

Le float: une invention révolutionnaire

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Remerciements:

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Journée 70 ans de SF2M et de Matériaux, Paris (20/3/2015)

Plan

- Perspective historique
- Deux voies en parallèle:
 - Soufflage: vitres
 - et coulée: glaces
- La révolution de 1959
- Aujourd'hui
- Enjeux

Perspective historique

70 ans: 1945-2015 → **Le float: brevet**

de 1959

500

800

1000

1600

1800



Modificateur: Natron / Cendres (verres modifiés par la potasse ou la soude) ▲ Soude synthétique

Combustible : bois (implantation en forêts: Eu, Lyons...)

● Charbon

CO... CH₄

Verre plat: coulé (glaces), cylindre et plateau (vitres)



Ruban

▲ 1791 Leblanc
1870 Solvay

● 1854 Siemens

■ 1903 Lubbers
(cylinder)

◆ 1910 Bicheroux
(cast)

■ 1913 Fourcault
1925 Pittsburgh
1959 Float Pilkington
(ruban flotté sur étain
liquide)

Bontemps, G. (1868) *Guide du Verrier*, Librairie du Dictionnaire des Arts et Manufactures, Paris, libre accès à la Bibliothèque Nationale de France

Glass : mechanics and technology, 2nd Edition, E. Le Bourhis, Wiley-VCH, 2014

Deux voies en parallèles

Vitres

- Cylindre
- Plateau

- Lubbers
- Fourcault, Pittsburg

Glaces

- Coulée
- +*Polissage*

- Bicheroux, Boudin
- +*Polissage*

Automatisation à partir de 1900

Révolution du Float 1959

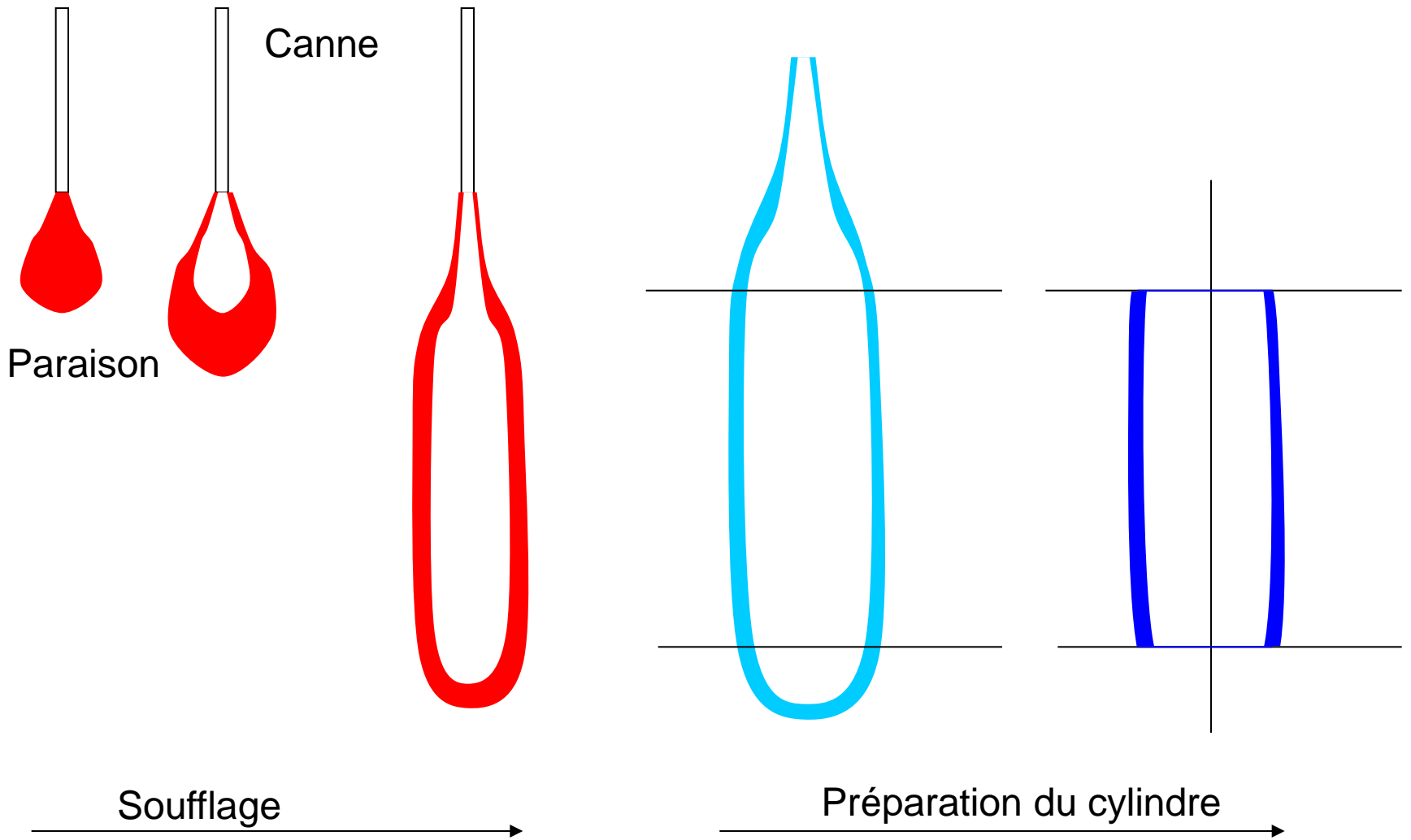
Bontemps, G. (1868) *Guide du Verrier*, Librairie du Dictionnaire des Arts et Manufactures, Paris, libre accès à la Bibliothèque Nationale de France
Glass : mechanics and technology, 2nd Edition, E. Le Bourhis, Wiley-VCH, 2014

