Chromatogeny
An History of an Innovative Technology

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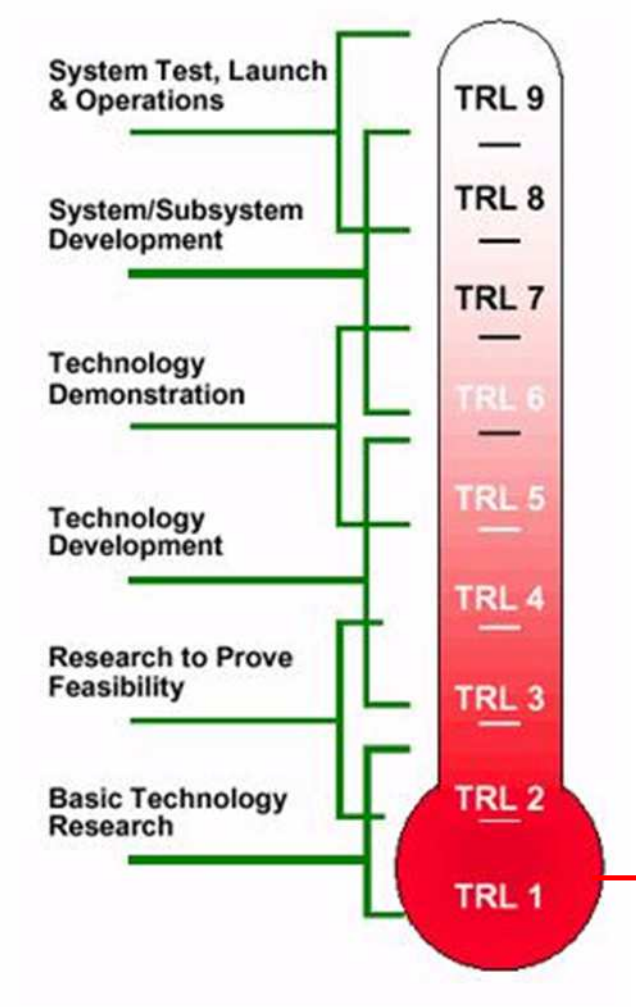
History of the Development of Chromatogeny



Invention 1997 – D. Samain

Worldwide patent in public domain now

ctp centre technique du papier

What is chromatogeny?

Paper tissue grafted by chromatogeny

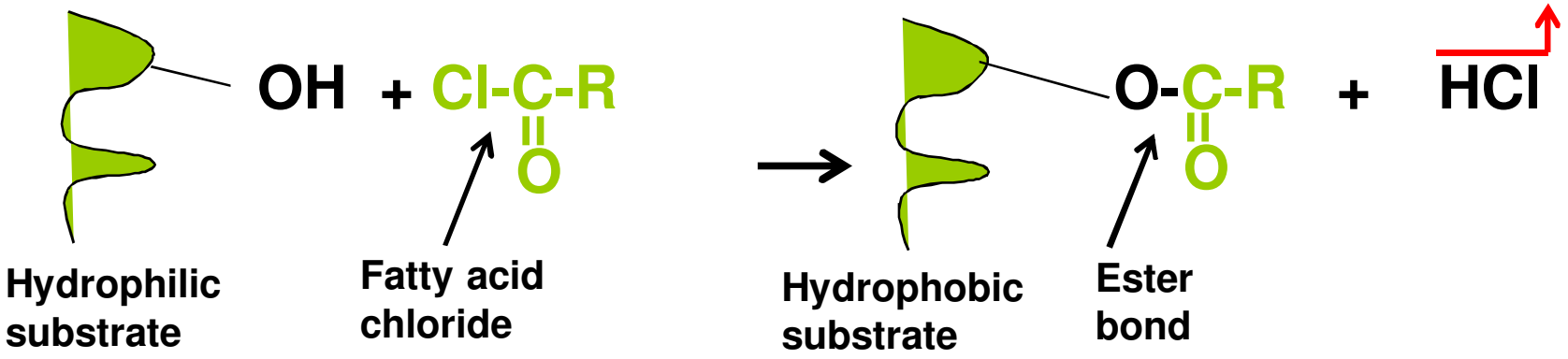
Source : Daniel Samain

What is chromatogeny?

