Adhesion of inkjet inks: Pain or gain?

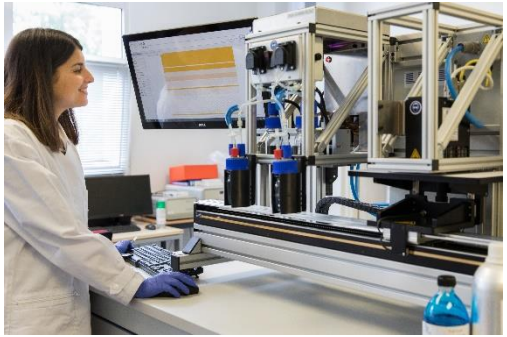
Dr. Yolanda Justo

CHEMSTREAM
SUSTAINABLE CHEMISTRY

Chemstream: The Chemical R&D Company

Profile

- Founded in April 2010
- **Staff profile:**
  - Chemistry
  - Material Science
  - Bio Engineer
- **Located near Antwerp – Belgium**
- **Lab-facilities (500 m2)**
  - Organic Synthesis
  - Chemical Formulation
  - Characterization



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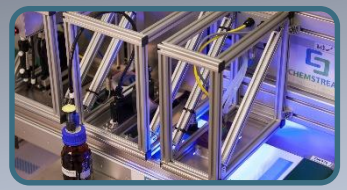
Chemstream: The Chemical R&D Company

Mission

To translate customer requirements into chemical formulations with dedicated functionalities, from **design to prototyping and implementation**

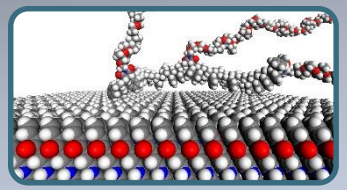
Organic Synthesis

* Crystal, colorant and dispersant design
* Photochemistry
* Interfacial chemistry, wetting and adhesion
* Superabsorbing polymers



Technology

* Dispersion technology
* Coating, printing, jetting (Modular printing unit MPU)
* Radiation curing (UV, UV-LED, e-Beam)
*Atmospheric plasma



Methodology

* Molecular Modeling
* Design of Experiment (D.O.E.)
* Smart throughput screeining
* Hansen solubility parameters (HSP)

Analytical and physical chemical tools

* UVVIS, FTIR, GCMS, LCMS, GPC
* Particle size distribution (PSD)
* Contact angle, surface tension, Viscosity

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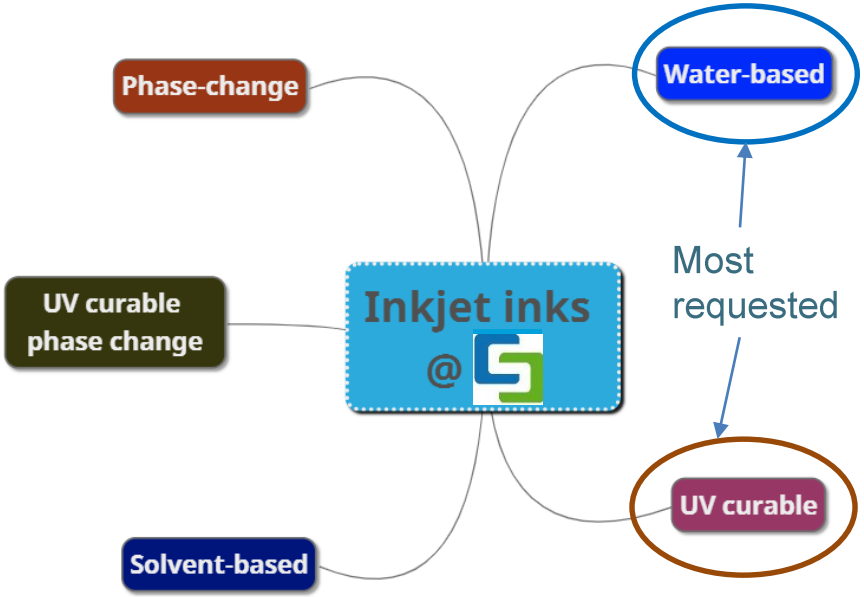
Inkjet @ ChemStream



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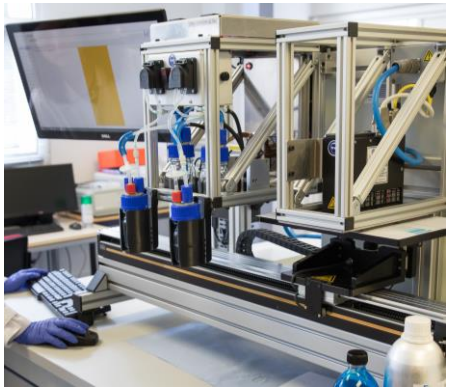
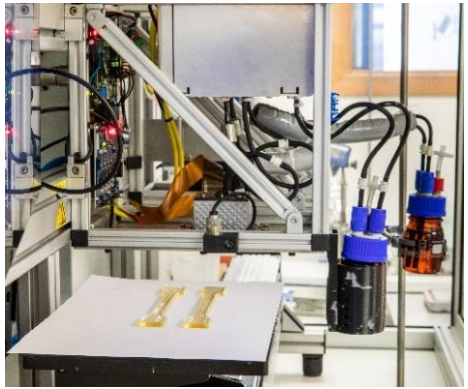
Modular Printing Units

- Mimic of an in line printing process
- Fast iterations of ink prototypes
- Different inkjet printheads
- Low investment level for customer
- 3D printing





Adhesion: the challenge

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Water-based

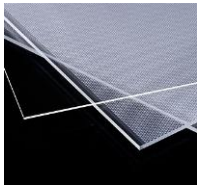
- ✓ Good adhesion porous or specially treated substrates


- ✓ Challenging adhesion on non-absorbing substrates.
- ✓ Use of binders.