Vitres : soufflées

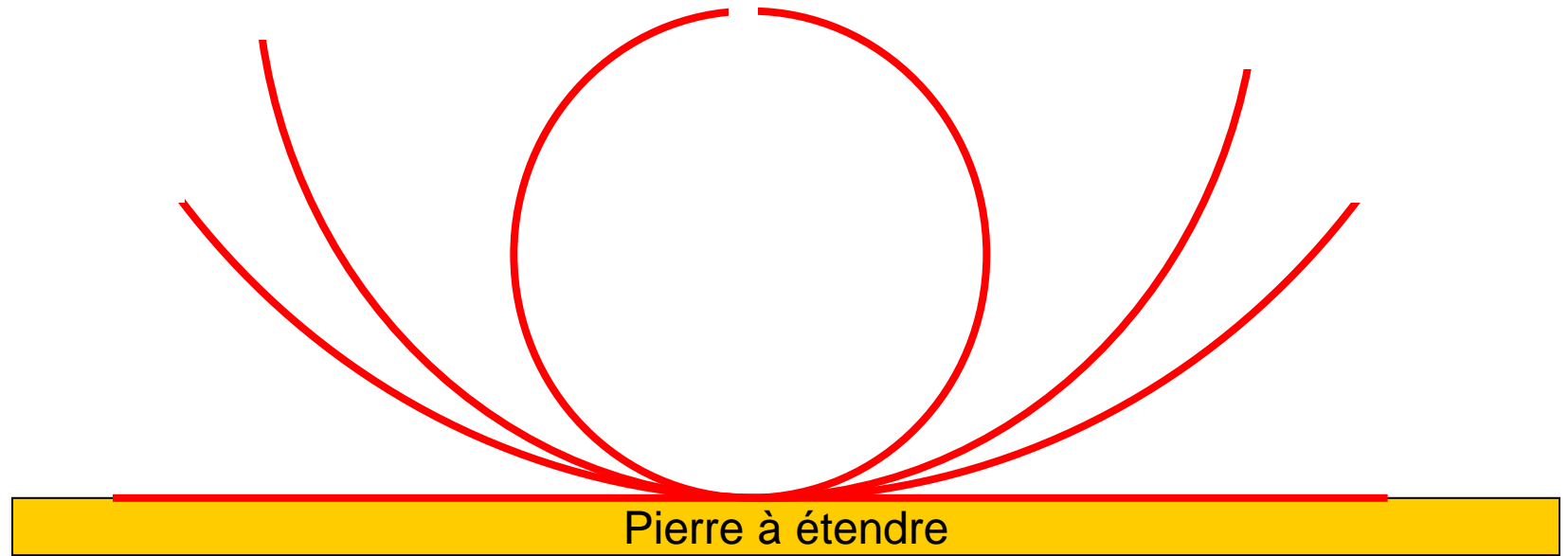
Diderot, D. and d'Alembert, J. (1765) *L'Encyclopédie, Art du verre Fabrication des glaces*, Paris, (2002) Inter-Livres, Paris

Fig. 2.





Ouverture du manchon



Procédés encore usités

Video 14.45 -15.28, <http://www.saint-gobain350ans.com/>

Automatisation progressive à partir de 1900 des opérations les plus éprouvantes

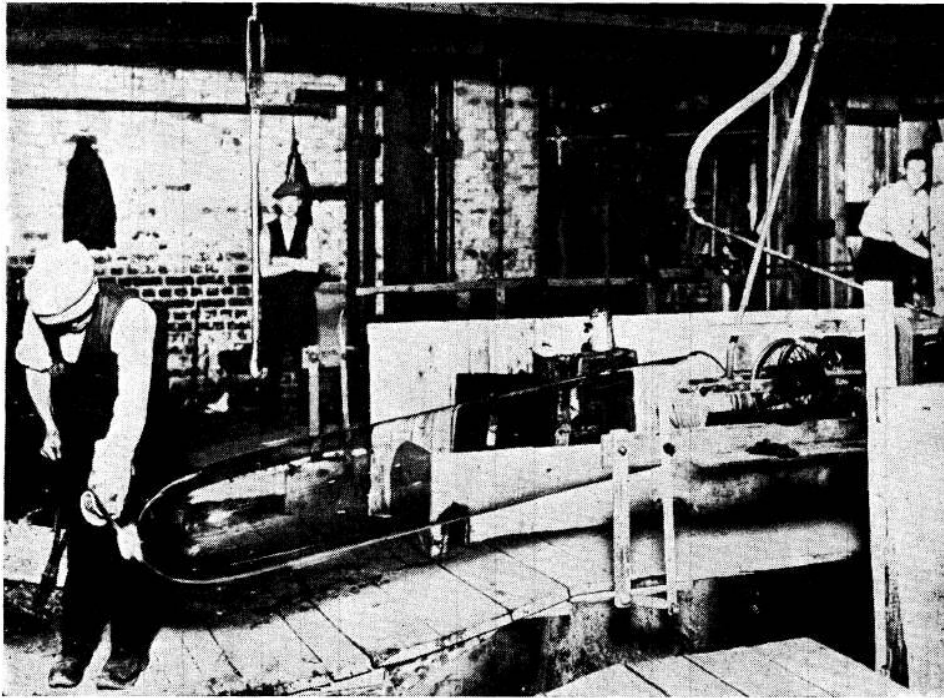


FIGURE 3. Glass made by the cylinder process had to be split and flattened for windows.

Pilkington, L.A.B (1969) *Proc. R. Soc. Lond. A*
Cable, M. (1999) *J. Am. Ceram. Soc.*, **82**, 1093.

