Low Migration UV inkjet inks
Examples of food packaging printed with LM UV inkjet inks

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Agfa Graphics
2015-11-18
Outline

- Who is Agfa Graphics and where active in industrial printing?
- Food packaging printing by inkjet – why inkjet / why UV?
- Ink requirements for food packaging
- Ink requirements for UV inkjet printing
- Development of Low Migration UV inkjet inks
- Summary and conclusions
Part of the Agfa-Gevaert Group

- Founded in 1867, IPO in 1999 (Brussels)
- Headquartered in Antwerp, Belgium
- Sales of EUR 2.620 billion in 2014
- 10,506 employees (FTEs) worldwide
- Wholly owned sales organizations in more than 40 countries
- 21 R&D and production sites around the globe
- Global market leader in each of its divisions

<table>
<thead>
<tr>
<th>Agfa Graphics</th>
<th>FY 2013</th>
<th>FY 2014</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sales</td>
<td>1,491</td>
<td>1,355</td>
<td>-9.1%</td>
</tr>
<tr>
<td>Recurring EBITDA*</td>
<td>97.9</td>
<td>100.4</td>
<td>+2.6%</td>
</tr>
<tr>
<td>Recurring EBIT*</td>
<td>60.7</td>
<td>70.0</td>
<td>+14.3%</td>
</tr>
</tbody>
</table>

€ 2.9 billion
### Integrated & innovative solutions

#### Best-in-class portfolio by segment

<table>
<thead>
<tr>
<th>Commercial Printing</th>
<th>Packaging &amp; Labels</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Prepress equipment, consumables, software and services</td>
<td>- Prepress and inkjet equipment, consumables, software and services</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sign &amp; Display</th>
<th>Industrial Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Wide-format UV inkjet printing equipment, consumables, software and services</td>
<td>- Industrial inkjet inks; integration of printing into existing industrial manufacturing processes</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Newspapers</th>
<th>Security Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Prepress equipment, consumables, software and services; mobile and cloud solutions</td>
<td>- For high-end security printers who want to protect their designs against counterfeiters</td>
</tr>
</tbody>
</table>
Industrial inks for graphic and non-graphic applications

Integration of printing into existing industrial manufacturing processes
- Integration of print equipment
- Ink development
- Imaging software and color control
- Workflow solutions

Your partner to integrate print in manufacturing
Analog or digital?

Why printing?
→ decoration, information, marketing, identification…

Analog printing:
– Examples: gravure printing, pad printing, offset, flexography, screen, …
– Master to be made for each print colour
– Fixed set-up cost divided by number of prints → preferably large print runs

Digital printing: no master – variable run lengths
– Laser/toner/EP vs. inkjet

Each printing technique requires specific inks
ABC of inkjet printing

Inkjet = ink droplets jetted by small nozzles

Digital, non-contact printing method
- no master (plate or sleeve)
- direct from image file to substrate

Ink properties for jetting process
- No 1 = low viscosity,…

Ink properties for application
- surface tension for image quality
- UV curable for non-absorbing substrates

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<td>web offset</td>
<td>10000 - 80000</td>
</tr>
<tr>
<td>sheet-fed offset</td>
<td>10000 - 80000</td>
</tr>
</tbody>
</table>

viscosity in mPa.sec
Industrial printing: INK plays a key role

**PRF = Process Result Fit-for-use**

**PROCESS**
INK fitted to the printhead, print system and substrate

**RESULT**
INK fitted to the application, delivering the end-user performance

**FIT-FOR-USE**
INK fitted to cost, environment, legislation, people, business model, company, …

Competitive solution

PRF model
Drivers to industrial inkjet printing

• Market trends
  – extremely large run lengths → varying run lengths
  – Just-in-time production & short lead times
  – Personalisation, flavoring, seasoning, marketing (launch), …

• Applications
  – Growing number of applications
  – Interior decoration: non-printed → printed, mass → personal
  – Product decoration: direct-to-shape ono large range of objects
  – Packaging: large variety from label to direct print, corrugated, …

• Inkjet Technology
  – All the advantages of digital (no master, low waste, first print OK, low energy drying / curing, short production cycle, …)
  – Industrial reliability gets proven every day
  – Printheads, software, curing/drying, inks, … available now
  – Customization: tuned system and inks
### Drivers to digital printing for packaging

**Inkjet printing is a response to packaging needs / trends**

- growing number of SKU’s → shorter run lengths
- variable run lengths
- “just in time” printing (high flexibility)
- print all info in one step (including promotions etc)
- new possibilities (customer communication - interaction)
  - events, seasonal, personalisation, …

**Packaging printed by inkjet = more sustainable**

- no need for master, direct from image file
- low waste of ink and substrate
- direct print = no wrapper or label needed
- print the exact amount of prints needed
- low energy curing, no VOC’s
- delivering possibility to lower stocks
- printing on location -> less transport
- shorter chain -> less food waste
Comparison full cost of printing (ROI) between traditional printing and inkjet printing (in function of the run length) -> so-called cross-over point

Inkjet adoption – economics must be right

“every cent lower will increase inkjet use”

Trend to shorter run lengths

New demand?
### Why UV inkjet for industrial printing?