UV curable

- ✓ Ideal for non-absorbing substrates: metals, glass, plastics…





- ✓ Shrinkage of the cured film due to retraction during the polymerization of monomers.
- ✓ Pre-treatment often needed for a better wetting.
- ✓ In some cases, use of adhesion promoters needed.

Adhesion: the challenge

Tunable adhesion

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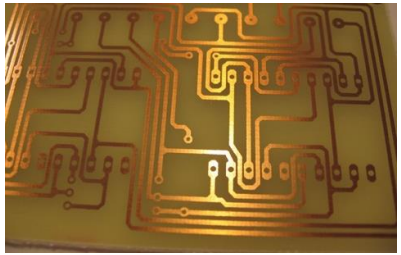
Some applications require a tunable adhesion.

Extra challenge:

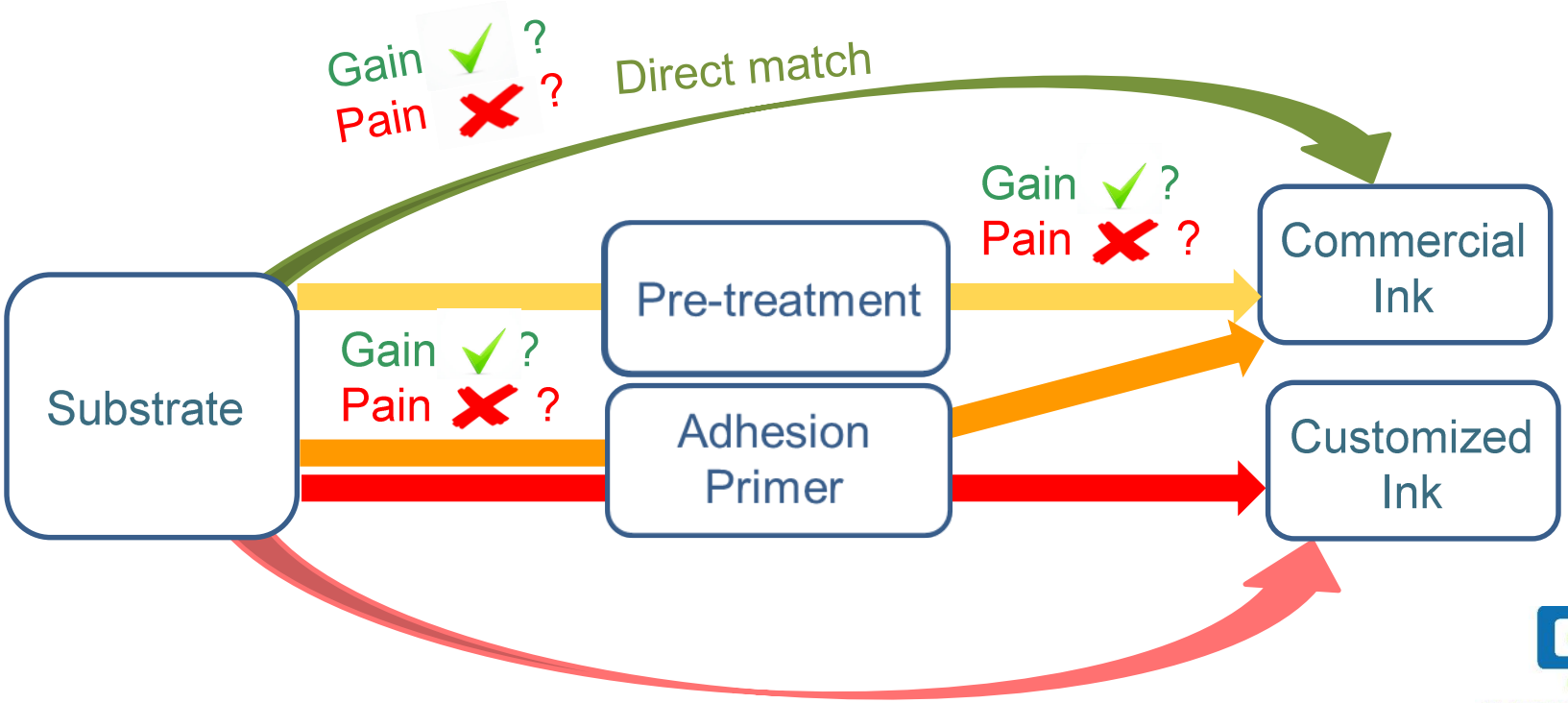
1. Excellent ink or primer adhesion
2. Deinkable @ high temperature, basic conditions