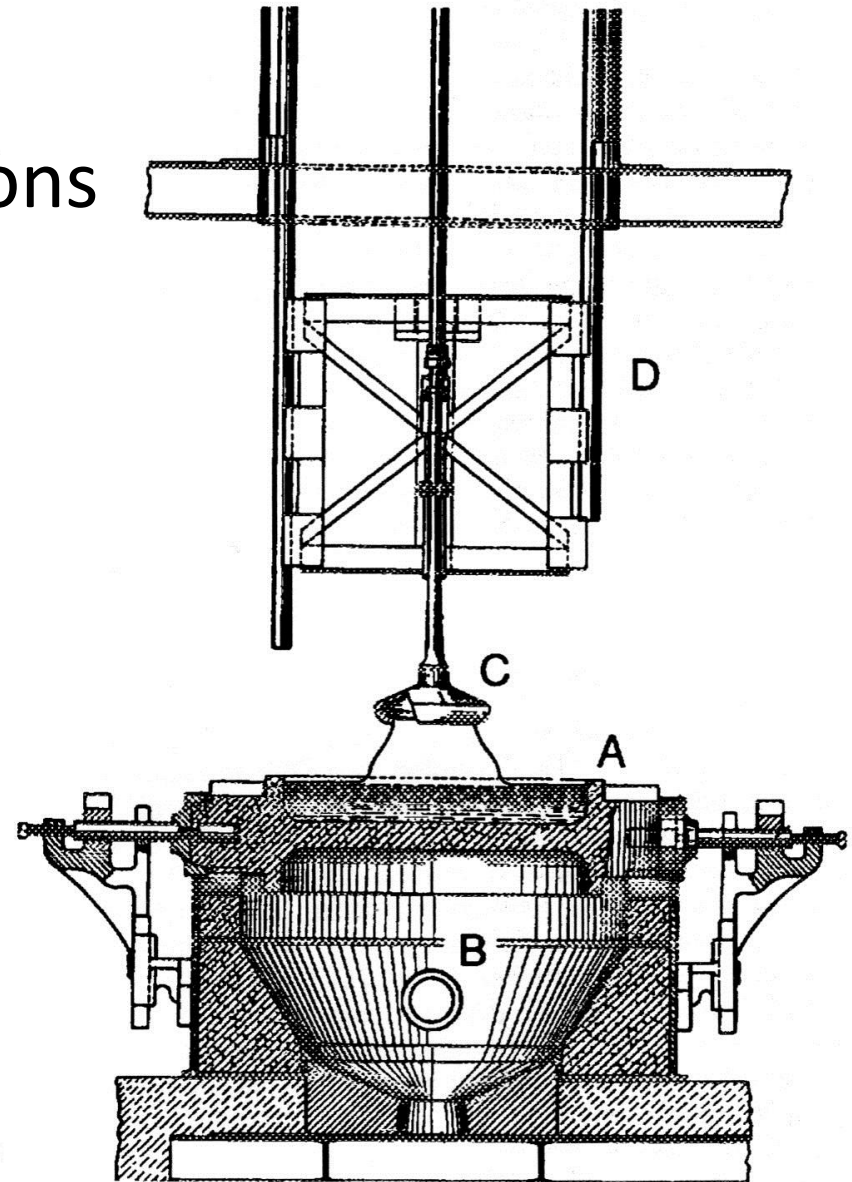
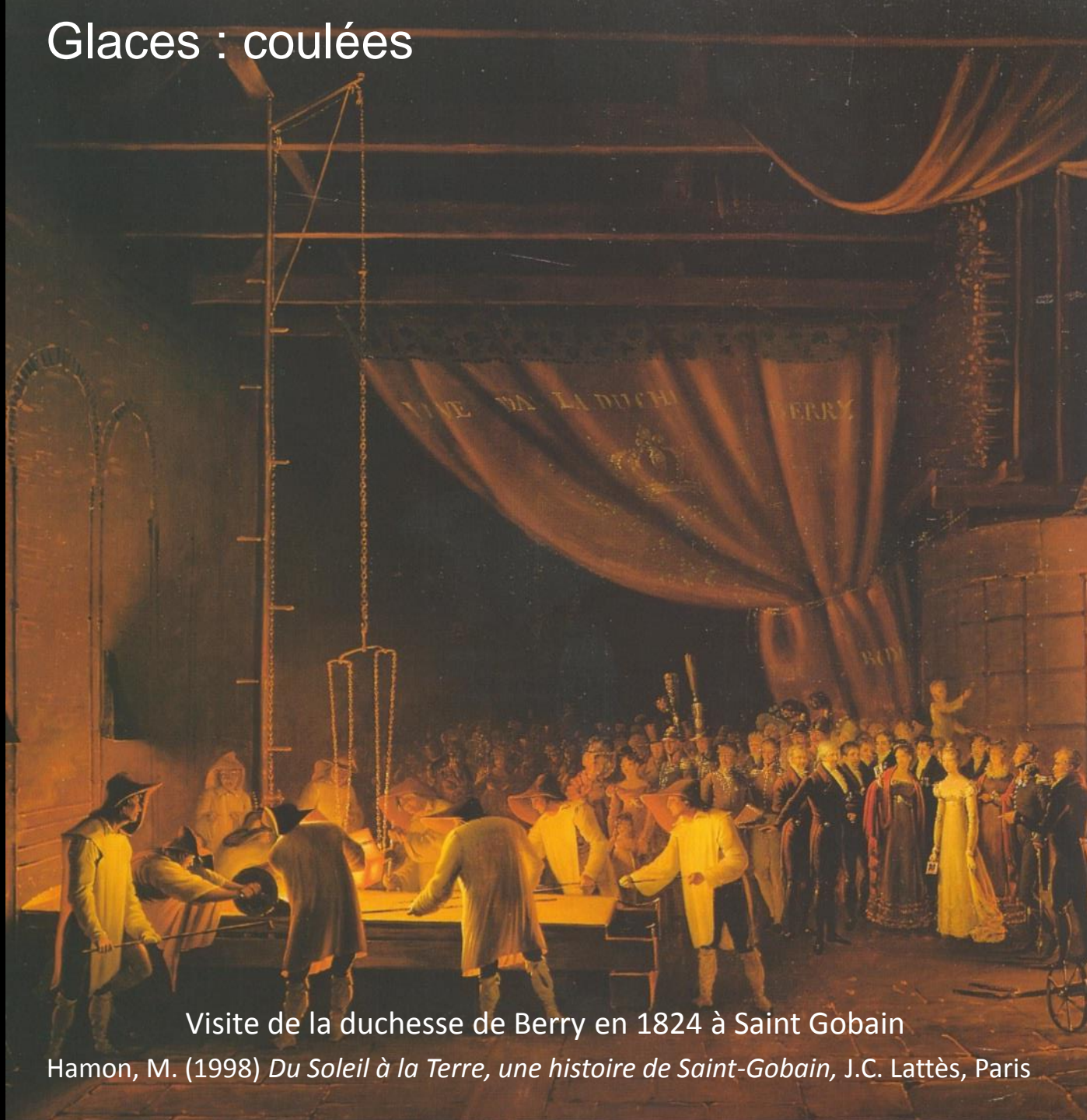


Fig. 14. Drawing a cylinder of glass by the Lubbers process. Glass is cast into a (A) reversible preheated bowl sitting on top of a (B) heated muffle. (C) Bait is dipped into the glass; when the glass has adhered, the blow-pipe unit is raised up the (D) vertical track.

