CHEMSTREAM
SUSTAINABLE CHEMISTRY

GLASSPrint2019
CONFERENCE

Adhesion of UV-curable inks and coatings on glass

Dr. Marin Steenackers
ChemStream

ChemStream: The Independent Chemical R&D Company

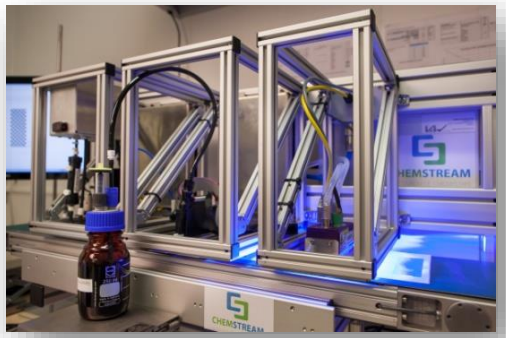
Translating customized requirements into chemical formulations with dedicated functionality, from **design to prototyping and implementation**

- Core activities:
  - Innovative contract research
  - Customized product development
  - Design and synthesis of functionalized (bio-based) polymers (dispersants, emulsifiers, surfactants...)
- Main deliverables:

- **Nano dispersions**

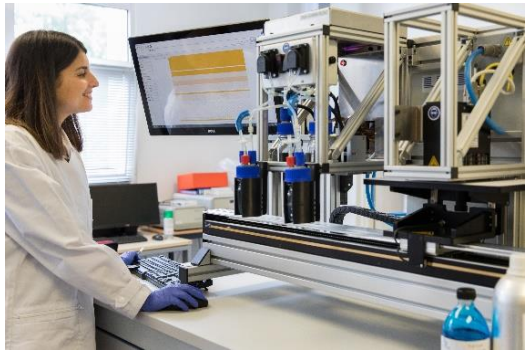
- **Coatings**

- **Inkjet inks**



ChemStream: The Independent Chemical R&D Company

- **Founded in April 2010**
- **Staff profile (14 FTE, 11 PhDs)**
  - Chemistry (12)
  - Material Science (1)
  - Bio Engineer (1)
- **Located near Antwerp – Belgium**
- **Lab-facilities (550 m^2)**
  - Organic Synthesis
  - Chemical Formulation
  - Characterization
- **Prototype production facility**
  - Coatings: 250 L batches
  - Inkjet inks: 25 L batches

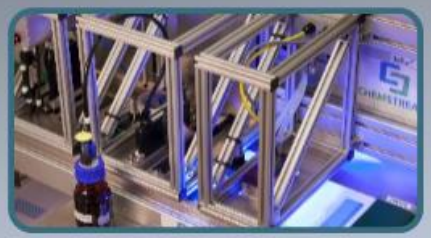


ChemStream: The Independent Chemical R&D Company

Expertises

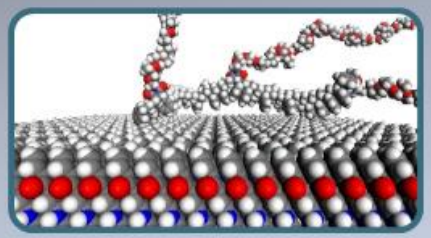
Organic Synthesis

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



Technology

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



Methodology

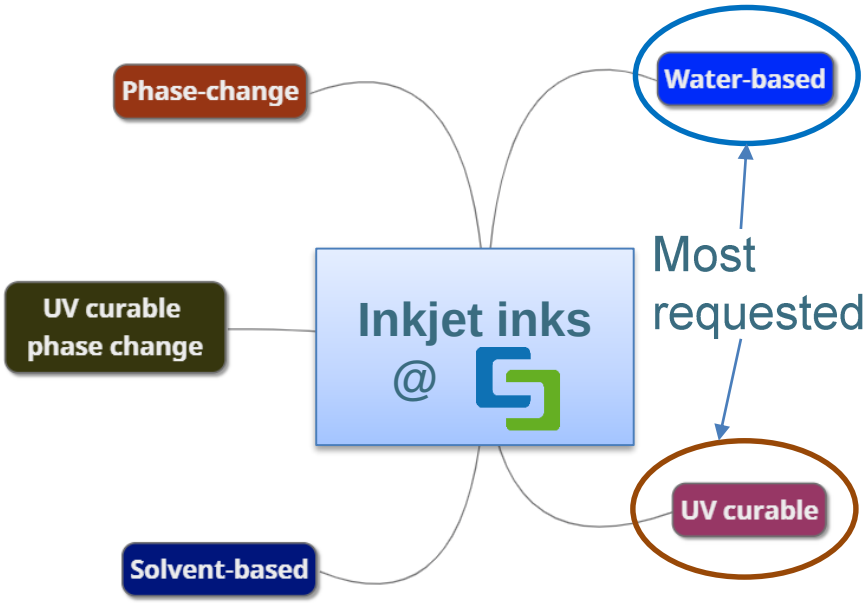
* Molecular modeling
* Design of Experiments (DoE)
* Smart throughput screening
* Hansen solubility parameters (HSP)