- **A breakthrough green chemistry process that brings hydrophobicity to hydrophilic reactive substrates**
  - Lignocellulosic fibres, papers, starch, minerals…
- **A solvent free technology, suitable for R2R processes**
- **First developments in the paper industry**
  - Applied to papers and boards
    - ✓ To bring water resistance while keeping converting ability, recyclability and biodegradability
  - Applied to coated papers
    - ✓ To protect water sensitive barrier layers from moisture keeping recyclability and biodegradability

Basic principle of chromatogeny

- **Use the reaction of Fatty Acid Chlorides with hydroxyl groups to obtain fatty esters**
  - Protect water sensitive material by grafting fatty alkyl chain (fatty acid chloride) at the surface of a layer containing OH groups



- **Use the liquid – vapour equilibrium to get an ultrafast solvent free reaction**

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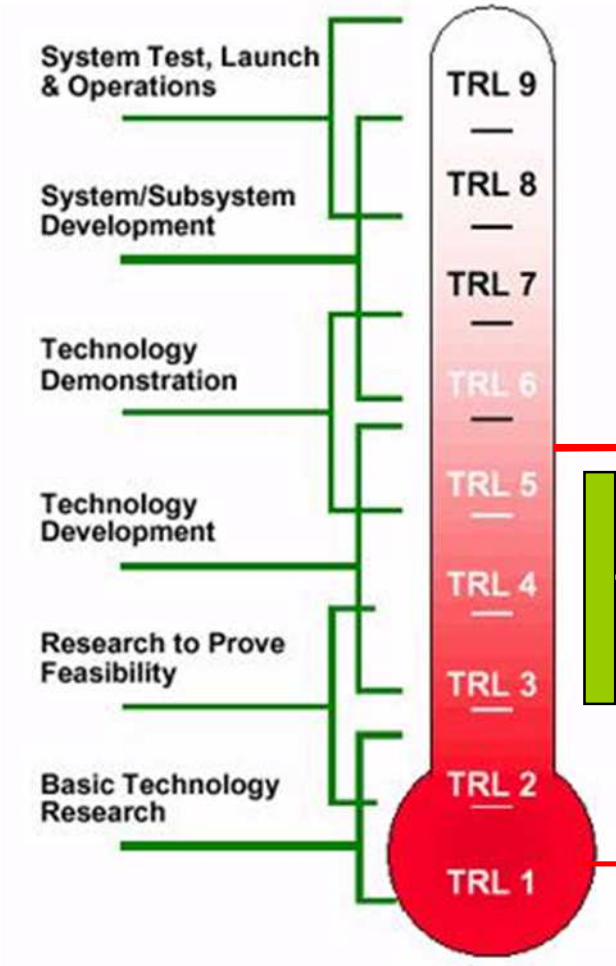

CTP's pilot machine 2010

Flexpakrenew 2008-2011

2 CNRS PhDs 2004-2008

Invention 1997 – D. Samain

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CTP's Chromatogeny pilot plant Overview

Hot air flushing

Cleaning paper

Rewinder

Gravure coater

eposition

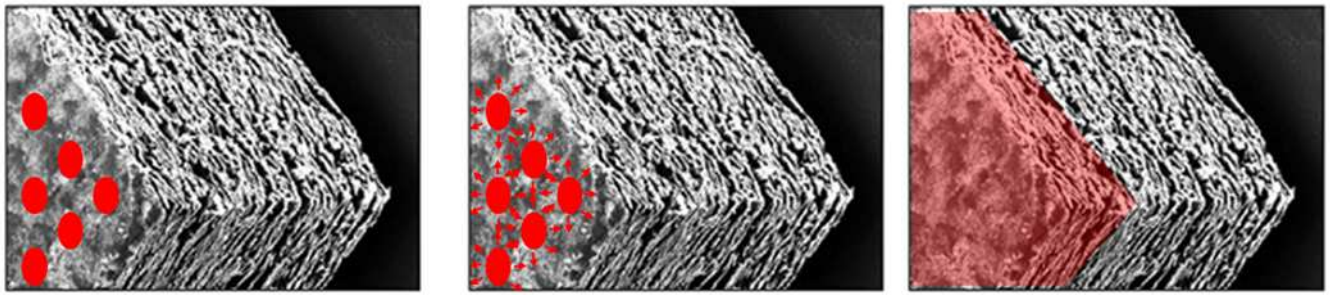
reagent

t

Patent CTP/CNRS

Basics of chromatogeny at pilot/industrial scale

- **Deposition of a weak amount of liquid reagent at the paper surface**
  - 0.2 to 0.8g/m²
- **Heating of the reagent (130°C to 190°C) and paper surface to increase the vapour concentration**
  - The vapour reacts within couple of seconds
- **Propagation of the reaction by diffusion, formation of ester bonds between fatty acid and cellulose and continuous withdrawal of HCl**
  - Diffusion depth ~ 100µm