Glaces : coulées



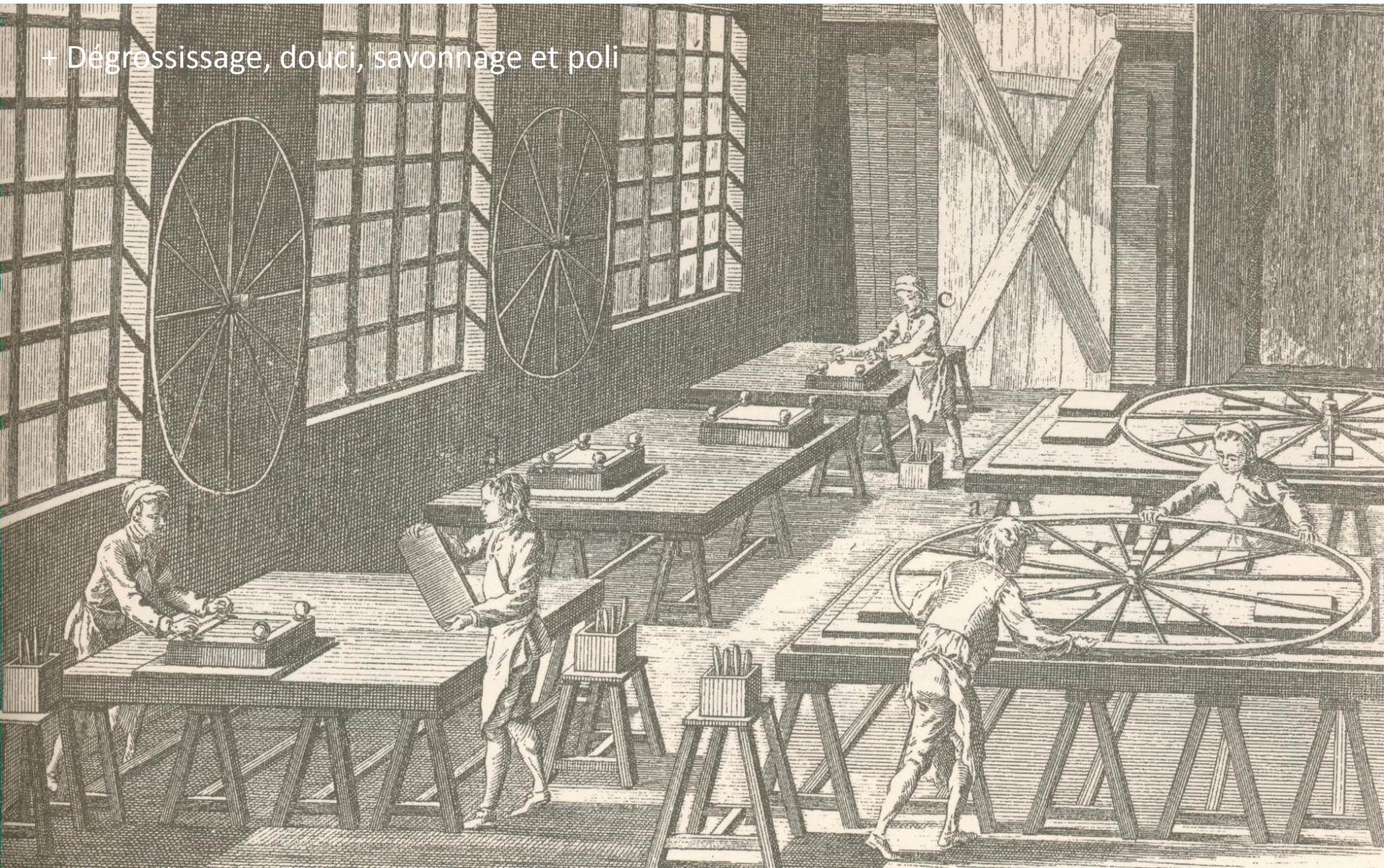
Visite de la duchesse de Berry en 1824 à Saint Gobain

Hamon, M. (1998) *Du Soleil à la Terre, une histoire de Saint-Gobain*, J.C. Lattès, Paris



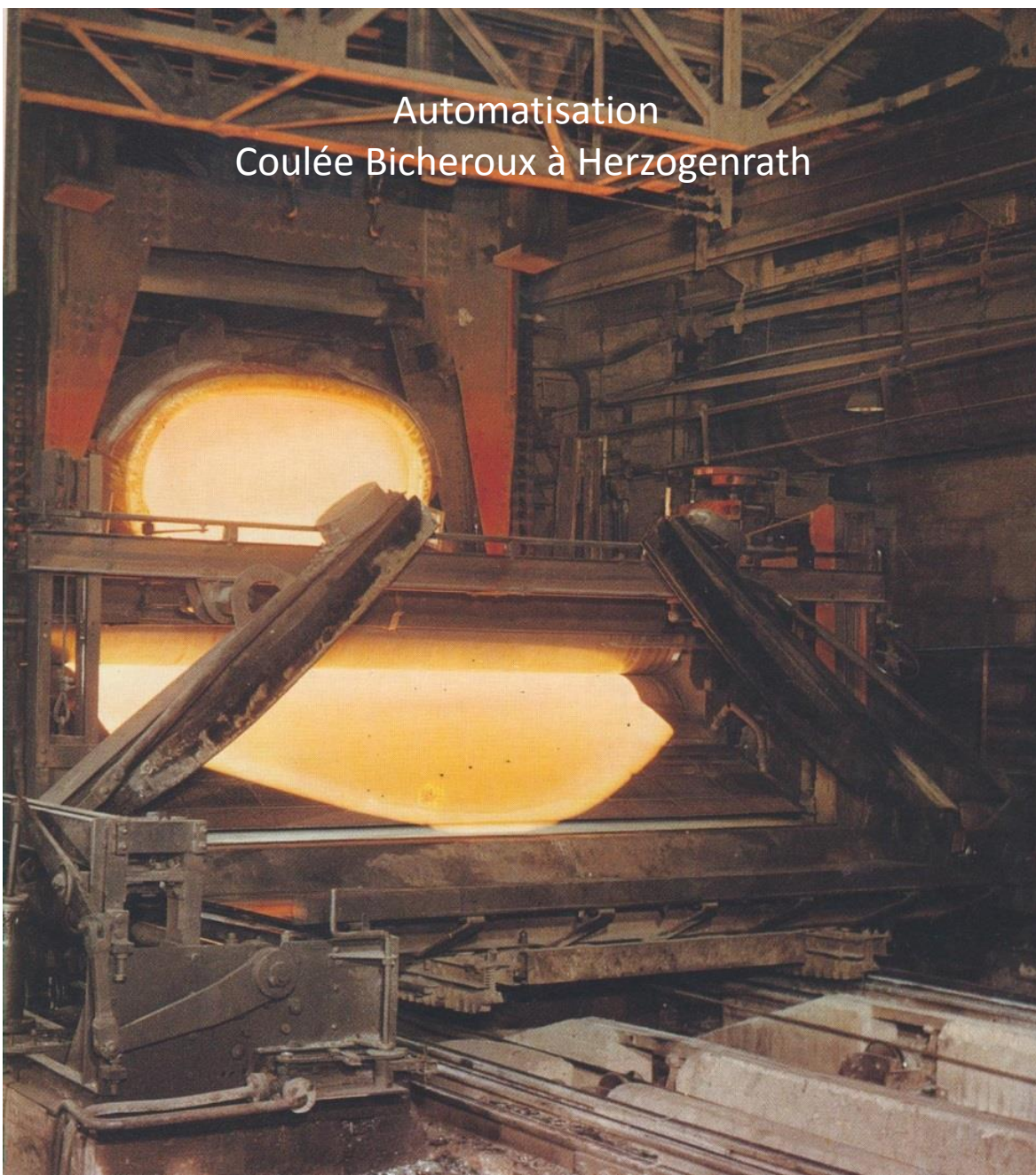
Voir aussi Saint Gobain, Saint Just aujourd'hui

