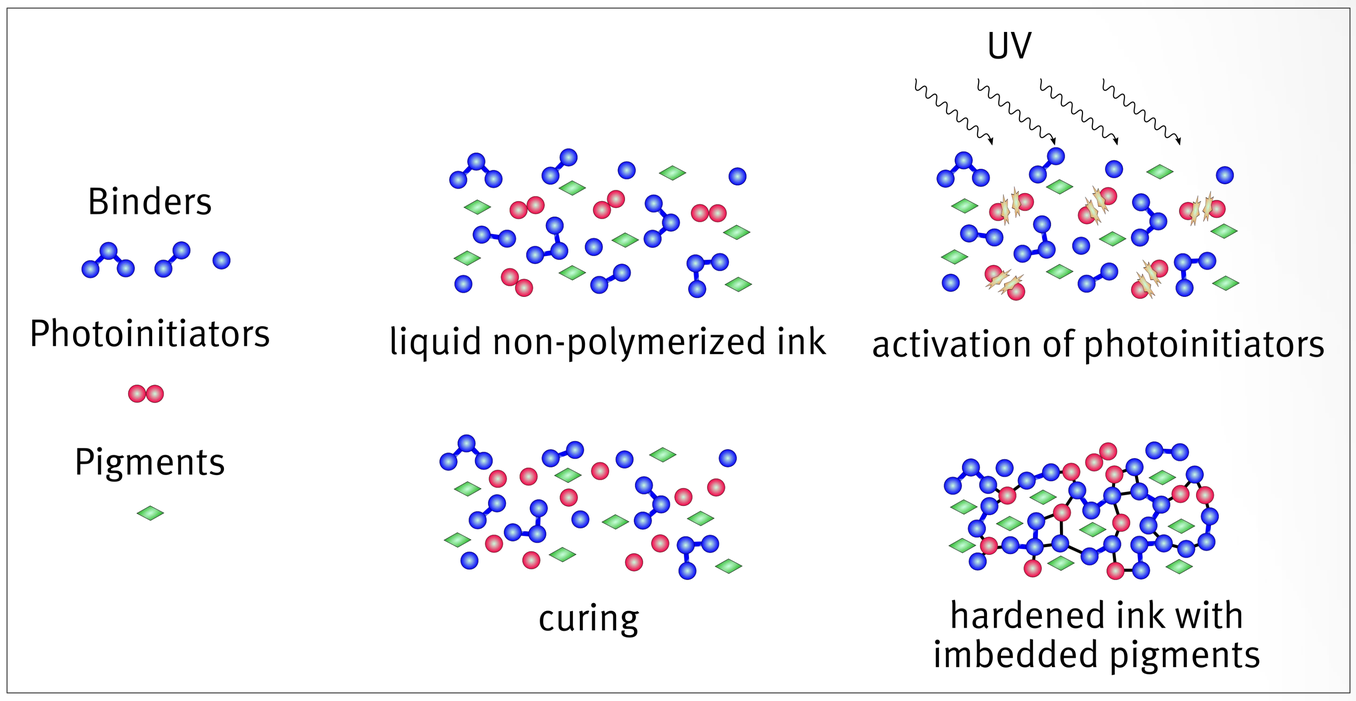
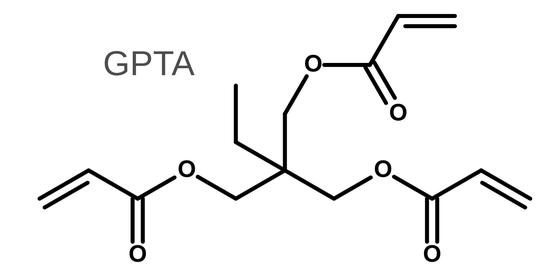
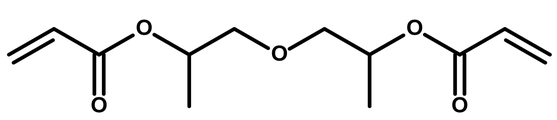