Analytical and physical chemical tools

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

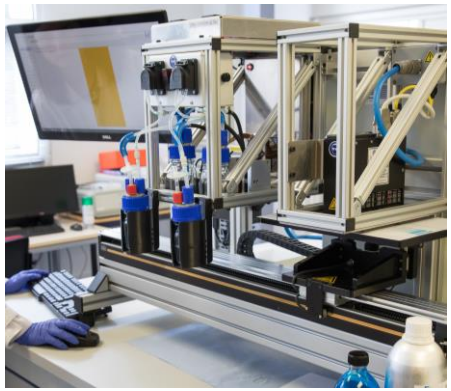
ChemStream: The Independent Chemical R&D Company

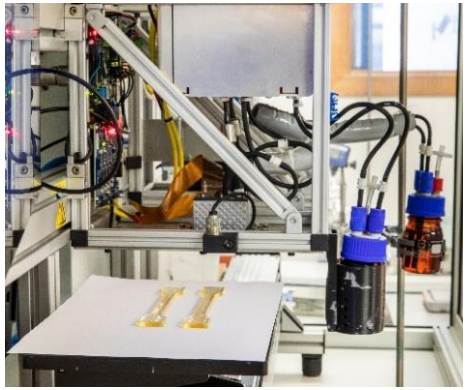
Inkjet @ ChemStream



Modular Printing Units

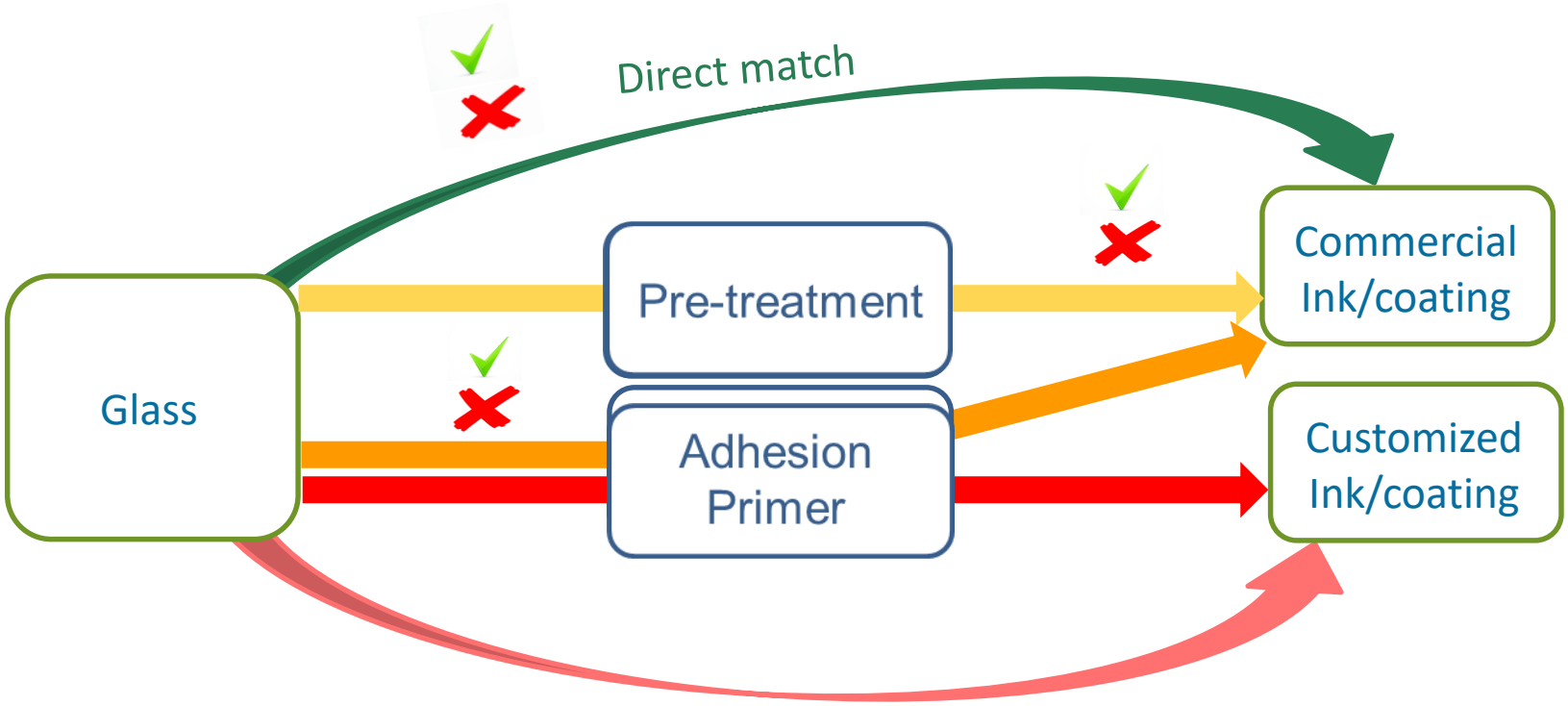
- Mimic of an in-line printing process
- Fast iterations of ink prototypes
- Different inkjet printheads
- 3D printing