+ Dégrèssage, douci, savonnage et poli

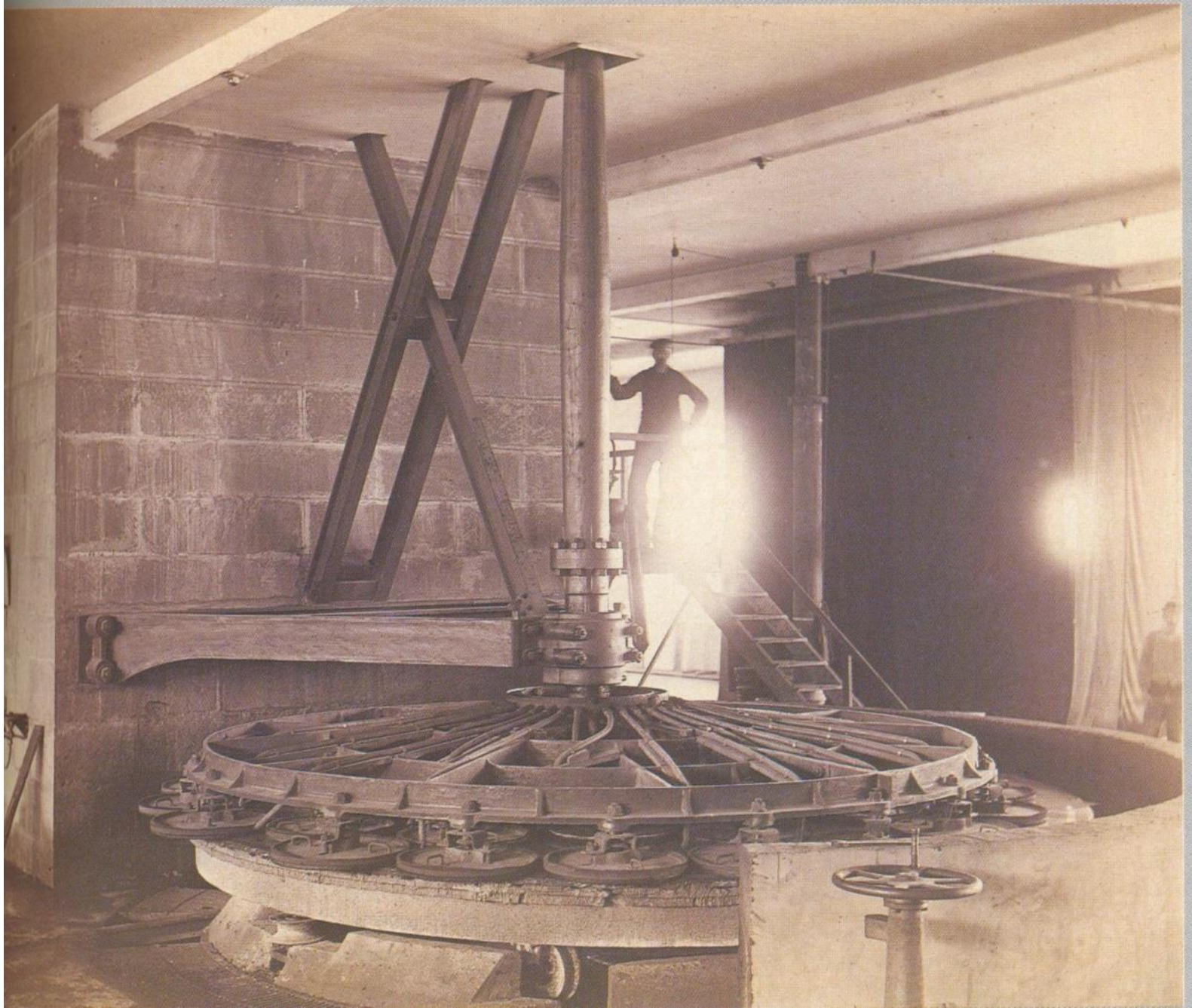


Diderot, D. and d'Alembert, J. (1765) *L'Encyclopédie, Art du verre Fabrication des glaces*, Paris, (2002) Inter-Livres, Paris

Automatisation
Coulée Bicheroux à Herzogenrath



Hamon, M. (1998) *Du Soleil à la Terre, une histoire de Saint-Gobain*, J.C. Lattès, Paris