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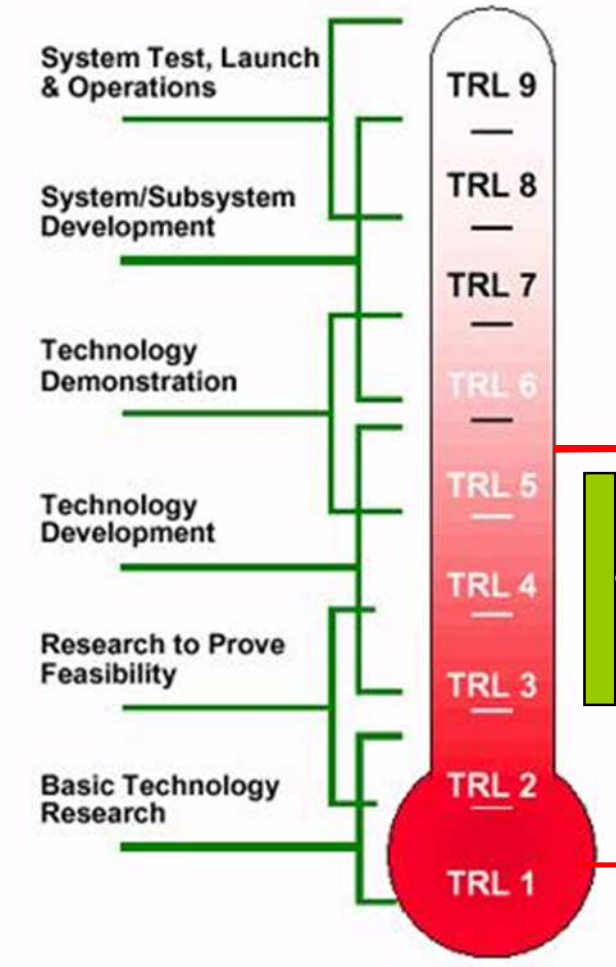

Waregraft 2013-2015

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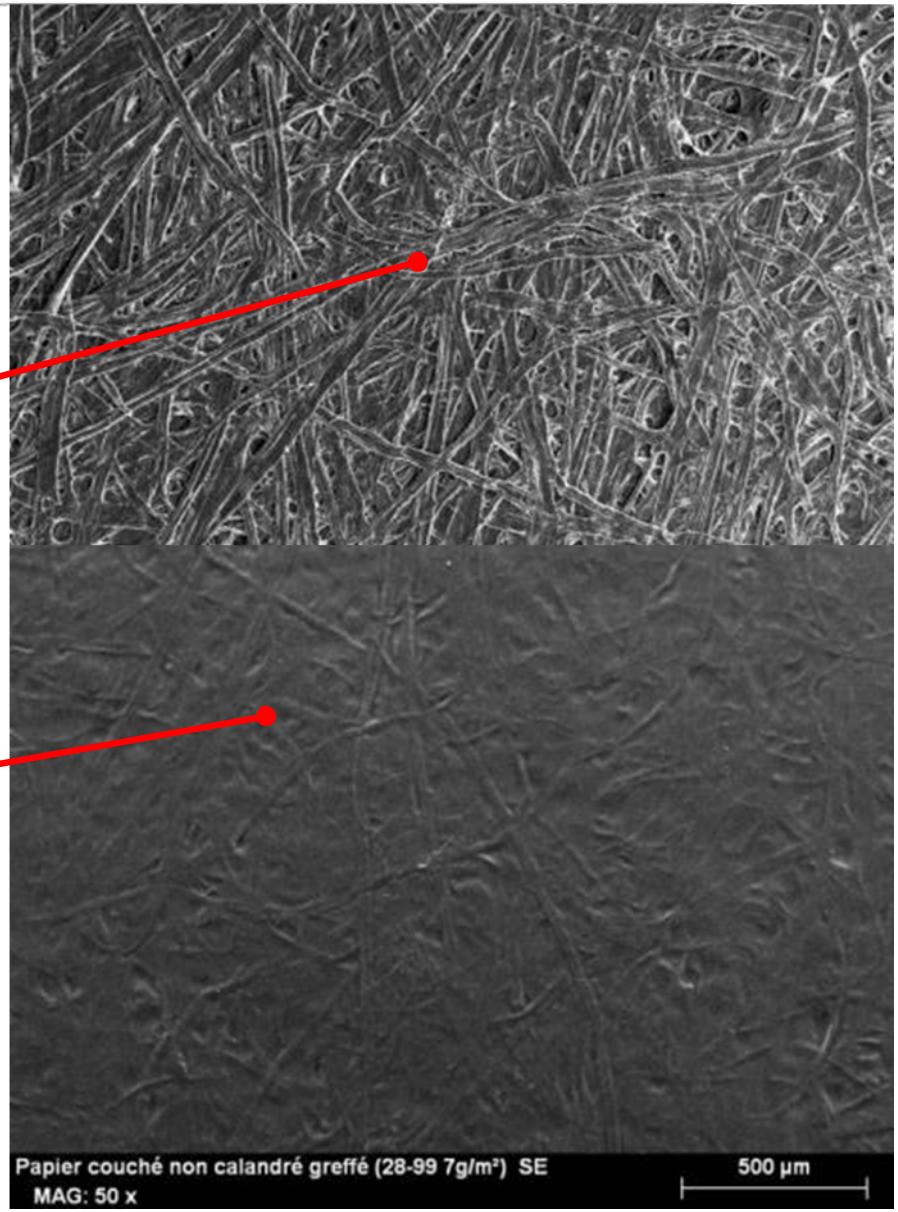
Potential of chromatogeny