#### UV inkjet: combination of quality, high print speed, industrial reliability

- **UV inkjet printheads**
  - Piezo printheads with industrial reliability
    - Resolution, drop placement, operating window
    - Importance of the waveform (printhead – waveform – ink)
  - UV inkjet inks
    - UV ink formulations
      - Tuning to the jetting: long latency time, low printhead maintenance
      - Tuning to the function: IQ, color, physical properties, durability, …
      - Tuning to the UV curing (pin / final)
    - UV printing for industrial applications
      - Printing direct on the substrate (no need for receiving layer)
      - High speed single pass printing
      - Fast drying by UV light (trend to LED, but also Hg bulb or combination)
      - Pre-treatment in-line to control ink wetting and adhesion, etc
Packaging printing
- Indirect printing (printing on the non-contact side)

- Primary food packaging (food & beverages)
  - Direct on ‘Food container’
  - Lids and closures
  - Pouches
  - Foils (wrap, flexible, laminates, etc.)
  - Labels
  - Secondary food packaging

- Pharmaceutical packaging
  - Direct print on medical bag, syringes, etc.
  - Foils (mostly alu based blisters)
  - Secondary packaging
Food safety

What can go wrong?

(In)visible set-off

Set-off

Migration
Food safety

Food packaging printing needs to be a controlled process

Combination and control of all parts of the print solution

- Substrate (barrier quality)
- LM UV-curable inkjet ink
- Printing and process conditions
- Environmental conditions

Food safe packaging
Ink specifications:
- Swiss Ordinance 817.023.21, German Bedarfsgegenstand
- EuPIA Guideline on Printing Inks applied to the non-food contact surface of food packaging materials and articles
  - EuPIA Exclusion List for Printing Inks and Related Products
  - EuPIA Suitability List of Photo-Initiators for Low Migration UV Printing Inks and Varnishes

Food packaging regulations where inks may be involved:
- General Framework Regulation 1935/2004/EC
- Plastics regulation 10/2011/EC
- GMP 2023/2006/EC

Company specific claims
- Company “List of Restricted substances” (e.g. soluble azo dyes, heavy metals such as lead, hexavalent chromium, mercury and cadmium).
- ITX, benzophenone or 4-methylbenzophenone
- Nestlé list, ...

Common ground in legislations: 10 µg / 6 dm² (6 dm² is the typical packaging area for 1 kg of food) \(\rightarrow 10 \mu g/1 \text{ kg} = 10 \text{ ppb}\): rule-of-thumb for the allowable specific migration limit for the different ink compounds. If sufficient toxicological data available, this limit can be higher.
Not free to formulate for LM inks

Ordinance on articles and materials - Annex 6, List of binders (monomers), Part A: evaluated substances

<table>
<thead>
<tr>
<th>Designation</th>
<th>CAS n°</th>
<th>SML [mg/kg]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,7,9-Tetramethyl-5-decyne-4,7-diol</td>
<td>0000126-86-3</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>beta-Pinene</td>
<td>0000127-91-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phthalic acid, diallyl ester</td>
<td>0000131-17-9</td>
<td>n.d. (DL = 0.01)</td>
<td></td>
</tr>
<tr>
<td>4-(1,1,3,3-Tetramethybutyl)phenol</td>
<td>0000140-66-9</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Acrylic acid, ethyl ester</td>
<td>0000140-88-5</td>
<td>6 (T)</td>
<td>s. annex 1, list III.17</td>
</tr>
<tr>
<td>Ricinoleic acid</td>
<td>0000141-22-0</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>Acrylic acid, n-butyl ester</td>
<td>0000141-32-2</td>
<td>6 (T)</td>
<td>s. annex 1, list III.17</td>
</tr>
<tr>
<td>2-Aminoethanol</td>
<td>0000141-43-5</td>
<td>0.05</td>
<td>s. annex 1, list III.11</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>0000142-62-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lauric acid</td>
<td>0000143-07-7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Nonanol</td>
<td>0000143-08-8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Oxalic acid
2-Ethylhexanoic acid
Ethyleneimine
n-Decanoic acid
Palmitoleic acid