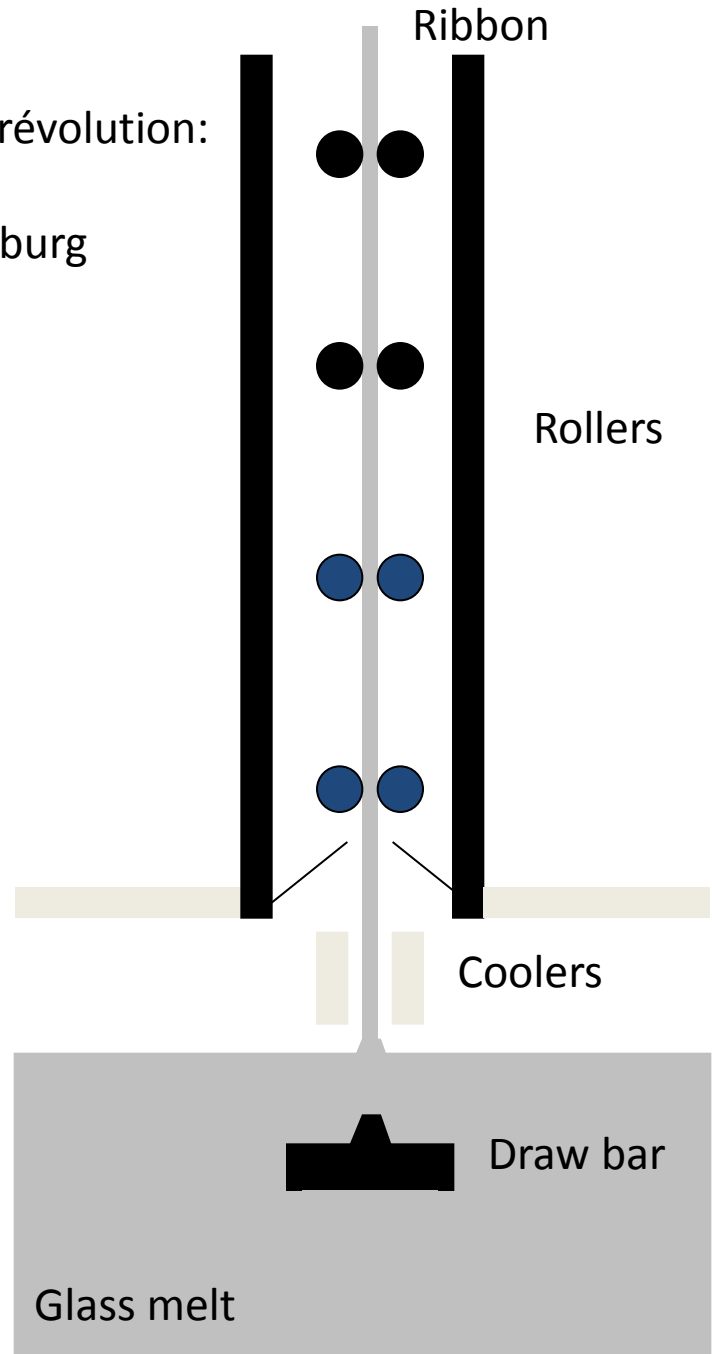
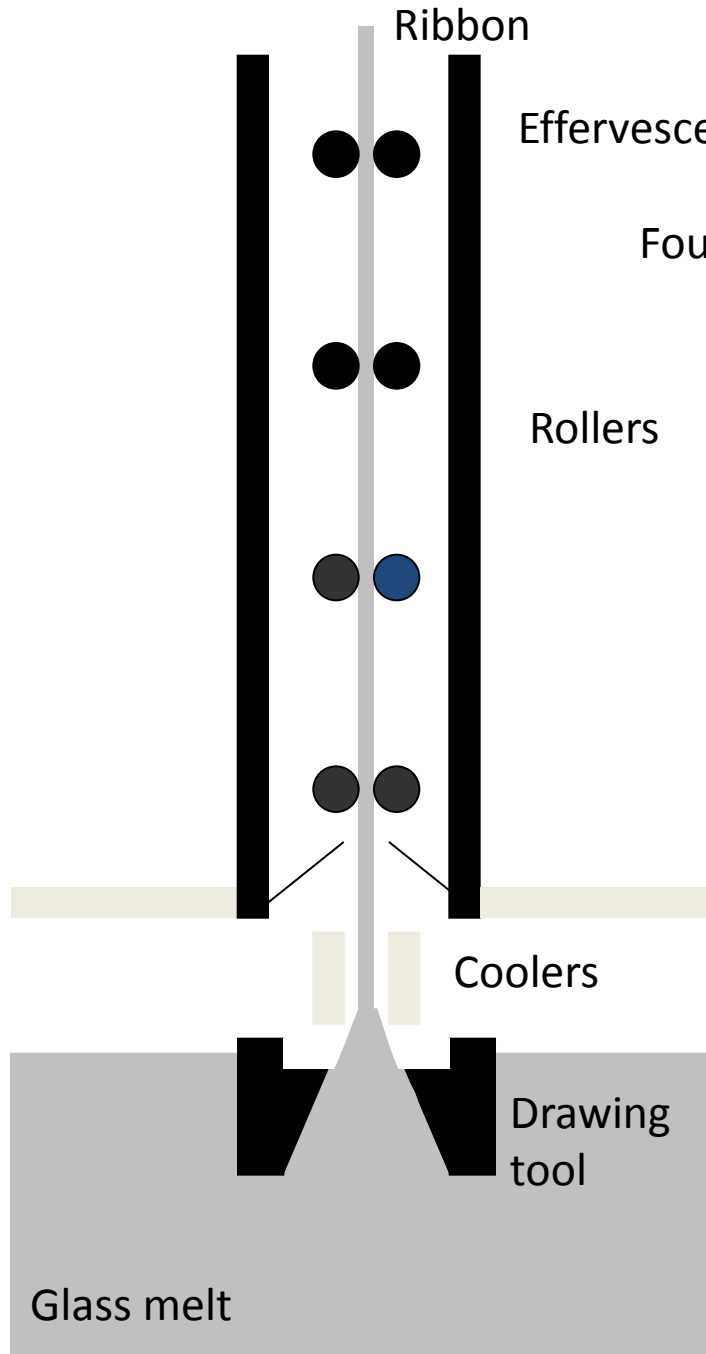
Hamon, M. (1998) *Du Soleil à la Terre, une histoire de Saint-Gobain*, J.C. Lattès, Paris

Danse des sabots



Video 4.38 – 5.04, <http://www.saint-gobain350ans.com/>

Hamon, M. (1998) *Du Soleil à la Terre, une histoire de Saint-Gobain*, J.C. Lattès, Paris