Adhesion: the challenge

Direct to object adhesion



Technology: UV curable inks, coatings, …

Adhesion: the challenge

Direct to object reversible adhesion

→Tunable Deinking
→Tunable Stripping
} E.g. in acid/base, @ high T, etc.

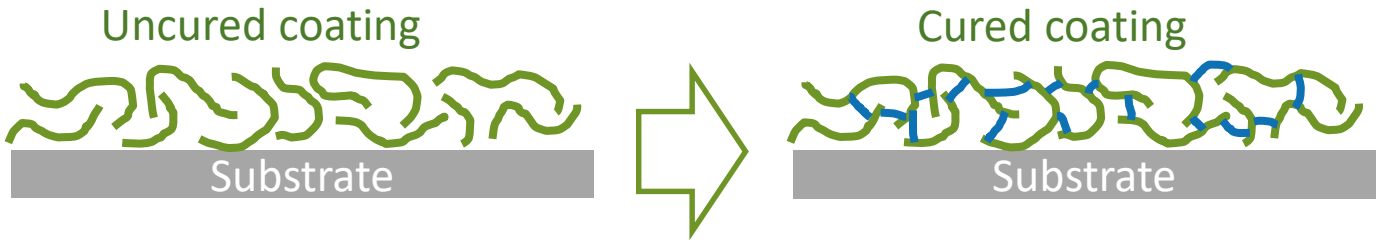
Examples:

