The Solution in Energy Curing

Miwon Specialty Chemical Co., Ltd.





Nestle Compliant Chemistries to Enable Next Generation Formulations

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Current Guiding Regulations

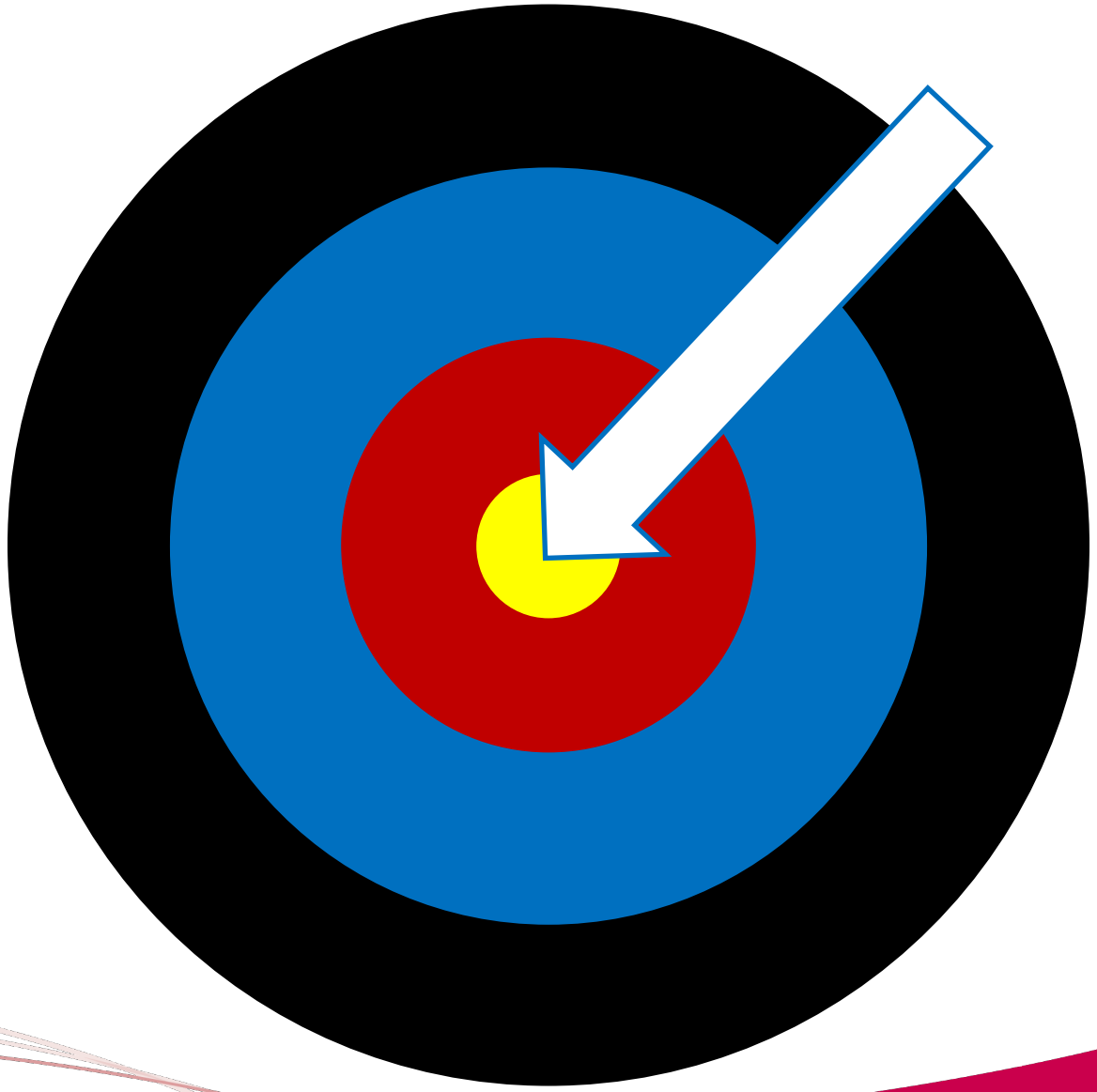
- EuPIA Plastics Regulation No 10/2011
  - Covers the entire plastic article, including the non-contact printed area
  - Does not specifically cover the printing ink itself
    - Can be guided by company or nation
  - OML and SML's set for included materials
  - Extraction and manufacturing requirements must be met