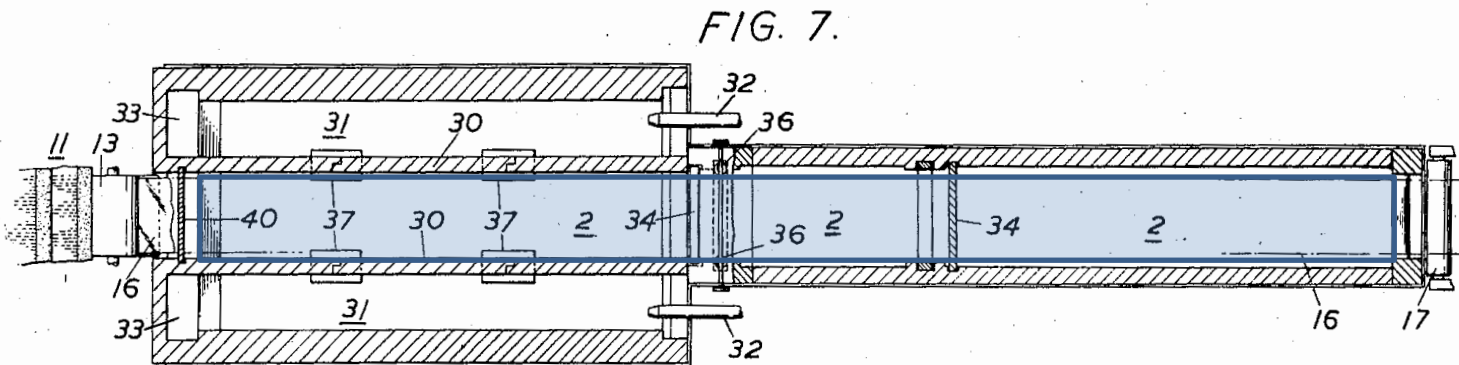
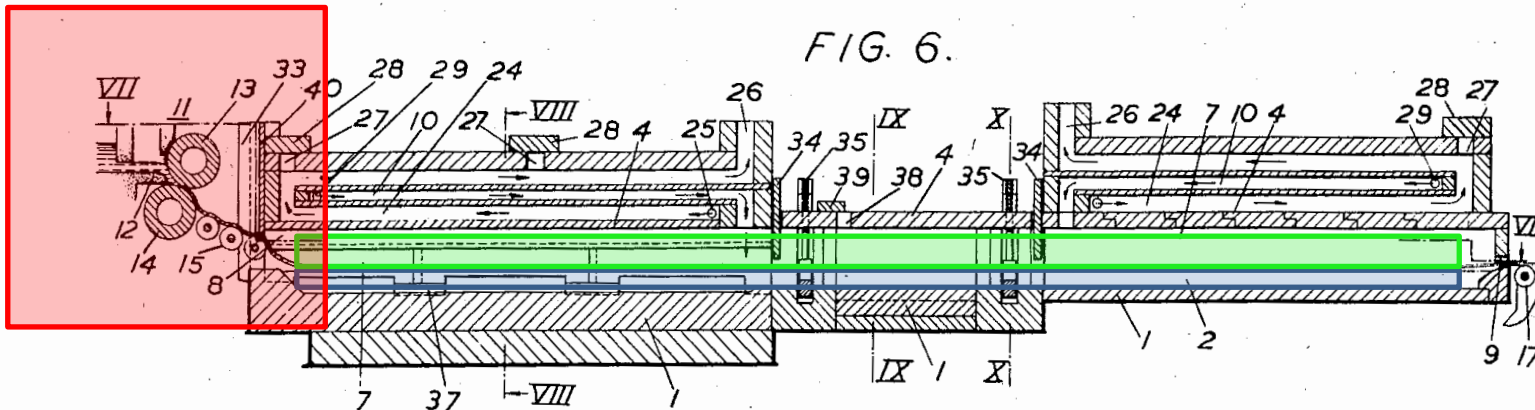
La révolution de 1959

Nov. 10, 1959
 Filed Dec. 6, 1954

L. A. B. PILKINGTON ET AL
 MANUFACTURE OF FLAT GLASS

3 Sheets-Sheet 2

2,911,759



Bain d'étain

Atmosphère réductrice

Excellente qualité des faces
 (Face atmosphère vs Face étain)
 → Pas d'opérations supplémentaires
 (polissage)