Printing on returnable bottles

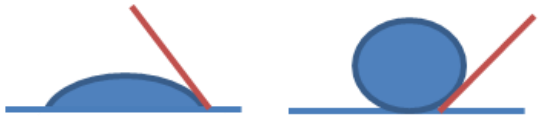
Temporary mask – frosted glass

Factors influencing adhesion

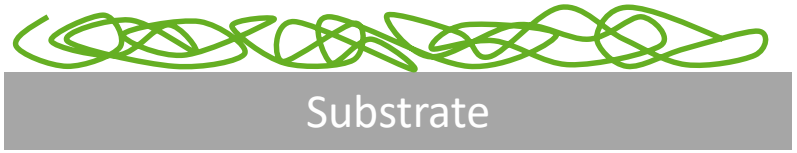
- Shrinkage



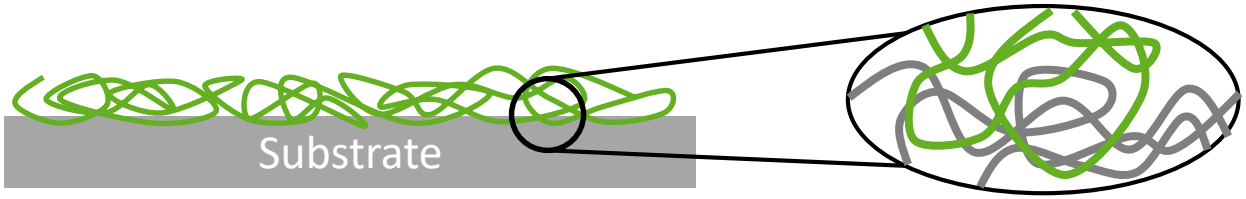
- Wetting



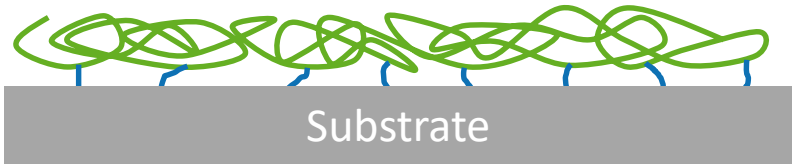
- Non-covalent interactions



- Entanglement



- Covalent bonding

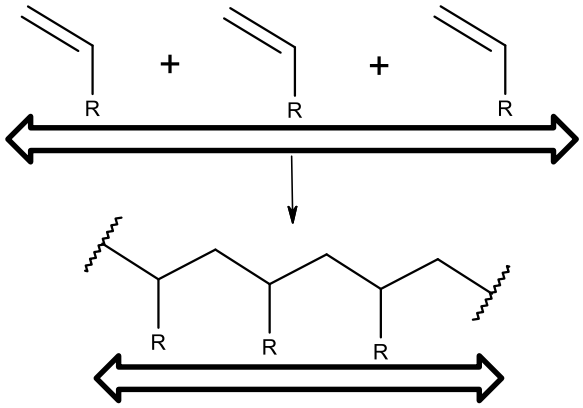


Adhesion: Shrinkage

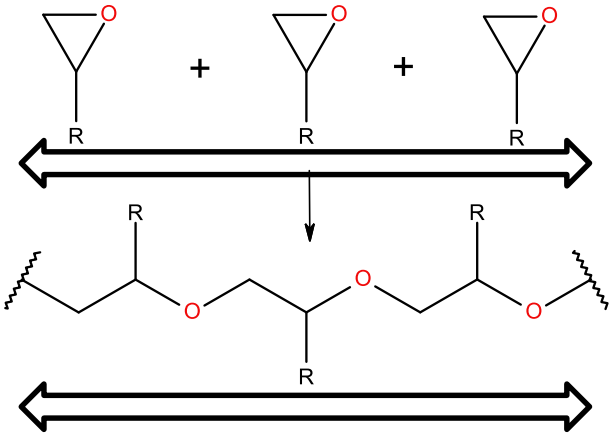
Property	Radical Polymerization	Cationic Polymerization
Oxygen Inhibition	Yes	No
Inhibition by humidity	No	Yes
Cure speed	Milliseconds	Seconds
Shrinkage	> 10 %	< 10 %
Adhesion	Good	Very good
Raw Material Cost	Acceptable	High

Shrinkage:

(Meth)acrylates



Epoxides

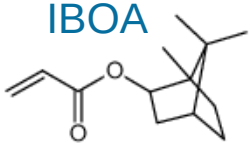


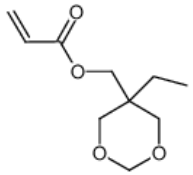
Adhesion: Shrinkage

How to minimize shrinkage for (meth)acrylates

✓ Use of monofunctional monomers

IBOA

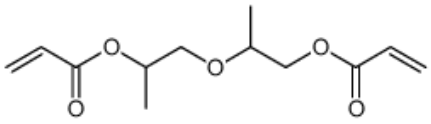




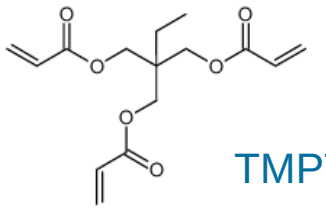
CTFA

✓ Use of multifunctional oligomers (high viscosity ⚠)

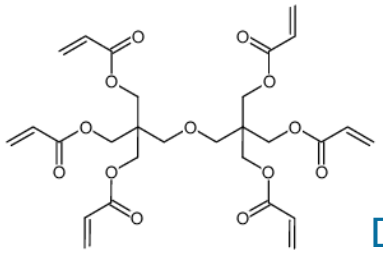
✓ Minimize the use of small crosslinkers