figure 1. UV-curing process

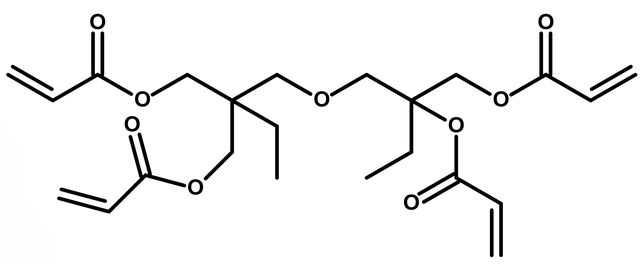
Nestlé, the world's largest food company, adjusted its *Guidance Note on Packaging Inks* accordingly, excluding the use of various photoinitiators (e.g. ITX) and acrylates (e.g. TMPTA and DPGDA).



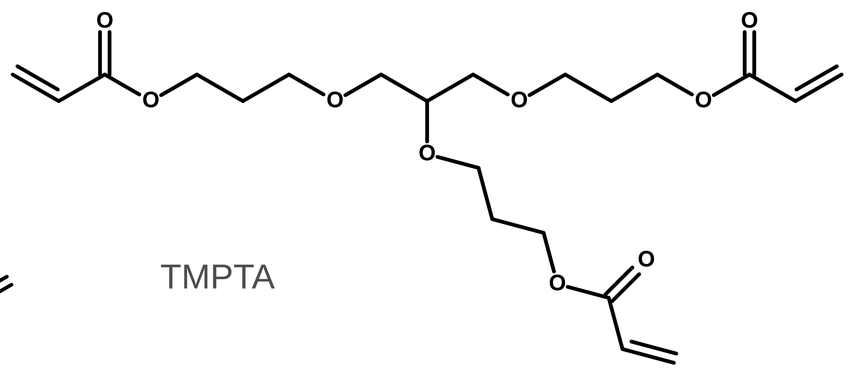


DPGDA

di(trimethylolpropan) tetraacrylate



TMPTA



A sensitive LC-ESI-MS/MS method was developed and validated for the target screening of different acrylate monomers in food simulants used for migration tests.
Food simulants are measured directly using an internal standard (ITX-d7). Substance separation is performed with RP-HPLC and a gradient program (8 min). Quantification is performed by external calibration. As a quality assurance measure, one sample per measurement series is spiked with the analytes.
The method contains the following analytes:

di(trimethylolpropane) tetraacrylate (CAS 94108-97-1)
pentaerythritol tetraacrylate (CAS 4986-89-4)
diurethane dimethacrylate (CAS 72869-86-4)
pentaerythritol triacrylate (CAS 3524-68-3)
NPGPDA (CAS 84170-74-1)
GPTA (CAS 52408-84-1)
TMPTMA (CAS 3290-92-4)
ITX (CAS 5495-84-1)
DPGDA (CAS 57472-68-1)
TMPTA (CAS 15625-89-5)
TPGDA (CAS 42978-66-5)

For each analyte, we reach a limit of determination of at least 0.01 mg/kg migrate, usually significantly lower.
This year we analyzed different food simulants from our customers. We detected GPTA and TMPTA in an in-mould label. In another sample we detected DPGDA and di(trimethylolpropane) tetraacrylate .

There is a need for the analysis of acrylates from radiation-curing inks. The tested substances are used and can be detected in food simulants. We developed a fast, sensitive and reliable screening method. In the future the spectrum can be extended by further acrylates detectable with LC-MS and common photoinitiators.

[1] Soltani, M. et al. (2013) UV-curable coating process on CMYK-printed duplex paperboard, Part 1: Mechanical and optical properties, BioRes. 9(1), 86-92.
[2] T. Jung , T.J. Simat & W. Altkofer (2010) Mass transfer ways of ultraviolet printing ink ingredients into foodstuffs, Food Additives & Contaminants: Part A, 27:7, 1040-1049, DOI: 10.1080/19440041003596543
[3] Kromhout, H. et al. (2018) Carcinogenicity of isobutyl nitrite, β-picoline, and some acrylates. The Lancet Oncology. 19. 10.1016/S1470-2045(18)30491-1.

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