Ordinance on articles and materials - Annex 6, List of photoinitiators, Part B: non-evaluated substances

<table>
<thead>
<tr>
<th>Designation</th>
<th>CAS n°</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(oxy-1,2-ethanediyl), a-[2-(4-chlorobenzoyl)benzoyl]-w-[2-(4-chlorobenzoyl)benzoyl]oxy]-</td>
<td>1007306-69-5</td>
<td></td>
</tr>
<tr>
<td>2-Propenoic acid, 1,1',9'-(1-fluoro-9-oxo-9H-thioxanthene-4-yI)oxy]methyl]-7,12-dimethyl-3,6,8,11,13,16-hexaaoxactadecane-1,18-diyl ester</td>
<td>1253390-33-8</td>
<td></td>
</tr>
<tr>
<td>2,3-Dihydroxy-6-(2-hydroxy-2-methyl-1-oxopropyl)-1,1,3-trimethyl-3-[4-(2-hydroxy-2-methyl-1-oxopropyl)phenyl]-1H-indene</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>2-Hydroxy-[4'-2-Hydroxypropoxy] phenyl]-2-methylpropanone</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>Mixture of 3-(4-(2-Hydroxy-2-methylpropionyl)phenyl)-1,1,3-trimethyliindan-6-yI 2-hydroxyprop-2-yl ketone and 3-(4-(2-Hydroxy-2-methylpropionyl)phenyl)-1,1,3-trimethyliindan-5-yI 2-hydroxyprop-2-yl ketone</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>Polyethylene glycol (200) di(β-4-[p-acetylphenyl]piperazine) propionate</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>Reaction product from ethoxylated dipentaerythritol with 10-biphenyl-4-yl-2-isopropyl-9-Oxo-9H-thioxanthen-10-ium hexafluorophosphate</td>
<td>n.a.</td>
<td></td>
</tr>
</tbody>
</table>
Migration testing

Single sided extraction

- dependent on the application different simulants can be used at different temperatures e.g. water, water + acid, water/ethanol mixtures, ethanol, …
- identification and/or quantification of extracted compounds

<table>
<thead>
<tr>
<th>Reference number</th>
<th>Description of food</th>
<th>Food simulants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>02.05</td>
<td>Pastry, biscuits, cakes, bread, and other bakers’ wares, dry:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. With fatty substances on the surface</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B. Other</td>
<td></td>
</tr>
<tr>
<td>02.06</td>
<td>Pastry, cakes, bread, dough and other bakers’ wares, fresh:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. With fatty substances on the surface</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B. Other</td>
<td></td>
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Direct print on (plastic) object / packaging

Direct-to-shape printing: screen, pad,… → inkjet printing

COMPLEXITY of the solution

Key aspects

- Ink performance (e.g. adhesion)
- Ink – substrate interaction
- Industrial reliability
- Link to pre- and post- processes
- Productivity (output)
- Workflow integration
Sustainability inkjet of direct food container printing

Inkjet sustainability
- Direct from file
- Low ink waste
- Low substrate waste
- Low energy
- No VOC's

Sustainability chart

Low use of resources and low waste
Short time chain \(\rightarrow\) Less food waste
The PRINT process – the INK formulation

• Single pass printing

System solution: a range of options in the system design

Pre-treatment → White curing → CMYK curing → Varnish curing

Customized system
Combination of elements
Conveyor, robot, direct-to-shape

Customized result
Print speed, image quality
Application, Substrates

Ink selection: application, substrate(s), curing speed, printhead, pin or not, full list of functional specifications, ink set (Wh / colors / Varnish)
The PRINT process – the INK formulation

- Controlling ink wetting: matching ink formula to the system

System: increase surface energy, adjust cure delay, curing degrees
Ink formula: dynamic surface tension, wetting “plateau”

Optimized ink wetting
→ image quality, full patches, adhesion, gloss, …
Ink tuning: what is in the ink?

**UV curable inkjet ink**

Inkjet ink droplet (picoliter size)

- **Monomers**
- **Photo-initiators**
- **Color pigment & Polymeric dispersant**
- **Additives**
  - Surfactants
  - Adhesion promoters

...
LM UV-curable inkjet inks

The low viscosity – low migration dilemma

- Low Migration UV-curable inks for flexo, offset printing
  - comprising oligomers and pre-polymers

- Inkjet inks = need for low viscosity (in mPa.sec)

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How to solve for inkjet printing?