Examples:
Returnable bottles

Examples:
Printed PCBs
(ink → stripping)



Adhesion: the challenging process



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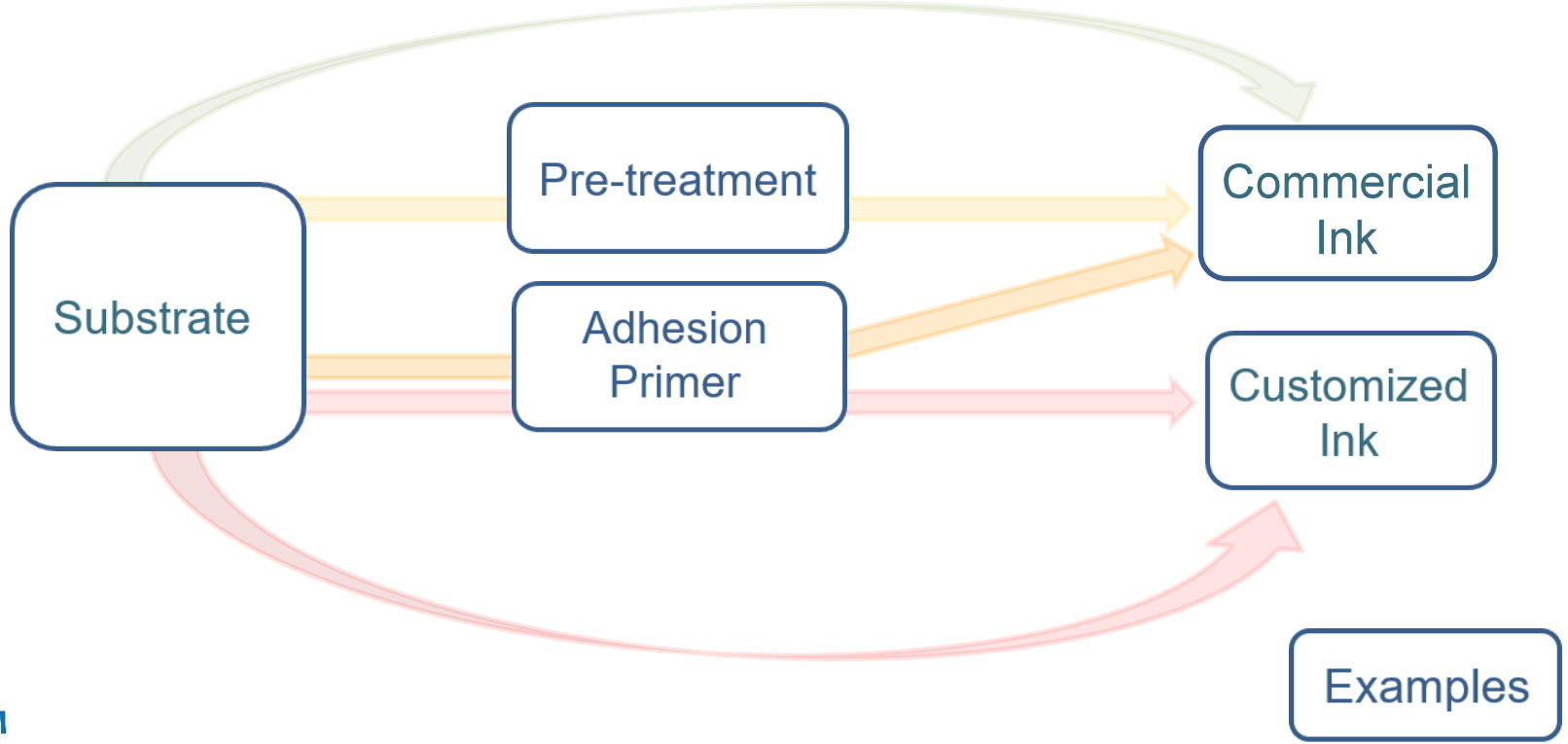
Adhesion: the challenging process