- **Chromatogeny helps protecting water sensitive materials**
- **To treat uncoated papers**
  - Cellulose is a natural reactive substrate for chromatogeny
- **To treat coated papers**
  - Requires to use a coating layer that is reactive to chromatogeny
  - Compatibilizing agents for non-reactive surfaces



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Performances of grafted uncoated papers and boards

Property	Tests/ Standard	Influence of grafting	Comments
Water absorption capacity	Cobb 60s Iso 535	↘12-15g/m²	Data for a 75g/m² blotting paper
Water absorption capacity	Cobb 300s Iso 535	↘15-18g/m²	Data for a 75g/m² blotting paper
Oil absorption capacity	Cobb 60s Modified Iso 535	⇔	
Water contact angle		↗ 120-130°	Hydrophobic
Capillary rise	Klemm method ISO 8787 – 1987	↘ 0cm	No edge wicking
Surface energy		↘ 22-23 mJ/m²	Polar component decreased to 0mJ/m²
Wet strength	ISO 3781 – 2011 ISO 12625 – 5	↗ 17-25%	But repulpable

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Performancesof grafted uncoated papers and boards

Property	Tests/ Standard	Influence of grafting	Comments
Breaking length	ISO 1924-2:2008	⇔	No ageing
Tear strength	ISO 1974:2012	⇔	No ageing
Brightness	ISO 2490	⇔	No change of colour neither
Roughness	ISO 8791-2:2013	⇔	
Friction coefficient	ISO 15359	↘⇔	Depends on paper composition
Recyclability	EN 13430	⇔	What is recyclable remains recyclable
Biodegradability	EN 13432	⇔	What is biodegradable remains biodegradable
Printability		⇔	Offset, flexo (water/uv), roto
Glueability	FINAT test method n°1	⇔	Water based/hotmelt

Case of uncoated papers and boards

- **Main target : to improve water resistance of cellulosic based materials, i.e. manufacture of waterproof papers**
- **Main Markets :**
  - Corrugated board resistant to rain/water
  - Health and medical papers
  - Technical paper for the industry and buildings
  - Filters
  - Papers for households, Papers for agriculture
  - Hydrophobic fibres/mats for composite market
  - And many others…

Performances of grafted PVOH coated papers and boards

Property	Tests/ Standard	Influence of grafting	Remarks
Water absorption capacity	Cobb 60s Iso 535	⇘0-1 g/m²	50g/m² paper covered with 3g/m² of PVOH
Water absorption capacity	Cobb 1800s Iso 535	⇘<5g/m²	ⓘ Paper coverage and grafting quality
Water contact angle		⇗120-130°	Hydrophobic
Oil absorption capacity	Cobb 1800s Iso 535	⇔ 1g/m²	Both grease and water barrier!
Kit test	Tappi UM 557	10-12	
Surface energy		20-22mJ/m²	No polar component
WVTR (23°C-50%RH)	T 448 om-97	<0.3g/m²/day	Quite similar to ungrafted
WVTR (38-90%RH)	T 464 om-01	<300g/m²/day	Value >3000 for ungrafted material
OTR (23°C-0%RH)	ISO 15105-2	5<cm³/m²/day/bar	Quite similar to ungrafted
Mineral Oil barrier		Excellent	Quite similar to ungrafted

Performances of grafted PVOH coated papers and boards

Property	Tests/ Standard	Influence of grafting	Comments
Recyclability	EN 13430	⇔	What is recyclable remains recyclable
Biodegradability	EN 13432	⇔	What is biodegradable remains biodegradable
Glueability	FINAT Test method n°1	↘↘ ↘	Water based Hotmelt (corona /plasma)
Release	FINAT Test method n°1 & 3	↗	Medium release grades