- Swiss Ordinance on the FDHA on articles and materials (RS 817.023.21)
  - National guideline on products for inclusion in formulations

- Nestle Guidance Note
  - Company guideline that excludes particular products

Formulation Exclusion

All Available
- Monomers
- Oligomers
- Photoinitiators
- Pigments
- Additives



Swiss Ordinance
- Allowable components
- SML

Application Requirements
- Registration
- Viscosity
- Adhesion
- Cure profile
- Pigment wetting

Nestle Guidance Note
- Exclusion of components

Products Excluded by Nestle Guidance Note

- SML guidelines outlined by Swiss Ordinance must be obeyed
  - Substances not listed on Swiss can not be used in Nestle formulations
  - Applies to each component
  - Part A → specific SML
  - Part B → default migration of 10 ppb
- Products listed on the Swiss Ordinance can be further excluded from Nestle formulations
- Selection of resins, pigments, and photoinitiators are under the purview of formulators
- Minimize (Nestle def): use the minimum quantity necessary to achieve an expected technical effect
- Exclusion (Nestle def): must not be intentionally used

Nestle Exclusion Products

Exclusion List	Exclusion List for Acrylates	Exclusion List for Solvents
Titanium Acetyl Acetonate	Butanediol diacrylate	Methyl glycol
Phthalate plasticizers	Diethylene glycol diacrylate	Ethyl glycol
Bisphenol A	Isodecyl acrylate	Monochlorobenzene
SVHC	Octyl acrylate	**Toluene**
NC resins in microwave articles	Phenoxy ethyl acrylate	1-methyl-2-pyrrolidone
Vegetable oil / fatty acid esters with strong odors		
Heavy / toxic metals		
Press washes and founts that have objectionable odor		

Nestle Minimize Products

Minimize List for Acrylates	**Minimize List for Solvents**	
TMPTA	Methanol	Butoxypropanol
DPGDA	**Cyclohexane**	Butoxy propoxy butanol
HDDA	MEK	Ethanediol
2-EHA	MiBK	Diethylene glycol
Mixtures of PETA	Hexanol	Triethylene glycol
TEGDA	2-ethyl-1-hexanol	Butyl glycol acetate
	N-octanol	1-methoxy-2-propylacetate
	Butyl glycol	Ethylbenzene
	Ethyl diglycol	Pentanol
	Butyl diglycol	
	Hexylene glycol	

Design of Acrylates for Nestle Compliance

Final acrylate will meet SML with expected cure and not listed on Nestle

Toluene Free Process

BPA free components

Remaining raw materials, solvents, or catalysts

- Listed Swiss SML
- Worst case extractable calculations

Stabilizer types and amounts

Calculation of Remaining Components

$$c_{max} = m_{ink} \times c_{ink} \times a_{spec} \times 0.01$$

c_{max}	Maximum concentration of migrant in foodstuff in worst case (µg/kg (ppb))
m_{ink}	Mass of liquid ink or coating applied to packaging (g/m^2)
c_{ink}	Content of migrant in ink or coating (ppm)
a_{spec}	Specific surface area of foodstuff (dm^2/kg). 6 dm^2/kg for EU cube
0.01	Conversion factor

- Worst case calculation allowed by Union Guidance on Regulation (EU) no 10/2011 (and updated versions)
- Must be backed by extraction testing
  - Extraction conditions determined by end-use
  - Cure conditions representative of commercial conditions

Calculation Example

How much MeHQ (CAS 95-71-6) can be used to stabilize an acrylate oligomer intended for Nestle inks?