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Substrates

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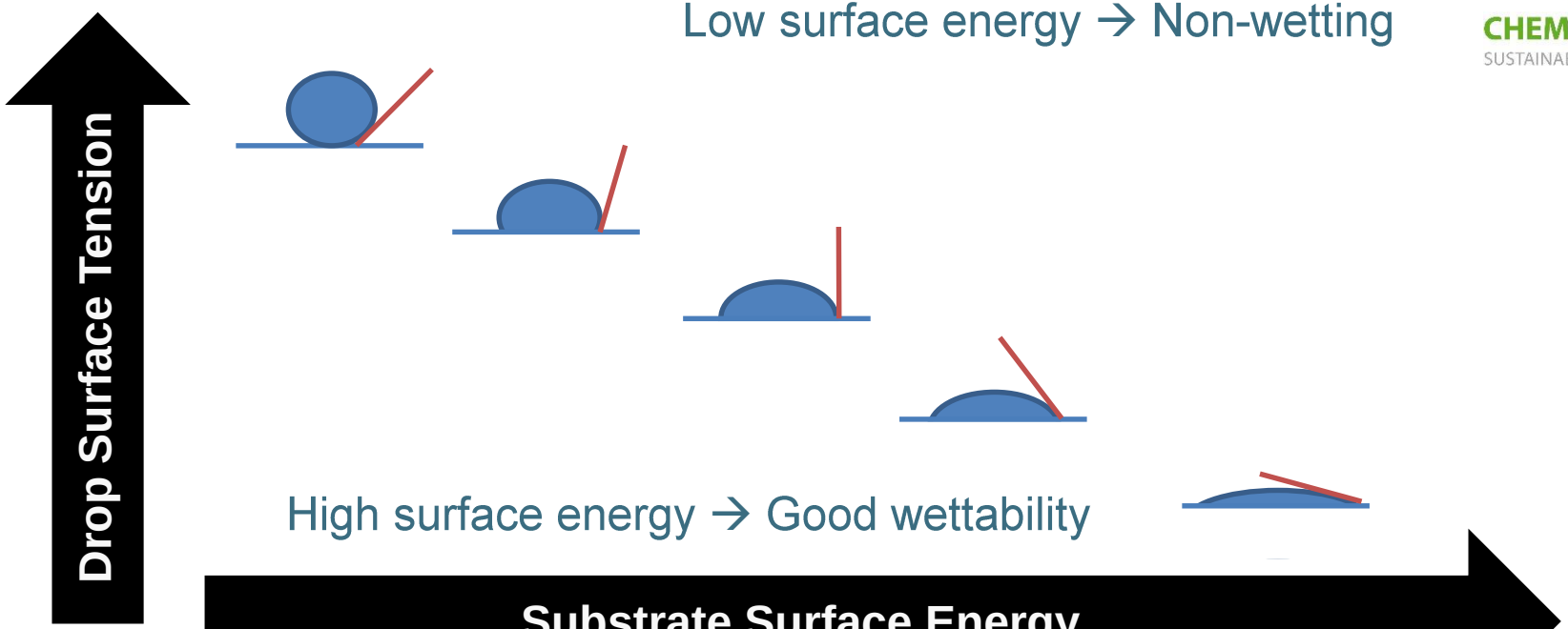
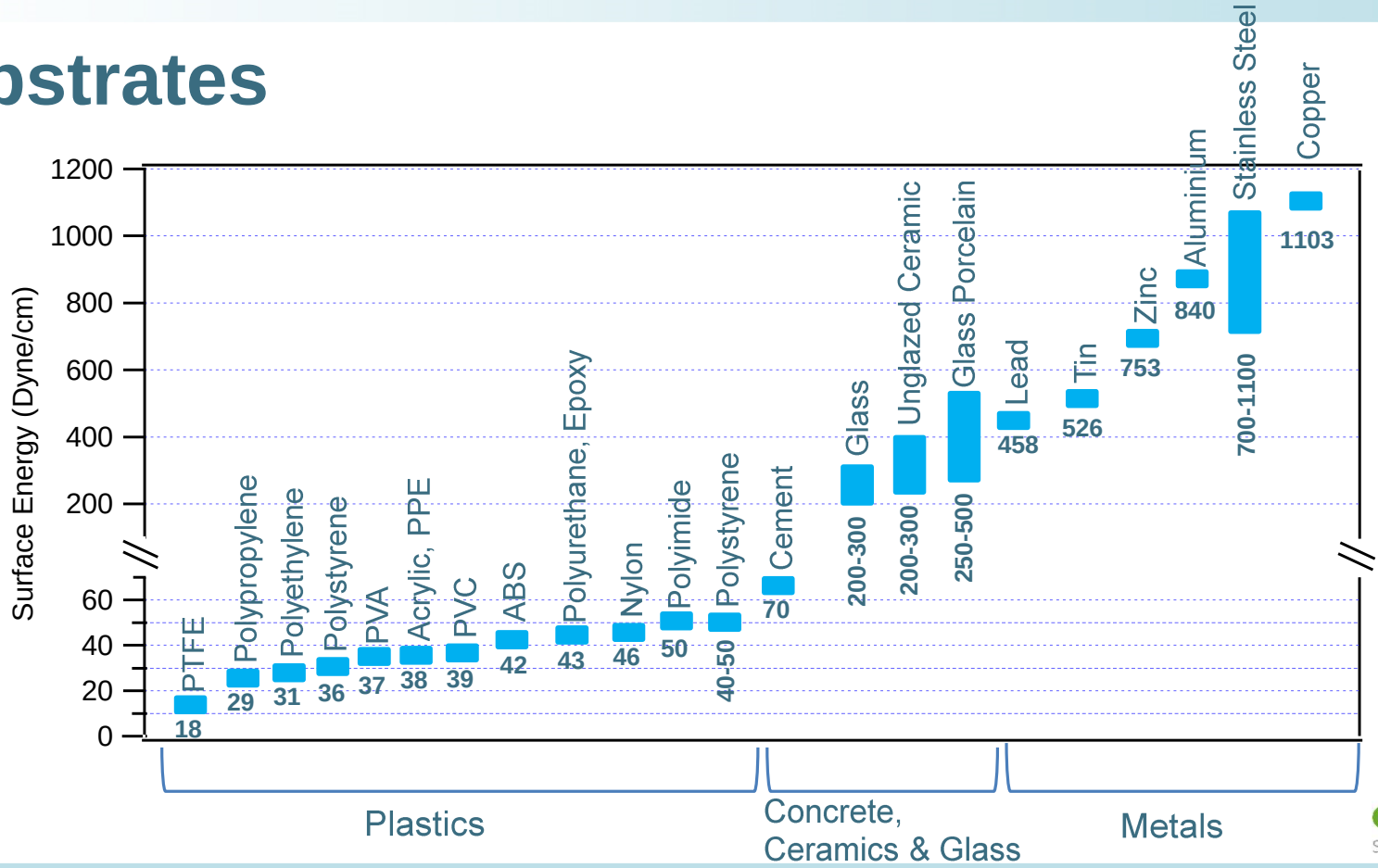
Low surface energy → Non-wetting