DPGDA



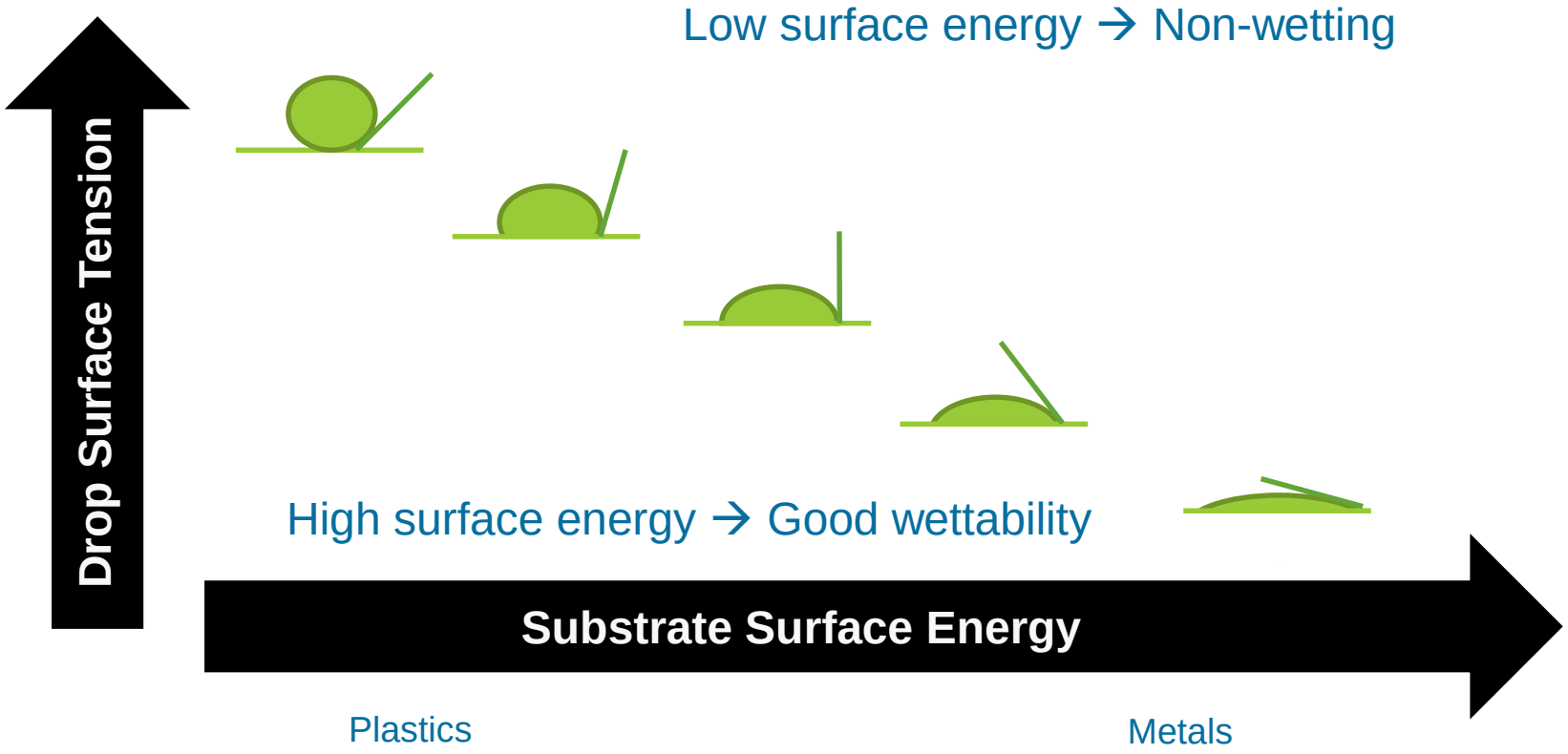
TMPTA



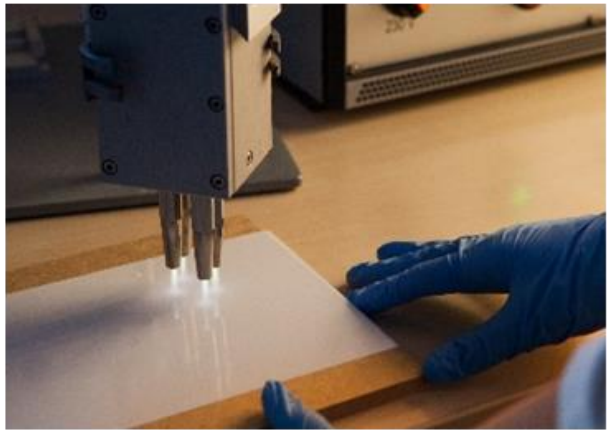
DPHA

Adhesion: Wetting

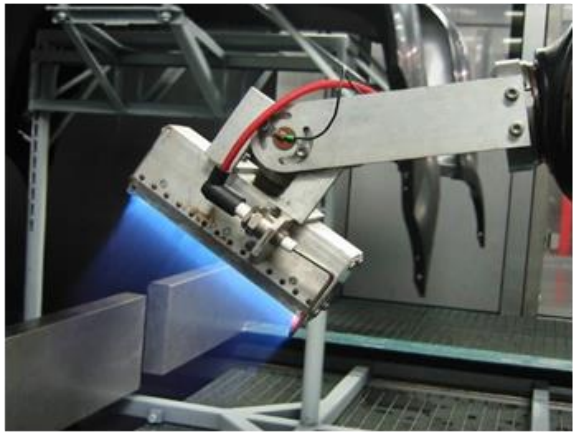
Substrates



Adhesion: Improve wetting by pre-treatment



Atmospheric plasma

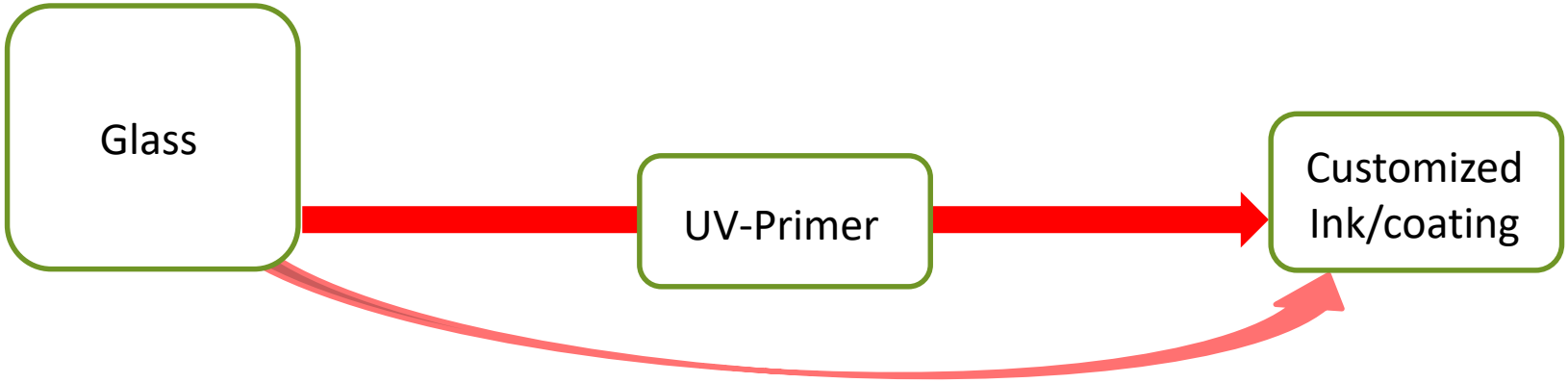


Flaming

Surface activation Surface cleaning

Removal of oil, dust and organic coatings (CEC)

Adhesion: Covalent bonding



Ink formulation:

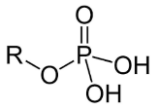
✓Use of monomers to minimize shrinking → better adhesion

✓Use of monomers with strong non-covalent interactions (polar, H-bonding)

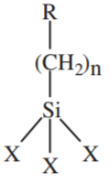
✓Use of adhesion promoters needed for a good adhesion (mostly acidic)

Phosphate & Silane best options (mono and multidentate)