Case of coated papers and boards

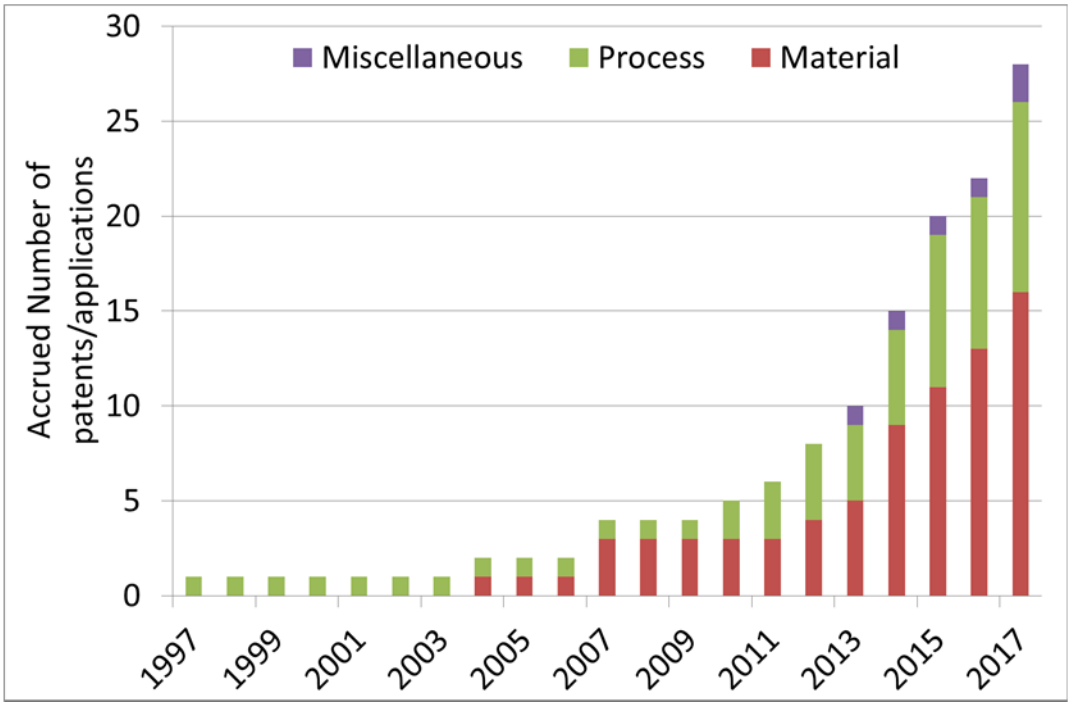
- **Main target: to develop medium and high barrier properties for coated papers and boards**

- **Potential markets:**
  - Release papers
  - Baking papers
  - Sacks, bags, wrapping papers
  - Lids
  - Box Boards, trays, cups, plates
  - and many others….

Patents around Chromatogeny

- **Patents and Main Players**

15 players identified



TOP 4 Companies/RTOs cited in patents	
Name	Number of patents/applications
CTP	10
Philip Morris	7
KNU	6
TKP	6

Chromatogeny = Solvent free use of fatty acid chlorides + cellulosic substrates

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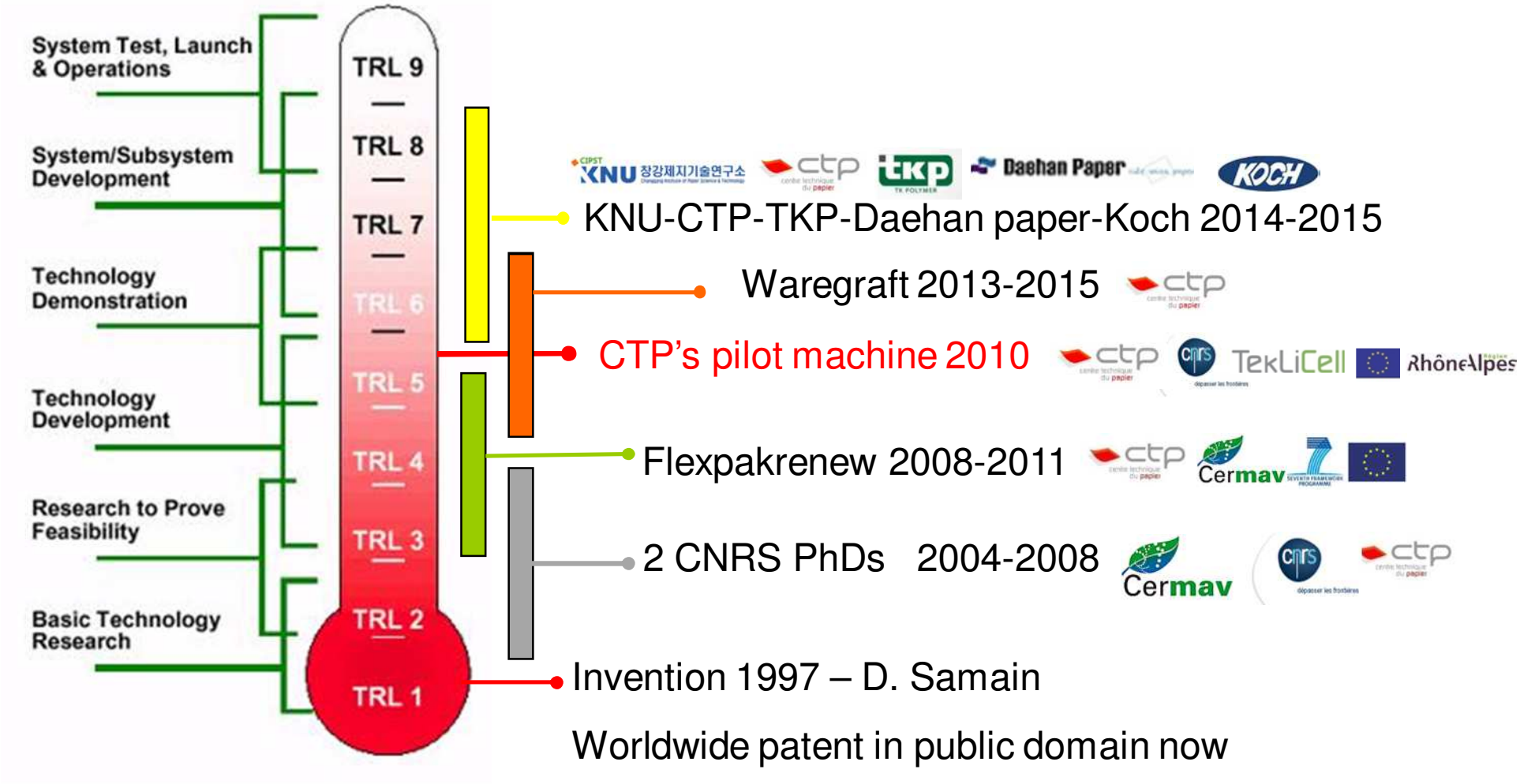