Substrates



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Pre-treatment: Activation and/or cleaning

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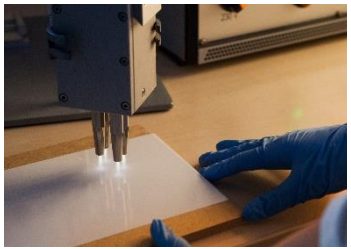
Examples of possible methods



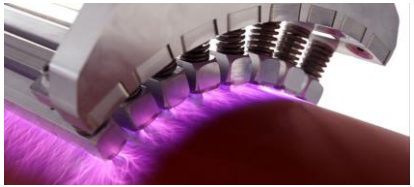
Atmospheric plasma

Surface activation

Air plasma forms:
-OH, -CO, -COOH
on the surface

Surface cleaning

Air plasma removes:
Impurities, lubricants, oils, etc. from the surface

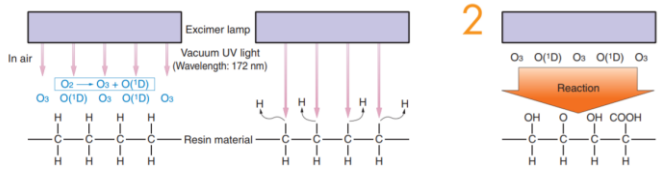


Corona

Surface activation

High-voltage discharge that ionizes the air forming:
-OH, -CO, -COOH
on the surface

UV-Ozone O_3 activation and cleaning



Pre-treatment: Activation and/or cleaning

Low surface energy substrates, e.g. Plastics
Creation of polar groups → wetting improvement
Breakage of polymer crystals, open of new surface → slight adhesion improvement

Drawback → Only a small amount of C atoms are functionalized:
✓ Enough for a better wetting
✓ Not enough for a good adhesion

❖ Adhesion → The most important is the ink formulation

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Adhesion Primer

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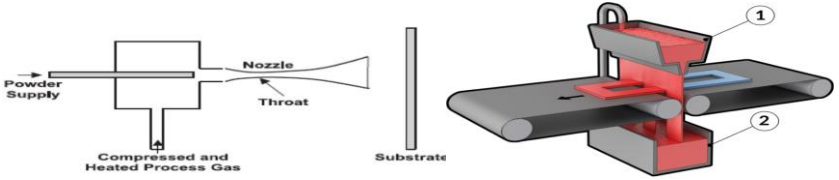
Adhesion coating

Compatible with coloured commercial inks.

Extra step needed
Coating method: e.g. Spraying or curtain coating



Jettable adhesion primer

Compatible with coloured commercial inks.