Phosphate functional



Silane functional

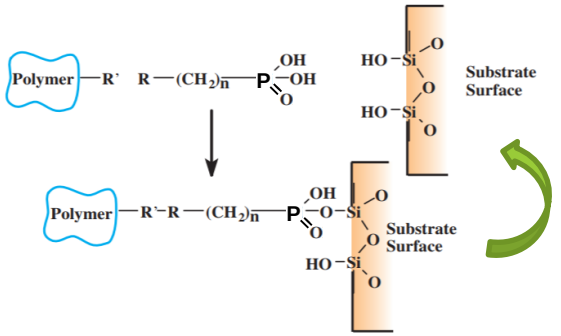


Adhesion: Covalent bonding

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



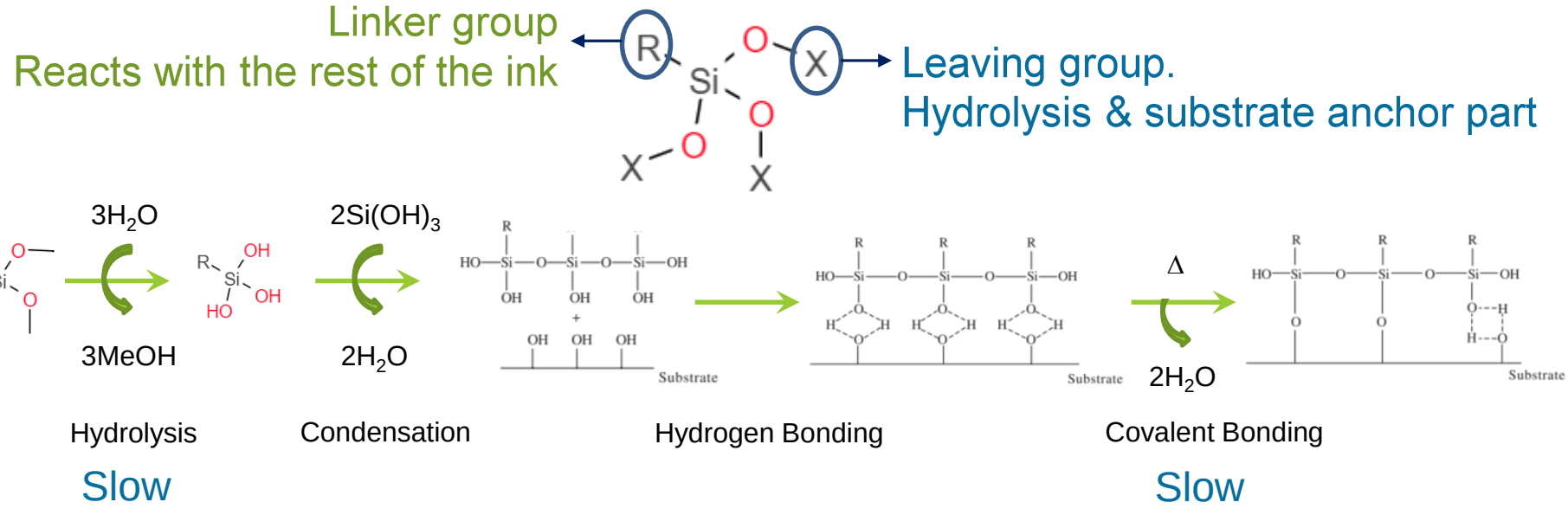
→ Perfect for applications which require a good dry adhesion

Adhesion: Covalent bonding

Silane functional groups

✓Once the covalent bond is formed, excellent & resistant adhesion.

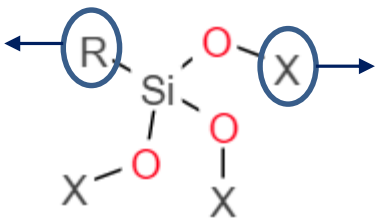
✓Drawback: Kinetics are very slow. Formulation adapted to speed up the hydrolysis and condensation of the silanes (e.g. catalyst)