- possible by use of standard UV-curable inkjet inks?
- need for specially designed LM inkjet inks?
Low Migration UV-curable inkjet inks – how?

Sign & Display UV inkjet inks

- Suited for migration sensitive applications?

<table>
<thead>
<tr>
<th>ink composition</th>
<th>standard UV inkjet inks</th>
</tr>
</thead>
<tbody>
<tr>
<td>monomers</td>
<td>low functional acrylates (with impurities) (often high amount of monofunctional acrylates)</td>
</tr>
<tr>
<td>photo-initiators (PI's)</td>
<td>ITX, benzophenone, and other small PI's</td>
</tr>
<tr>
<td>polymerization degree</td>
<td>92 - 98 %</td>
</tr>
<tr>
<td>smell of print</td>
<td>mostly smelling for a long time after printing</td>
</tr>
<tr>
<td>migration sensitive applications</td>
<td>unacceptable amounts of extractable/migrateable ink compounds</td>
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</table>

- Conclusion: NOT suited to be used for primary food and pharma packaging
  - note that for some applications with high barrier substrates and/or very low ink amounts, standard UV inkjet inks can be used safely, on the condition that all ink compounds are of the positive lists of the Swiss Ordinance list

→ Need for UV inks tuned to application = LM inks
Agfa Low Migration UV ink technology

Agfa inventions to develop LM inkjet inks:

- High degree of polymerization
  ➔ very low amount of unreacted monomers

- PI’s which have very low mobility but high reactivity
  • Diffusion-hindered PI’s with low viscosity
  ➔ very low migration of PI’s

➔ very limited migration and very limited set-off
Ink tuning: Low Migration UV inkjet inks

UV-curable LM inkjet ink

Combination of
Highly reactive low viscous monomer
Diffusion-hindered PI system
→ High curing degree
→ Low migration of monomers and PI’s

Additives
Surfactants
Adhesion promoters
Stabilizers

Inkjet ink droplet

Ink design to
Specific print system
Specific application

All compounds on Swiss list
GMP produced
Many other guidelines

Color pigment & Polymeric dispersant

Conceptual LM ink design
Agfa LM ink formulations

Agfa conceptual LM inkjet ink concept design

- **High degree of cross-linking** => very low amount of unreacted monomers  
  • => very low migration and set-off of monomers
- **Photo-initiators which have very low mobility but high reactivity**  
  • => very low migration and set-off of PI’s

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<tr>
<td>polymerization degree</td>
<td>92 - 98 %</td>
<td>up to 99.9999 %</td>
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<tr>
<td>smell of print</td>
<td>mostly smelling for a long time after printing</td>
<td>very low to zero smell (pass the Robinson test)</td>
</tr>
<tr>
<td>migration sensitive applications</td>
<td>unacceptable amounts of extractable/migrateable ink compounds</td>
<td>YES, but not for all</td>
</tr>
</tbody>
</table>

- substrate barrier quality also plays an important role
- if very low barrier quality (e.g. very thin PP foil, then not OK if LM ink only)
Monomers and Photo-initiators “chained together” in the ink layer after curing by UV light.
Agfa LM inkjet ink technology honored with *essenscia Innovation Award 2014* awarded for innovation in respect to innovation, sustainability, protected by IP, and showing big potential in next years selected from 25 innovations granted by essenscia (Federation of Belgian Chemical Industry) granted on December 03, 2014
Summary and conclusions

**Inkjet printing** on packaging = answer to packaging trends

**UV LM inkjet ink** formulation $\Leftrightarrow$ **low viscosity** for jetting

Thereby requires full conceptual development of LM ink concept

**Monomers** and **photo-initiators** need to be LM ink specific designed for combination of low viscosity and high curing degree

**Dedicated LM inkjet ink technology** can result in low migration levels, including **direct print on food packaging**

**Highly reactive monomer** is key driver to full curing

**Diffusion-hindered Photo-Initiating** system key to curing speed (UV LED curing) and low migration of PI’s
Examples of inkjet printing for food packaging applications
Food packaging printing needs to be a controlled process

Combination and control of all parts of the print solution

- Substrate (barrier quality)
- LM UV-curable inkjet ink
- Printing and process conditions
- Environmental conditions

Food safe packaging

What can go wrong?