In line with the other coloured inkjet inks

Extra step needed
Extra print head

Customized ink

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Ink with improved adhesion

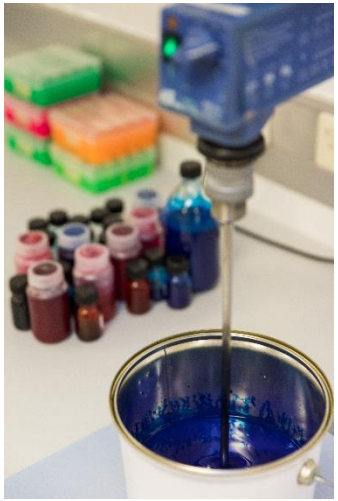
No extra step needed

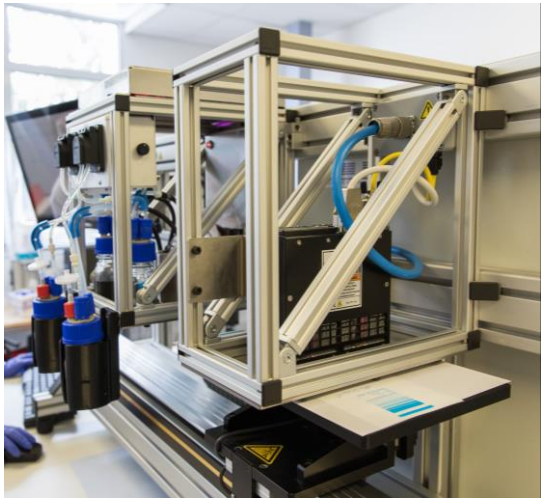
Less equipment space

All coloured inks should be adhesive

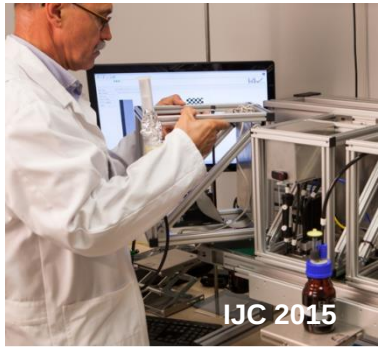
Challenging ink design

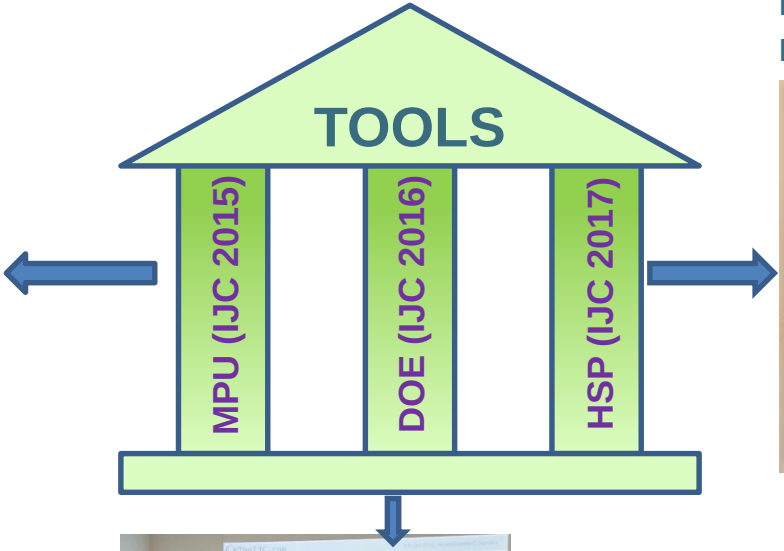
Adhesive coloured inks
Substrate



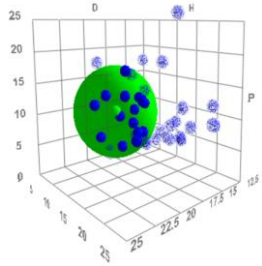


Ink Design @ ChemStream





Hansen Solubility Parameters
Best Speaker Presentation IJC 2017



➢ "Like likes like"

Modular Printing Unit:

➢Mimic of an in line coating/printing process
➢Fast iterations of ink prototypes
➢Fast iterations with different printheads

Smart throughput

➢Design of experiments
➢All parameters are changed simultaneously
➢Short development time of formulations

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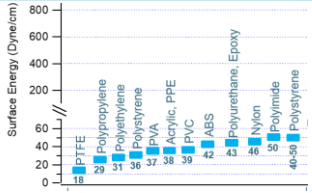
Adhesion on plastics

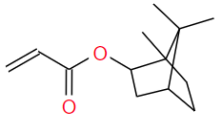


Low surface energy Substrate → Activation Pre-treatment → Customized Ink

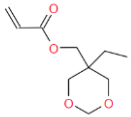
e.g. Printing on plastic bottles

Ink formulation:

✓ Use of monofunctional monomers for a better adhesion

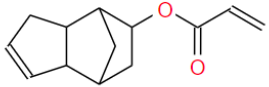


Isobornyl acrylate (IBOA)



Cyclic trimethylolpropane formal acrylate (CTFA)

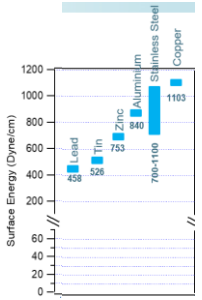
✓ Use of components to minimize shrinking → better adhesion

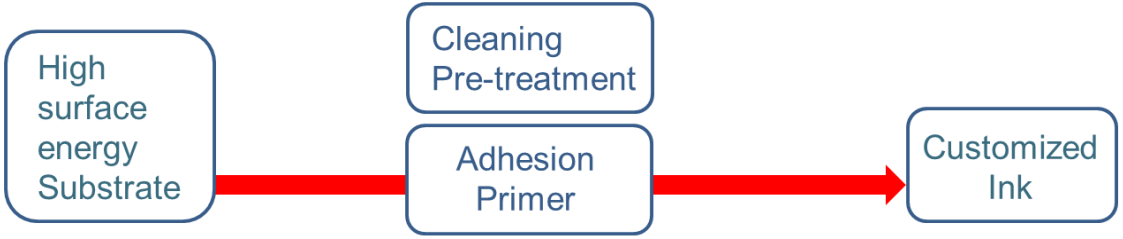
✓ 

Dihydrodicyclopentadienyl acrylate (DCPA)

Multifunctional oligomers (better crosslinking but high viscosity ⚠)

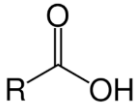
Adhesion on metals. Anodized Aluminium

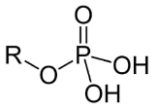


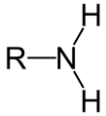


Ink formulation:

- ✓ Use of monomers to minimize shrinking → better adhesion
- ✓ Use of adhesion promoters needed for a good adhesion