Assumptions

- m_{ink} = 2 g/m^2 for offset ink, as laid out by EuPIA
- c_{max} = 10 ppb, SML listed in Swiss Ordinance
- Maximimum of 50% of the oligomer usage in the formulation

$c_{max} = m_{ink} \times c_{ink} \times a_{spec} \times 0.01$

$10 = 2 \times c_{ink} \times 0.06$

c_{ink} = 83 ppm = extraction amount of MeHQ allowed in total formulation

$83 = (200 \times 0.34) + (y \times 0.50)$

y = 30 ppm = MeHQ allowance after monomers

The Ongoing Toluene Drama

- Added as a Prop 65 material in 1991
  - Reproductive toxin as determined by a state qualified expert
  - Required warning of exposure to consumers
  - No safe harbor limits for toluene
- Recently more attention from private and public enforcers
- And more sensitivity from packaging producers and brand owners
- Prop 65 verbiage applied to SDS's
  - Traditionally a conservative approach to Prop 65 labelling
  - Now, if testing shows no toluene then no Prop 65 labelling is applied
- Now a member of the solvent exclusion list for Nestle

Nestle Formulation Component Strategies

	Inks	GA Coatings
Oligomers		
Polyester Acrylates	Pigment dispersion • Loading and product depends on ink type • **Toluene process** • **Excessive stabilizers** Adhesion • Chlorinated and non	Adhesion on difficult substrates
Epoxy Acrylates	Film properties and cure response • BPA and non-BPA types	Main oligomer used for all desired film properties • Mostly BPA-based

Nestle Formulation Component Strategies

	Inks	GA Coatings
Oligomers		
Amino Acrylates	Improvement in cure response • Additive or main resin	Lower levels to improve cure response
Urethane Acrylates	Film properties • Generally not the main oligomer • Enhance and different properties	Film properties differentiation from EA • Flexibility • Weathering • **BPA free**
Monomers	Reduce formulation viscosity to match application need • **Toluene process or in toluene facility** • Multifunctional monomers to achieve extractables • Monomer replacements	

Toluene Free Polyester Acrylate Chemistry

- Approach was to completely remove toluene from the process and facility
- Retain pre-established clearances
  - International registrations
  - REACh status
- Stabilizer types and levels to meet worst case calculations
- Monomers expected to yield low odor / low extractables
  - Tri or higher functional
- Minimize other undesirable remaining components
- High ink performance expected of polyester acrylate chemistry

	Toluene Process	Toluene Free Process
Viscosity, cP, 25 °C	50,000	40,000
Remaining solvent, ppm	200 ppm toluene	10 ppm CHX
Color	4G	4G

Toluene and Toluene Free Comparison – Offset Ink

	Toluene Process	Toluene *Free* Process
Polyester acrylate, %	26.0	26.0
Modified EA, %	26.0	26.0
TMPTA, %	17.0	17.0
Blue 15:3, %	18.0	18.0
Additive Package, %	13.0	13.0
Tack, 1200 rpm, g-m	22	22
Misting, 0 → least amount	1.5	1.5
Tan Delta	0.48	0.56
G′, MPa	5300	2600
Viscosity, P, 25 °C	112	82