Upscaling chromatogeny at large scale

- **Partnership project**
  - March 2014 → May 2017

Runs pilot trials at CTP
Advises TKP for the building of the machine
Assists TKP in the start up of the machine

Brings market expectations
Defines product specifications
Builds and operates chromatogeny machine

Coordinates the project
Drives product developments

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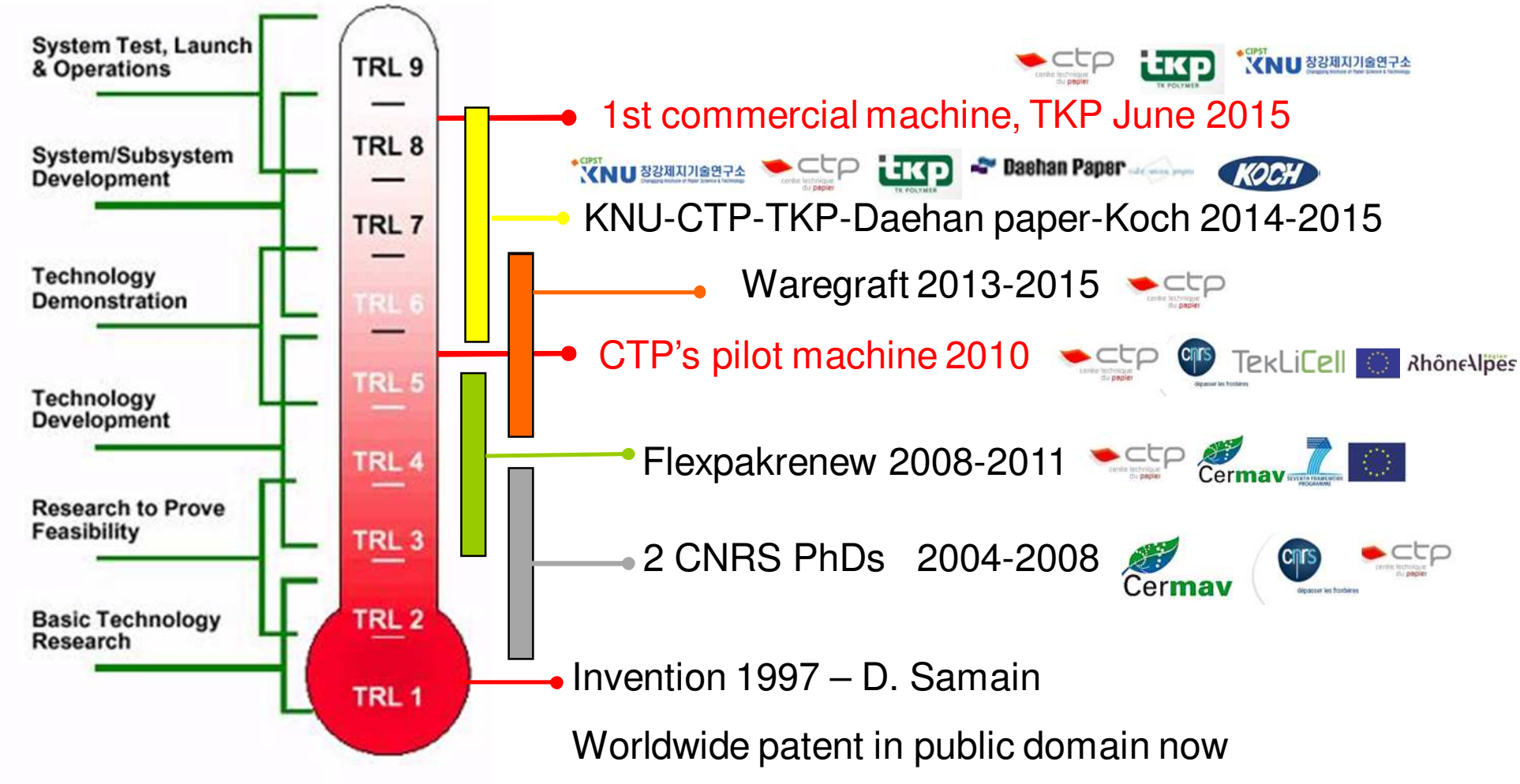
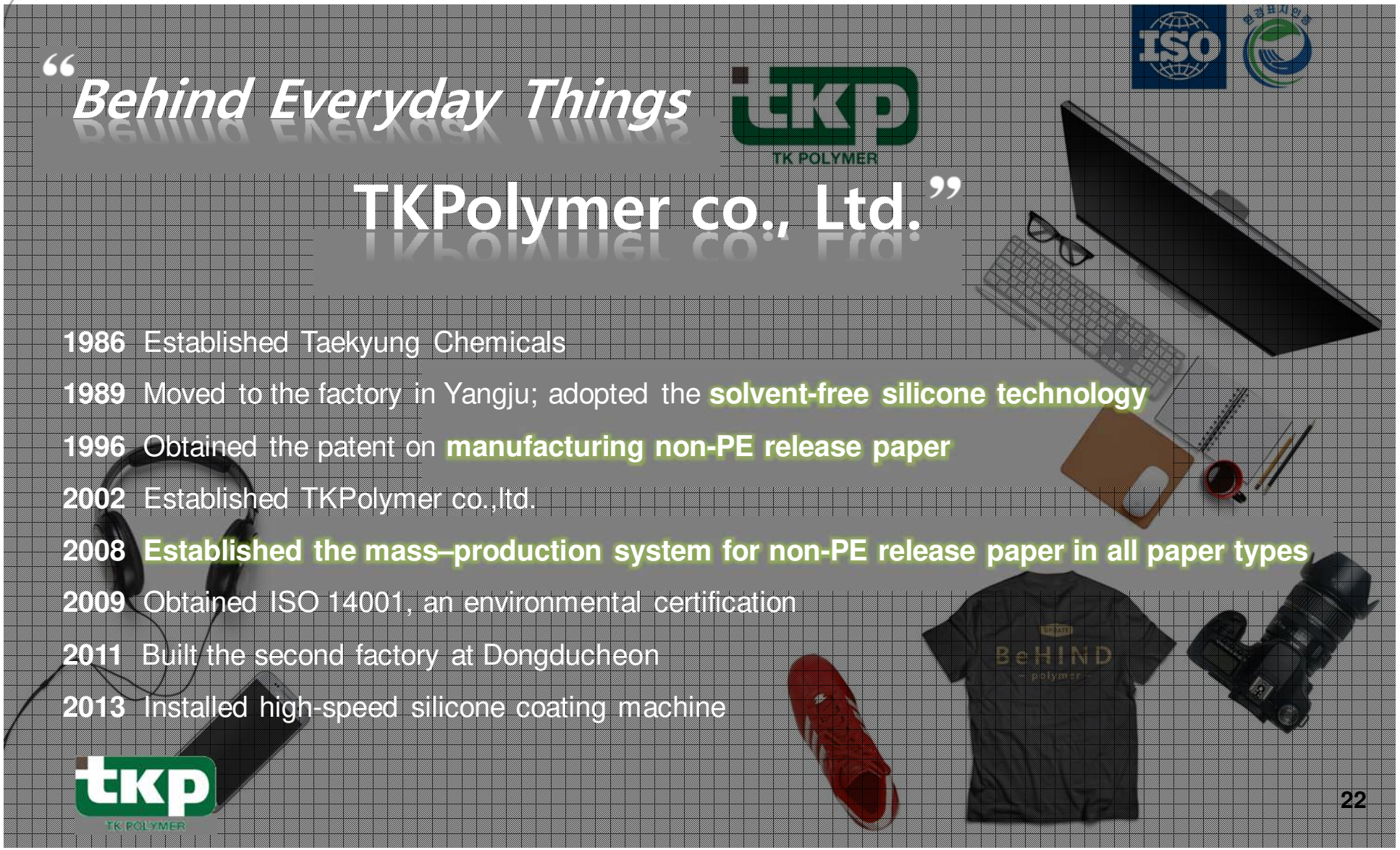


An Industrial reality

History of TKP



"*Behind Everyday Things*

TKPolymer co., Ltd."