Carboxyl functional 

Phosphate functional 

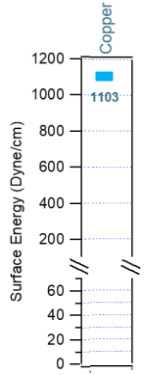
Amine functional 

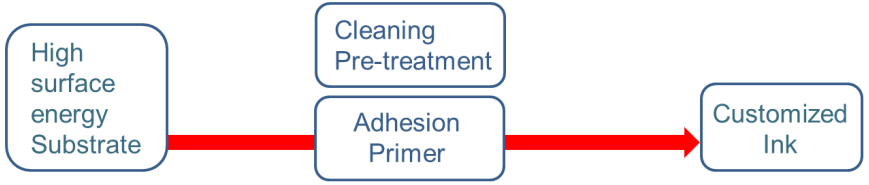
e.g. Printing on Al bike frame

- ✓ Most adhesion promoters are acidic → Not always compatible with pigment dispersions

Alternative: sandwich adhesion primer + coloured inks on top

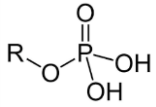
Adhesion on metals. Copper



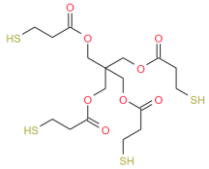


Ink formulation:

- ✓ Use of monomers to minimize shrinking → better adhesion
- ✓ Use of adhesion promoters needed for a good adhesion



Phosphate functional
(challenge: Acidity & pigments)



Polythiol
(challenge: Ink stability)

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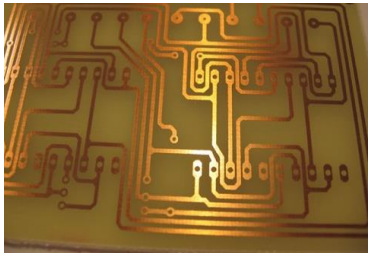
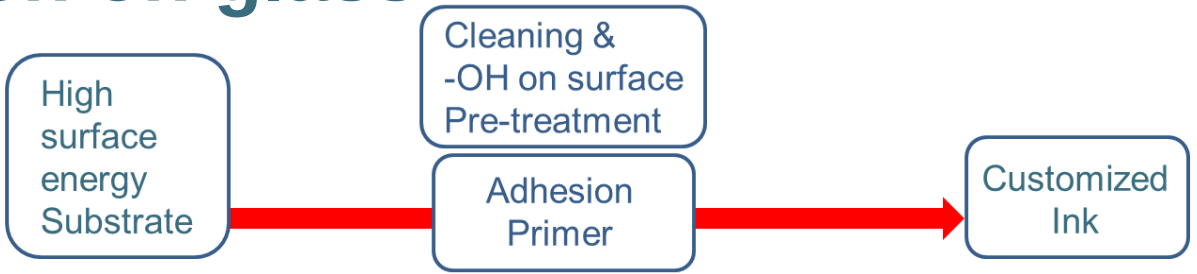
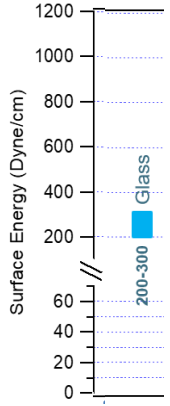


Printed PCBs
Reversible adhesion
(ink → stripping)
Important! amount of adhesion promoter (reversibility)

Adhesion on glass





Ink formulation:

- ✓ Use of monomers to minimize shrinking → better adhesion
- ✓ Use of adhesion promoters needed for a good adhesion (mostly acidic)
- ✓ Adhesion more difficult to achieve than on metals. **Phosphate & Silane best options**

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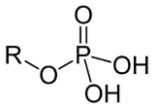
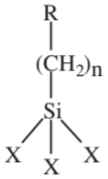
Phosphate functional



Silane functional



e.g. Printing on beer glasses

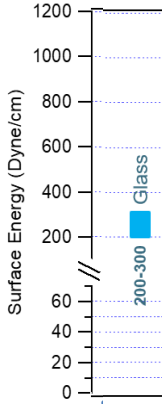
Adhesion on glass

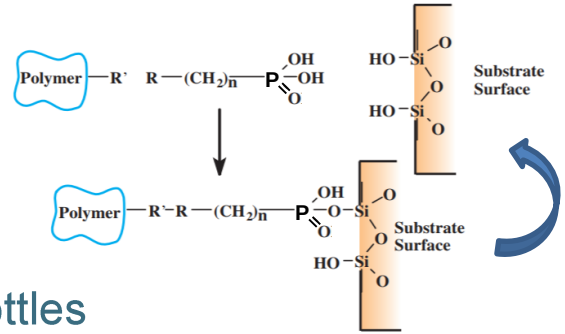
Phosphate functional groups

- ✓ Adhesion promoter with strongest adhesion on glass.
- ✓ Drawback → Phosphates desorb in prolonged contact with water.