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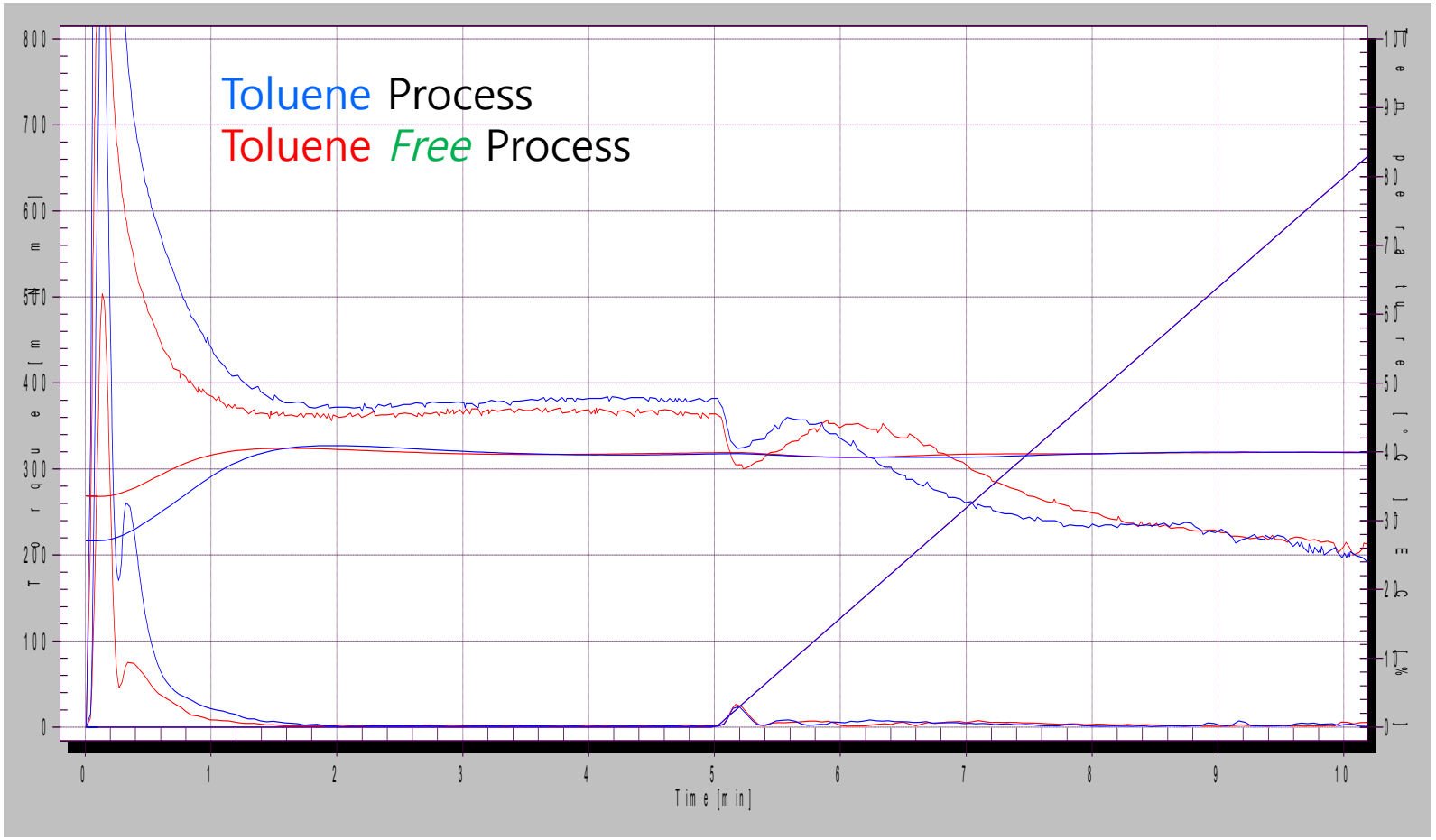

Toluene and Toluene Free Comparison – Flexo Ink

	Toluene Process	Toluene *Free* Process
Polyester acrylate, %	6.6	6.6
Amino Acrylate, %	65.3	65.3
Blue 15:3, %	20.2	20.2
Additive Package, %	7.9	7.9
Tan Delta	>200	>200
G', MPa	0.0020	0.0008
Viscosity, P, 25 °C	0.56	0.50
Gloss	38	43
Density	1.3	1.5

Unintended Casualty of BPA Uncertainty

- Chlorinated and non-chlorinated polyester resins are commonly used in UV/EB packaging inks and coatings for adhesion to plastics
  - The building blocks are not Bisphenol A but still contain trace amounts of Bisphenol A
  - Bisphenol A excluded for use by Nestle, even with the long history of use
- Alternate chemistry does exist!
  - Long history of using specialty acrylics with great results
  - But…high levels of toluene are present in these products
- Developed new chemistry address these issues while exceeding ink performance of traditional oligomers
  - Toluene free
  - BPA free
  - Global registration clearance
  - Still drawbacks

Toluene and Toluene Free Comparison – Offset Ink

	Toluene Process	Toluene *Free* Process
Acrylic oligomer, %	38.0	38.0
Polyester acrylate, %	15.0	15.0
EO TMPTA, %	15.0	15.0
Blue 15:3, %	18.0	18.0
Additive Package, %	14.0	14.0
Tack, 1200 rpm, g-m	17	15
Misting, 0 → least amount	1	0.5
Tan Delta	0.60	0.48
G', MPa	4200	3400
Viscosity, P, 25 °C	75	62

Toluene and Toluene Free Comparison – Offset Ink

	Toluene Process	Toluene *Free* Process
Adhesion, PVC, 0 → Excellent	4	0
Adhesion, BOPP	1	1
Adhesion, Aluminum	0	0
Adhesion, PP	5	1
Adhesion, Metalized PP	1	1

Lithotronic

Thank You

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