1986 Established Taekyung Chemicals

1989 Moved to the factory in Yangju; adopted the **solvent-free silicone technology**

1996 Obtained the patent on **manufacturing non-PE release paper**

2002 Established TKPolymer co.,ltd.

2008 **Established the mass–production system for non-PE release paper in all paper types**

2009 Obtained ISO 14001, an environmental certification

2011 Built the second factory at Dongducheon

2013 Installed high-speed silicone coating machine

Factory & Facilities

Dongducheon Factory (R&D Centre)

Yangju Factory

➢ 35,000m² of factory space, production capacity is 25,000,000m²/month

High speed silicone coating machine

➢ Producing up to 350 m/min

>> Rapid production / High quality

Regular speed silicone coating: 7 machines

Non-PE primer coating: 5 machines

Slitting: 5 machines

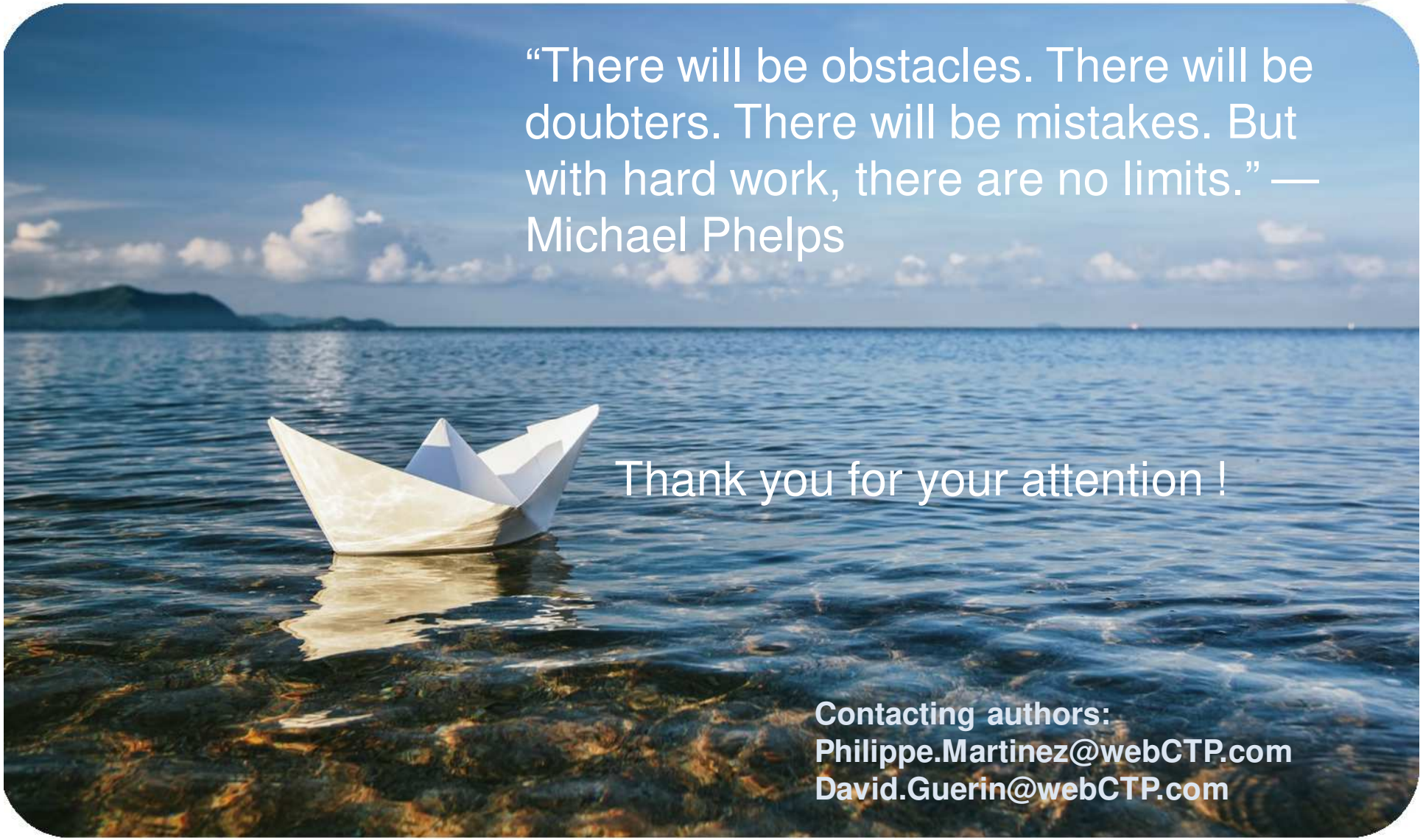
Gravure printing: 2 machines

Chromatogeny: 2 machines

Revision to real paper

Conclusions

- **A history of chromatogeny**
  - 18 years from invention to full scale
  - Several projects in progress
  - Several successes but also many failures
- **Some Difficulties**
  - Identify the created value
    - ✓ Value for lower environmental Impact
  - Find the right partners
    - ✓Culture of innovation, size of company
  - Find the right persons
    - ✓R&D, sales, marketing, production
  - Define the upscaling scenario
    - ✓List task to achieved, prioritize



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