Printed beer glass → Not suitable option → e.g. dishwasher removes ink

Perfect for e.g. printing on wine bottles





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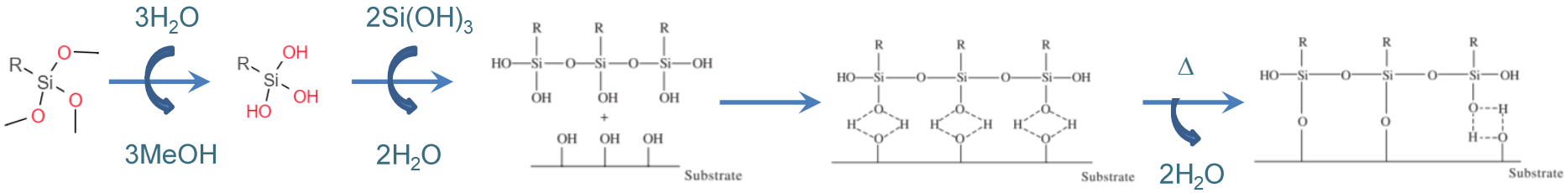
Adhesion on glass

Silane functional groups

- ✓ Once the covalent bond is formed, excellent & resistant adhesion.
- ✓ Drawback: Kinetics are very slow. Formulation adapted to speed up the hydrolysis and condensation of the silanes (e.g. catalyst)



Adhesion on glass. Silane functional group

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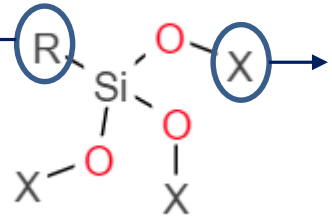
Linker group
Reacts with the rest of the ink



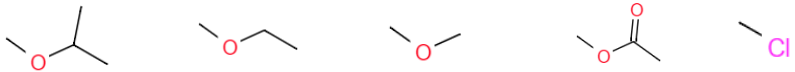
Leaving group.
Hydrolysis & substrate anchor part

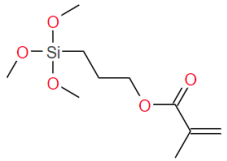
Linker Group → Chosen depending the composition of the ink.
UV curable ink: e.g. (Meth)acrylic, Vinyl, Mercapto…

Leaving group → Trade-off between reactivity & stability.

Reactivity (Hydrolysis): Cl^- > AcOH > MeOH > EtOH > iPrOH

Stability: iPrOH > EtOH > MeOH > AcOH > Cl^-

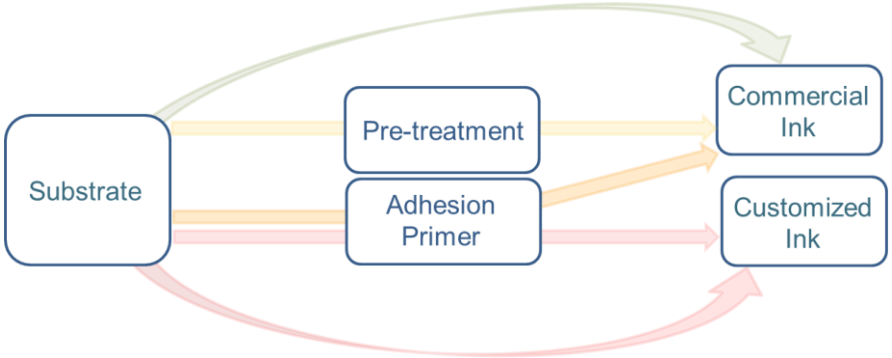




e.g. "MEMO"
✓ Price
✓ Ink interaction
✓ Slow hydrolysis

Conclusions

- ✓ Adhesion is one of the most critical attributes of an ink
- ✓ And also one of the biggest challenges
- ✓ A good adhesion between a substrate and an ink → complex process

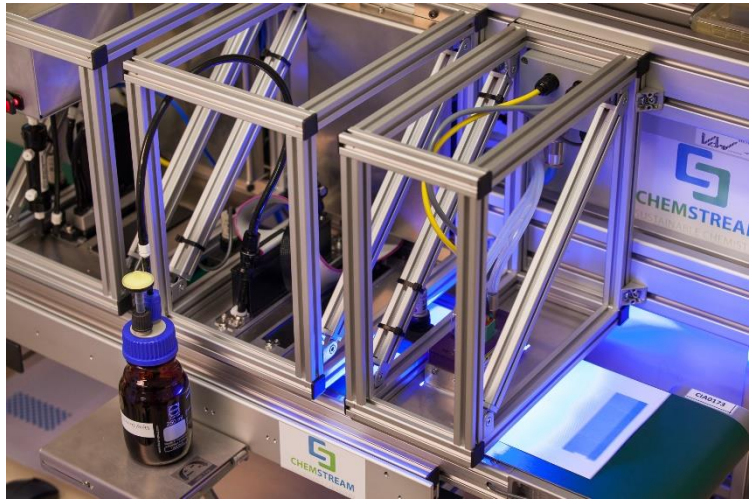


ChemStream → Experts in ink formulations with strong adhesion know-how

PAIN → CHEMSTREAM SUSTAINABLE CHEMISTRY → GAIN

Thanks for your attention

You are invited at our booth for further information and discussions.



Not enough time during IJC 2018?
Don’t worry! More info on our website:

www.chemstream.be

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