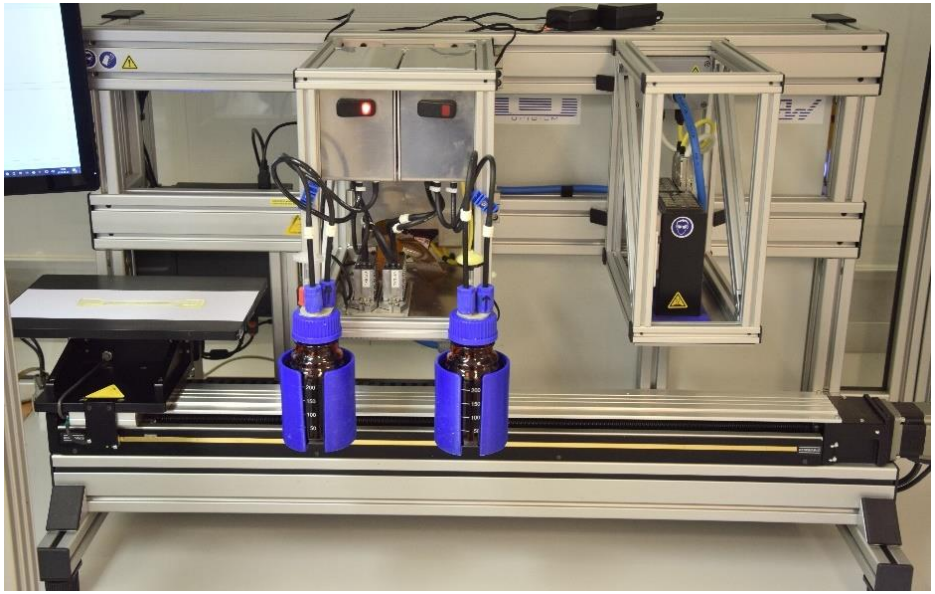
Adhesion: Covalent bonding

Silane functional groups

Linker group
Reacts with the rest of the ink



Leaving group.
Hydrolysis & substrate anchor part

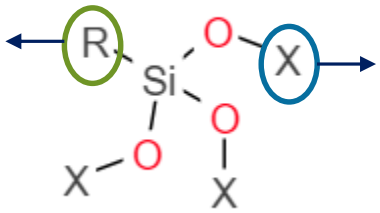


→ Anchoring has to take place during period between jetting and pinning

Adhesion: Covalent bonding

Silane functional groups

Linker group
Reacts with the rest of the ink



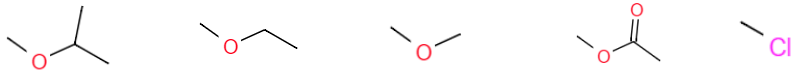
Leaving group.
Hydrolysis & substrate anchor part

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

Leaving group → Trade-off between reactivity & stability

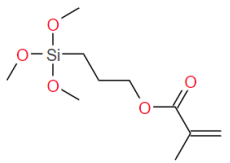
Reactivity (Hydrolysis): Cl^- > AcOH > MeOH > EtOH > iPrOH

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



Same compromise for catalysed silanes

→ Anchoring reaction is bottle neck towards adhesion

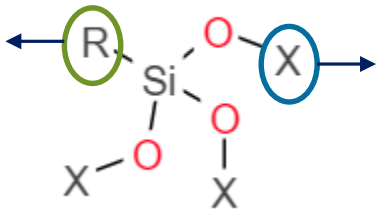


e.g. “MEMO”
✓ Price
✓ Ink interaction
✓ Slow hydrolysis

Adhesion: Covalent bonding

Silane functional groups

Linker group
Reacts with the rest of the ink



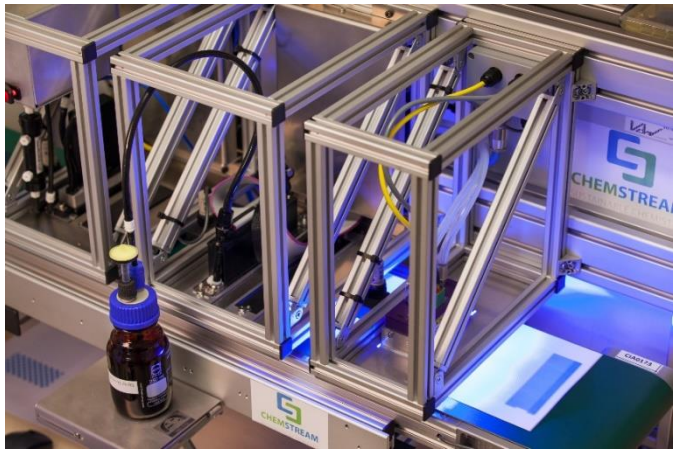
Leaving group.
Hydrolysis & substrate anchor part

ChemStream → synthesis of a new class of silane-based adhesion promotors to adhere directly on glass for UV-curable primers, inks and coatings

Thanks for your attention !!!

You are invited at our booth 23

www.chemstream.be



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