(In)visible set-off

Migration
Printing on alu blister foil (blister pack)

Printing product information

• Aluminium substrate is most common
  – complete barrier → no migration

• Risk of set-off: depending on process
  – off-line printing = roll-up → risk of set-off
  – near-line printing = roll-up (short time) → still risk of set-off
  – in-line printing → no risk of set-off
  – typically the ink amount is relatively low (diagonal print / print contact surface)

• Ink performance
  – alu foil typically has primer layer
  – → ink wetting and adhesion (pre-treatment)
  – heat sealing step on top of ink

• Note: pharma blister market
  – GMP mostly required → LM ink
  – trend to 1 QR-code / unit → inkjet
  – trend to multi color → inkjet
Label printing for food packaging

Printing product information

- Paper substrates and plastic substrates most common
- Typically printing on outside of the label
  - Protection against migration by label substrate + container
  - Risk of set-off during roll-up of the printed roll
- Today: inkjet UV label presses
  - Challenging digital print by toner printing
  - > 30 different suppliers (Label Expo EU in Brussels in September 2015)
- Ink performance
  - ink wetting on large range of substrates
  - heat sensitive substrates → LED curable inks
  - White + color printing: high resolution / color gamut
- Market
  - today no market pull to LM inks yet
  - brand owners start to require LM inks
# Direct printing on food packaging

<table>
<thead>
<tr>
<th>Direct print on PET beverage bottle</th>
<th>Direct print on plastic food cups / tubs</th>
<th>Direct print on plastic closure caps</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="PET bottles" /></td>
<td><img src="image2" alt="Cups" /></td>
<td><img src="image3" alt="Caps" /></td>
</tr>
<tr>
<td>production printing</td>
<td>Just-In-Time printing</td>
<td></td>
</tr>
</tbody>
</table>

**KHS**
- Bottling lines
- Direct Print

**POLYTYPE**
- Print equipment food containers
- DigiCup / DigiRound printer

**Sacmi**
- Food packaging equipment
- Colora Cap

11/18/2015
Direct print on closure caps (beverage bottles)

- HDPE substrate is most common
  - porous substrate $\rightarrow$ risk of migration
- Freshly printed caps fall into box
  - $\rightarrow$ risk of set-off of ink compounds
  - $\rightarrow$ need for immediate adhesion / scratch resistance
- Type of beverage can differ
- Printing : handling relatively easy
  - high output possible
- Printing : image quality in function of cap
  - clear / white / colored cap
  - pre-treatment extremely important
  - colored cap : white / cure / color inks / cure
- Mass customisation
  - easy : print folder $\rightarrow$ define nr / qty of images
Direct print on food containers (cups / tubs)

Direct print on food tubs / cups

- polypropylene substrate is most common
  - porous substrate → risk of migration
- stacking very short after printing → risk of set-off
- single use containers ↔ multiple use containers
- mostly for chilled products in refrigerator
- type of food: water based – oil based – diary: different risks of migration
- printing: handling of the tub / cup for constant print quality
- print performance: pre-treatment of the surface → ink wetting
Innovation in all aspects of the product

- Beer in PET bottles
  - light weight, unbreakable
- First Direct Print system powered by KHS
  - PET bottle blowing – inside coating – Direct Print – filling all at same location
  - Printing 4 images at the same time
  - Agfa LM UV inkjet inks for direct print on PET bottles
    - food / beverage safe (migration)
    - White + overprinting with CMYK
    - physical properties
    - image quality
    - LED curable
    - jetting performance Xaar head skyscraper
    - ...
- Campaign : Kampioenenbier
  - linked to release of second movie
  - “Talking Bottles” by the app on your smart phone
Direct Print by inkjet: Value proposition

State-of-the-Art

label order design

Delay

Cost

logistics

stock

glue

fill

ship

Drink Manufacturer

Printed bottle supplier

Value proposition = JIT + Cost effective Solution
Innovation in all aspects of the product

- Beer in PET bottles (bottles with internal coating)
- First Direct Print system powered by KHS
  - PET bottle blowing – inside coating – Direct Print – filling
  - Direct print with Agfa LM inks
    - White + CMYK ink set
  - Printing 4 images at the same time

- Augmented Reality by Agfa AR+ app
Summary and conclusions

Printing on food packaging by UV inkjet technology
  – full system approach
  – Low Migration (LM) ink is key element of the print solution

Inkjet ink tuning to the print system (printhead, substrate, drying, …)

Inkjet ink optimisation to the functional needs of a specific application
  – fitted to the production process
  – fulfilling the functional requirements of the print

LM UV-curable inks design towards specific applications
  – printing on many different types of food packaging
  – low migration performance proven
  – examples: PET beverage bottles, food containers, closure caps
  – more to come (also for pharma packaging)
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