*L. A. B. Pilkington
 & Co. Proprietors
 Messrs. James & Humphreys
 Attorneys*

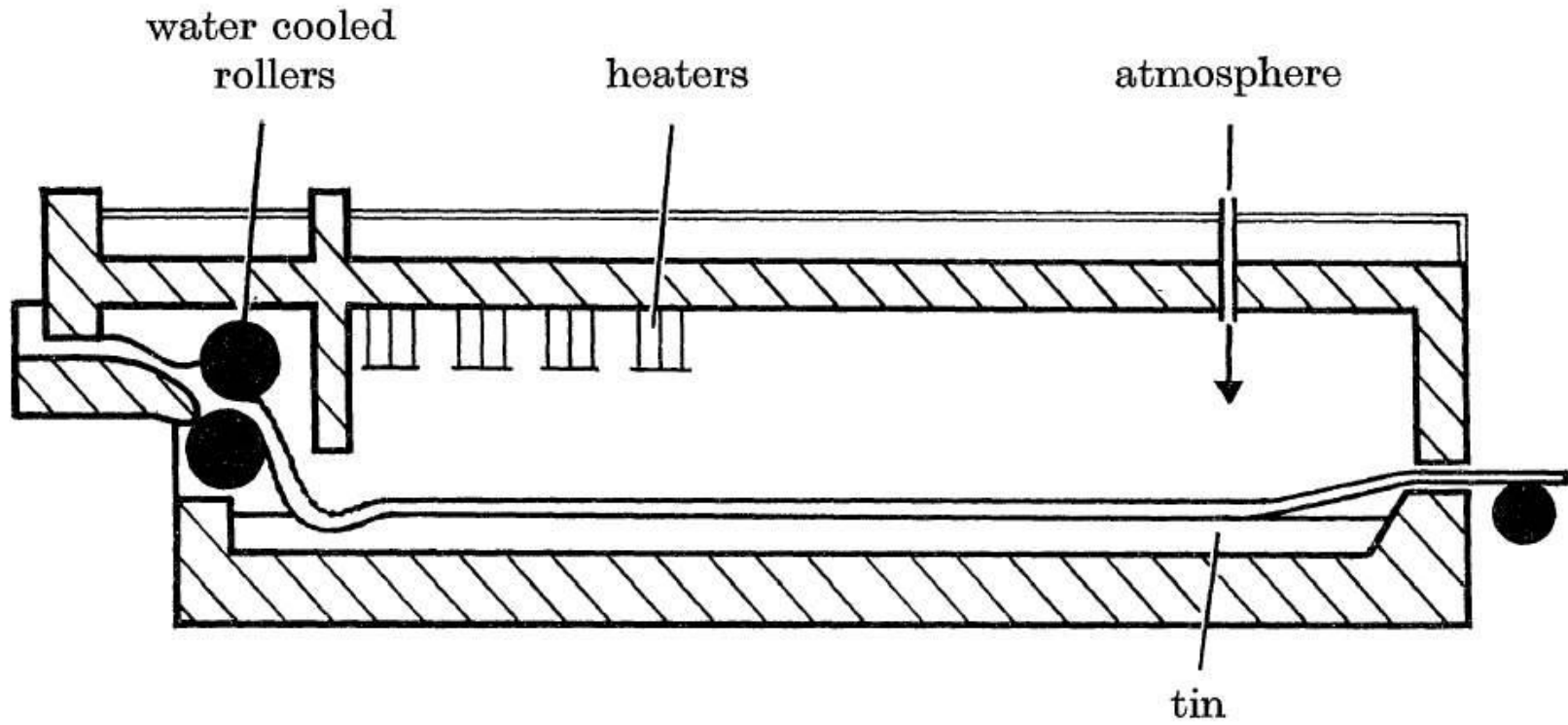


FIGURE 11. In experiments with the float process glass was rolled on to the molten tin.

Première tentative : verre pré laminé

- pas de contrôle d'épaisseur (cf. épaisseur d'équilibre)
- condensation d'étain et alliages sur les rouleaux marquant les surfaces

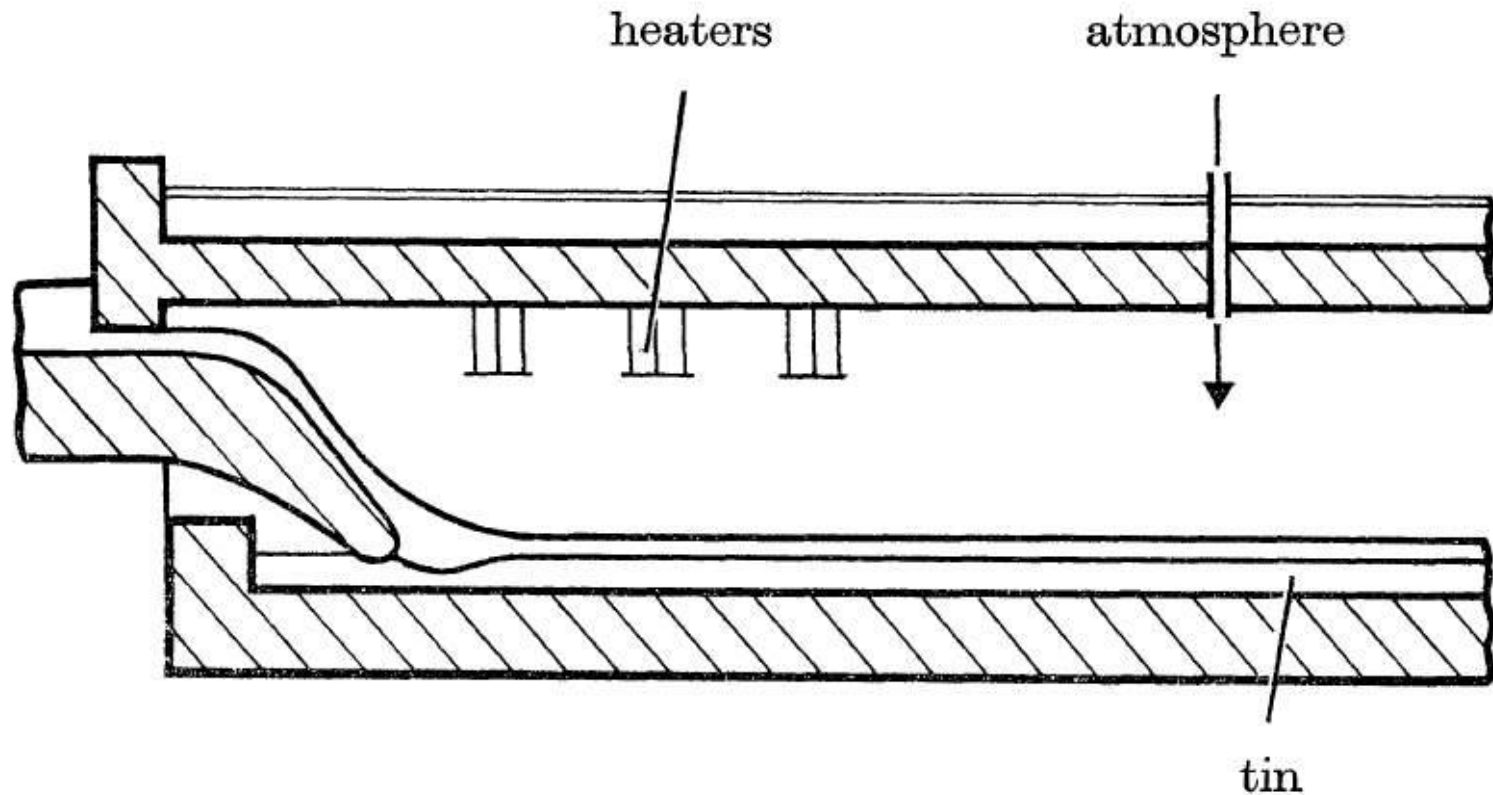


FIGURE 12. Direct pour of the glass replaced the roller method.
The spout dipped into the tin.

Deuxième tentative: verre versé avec l'outil plongeant dans le bain

- attaque du réfractaire préférentielle à l'interface étain/verre/réfractaire
- contamination des surfaces

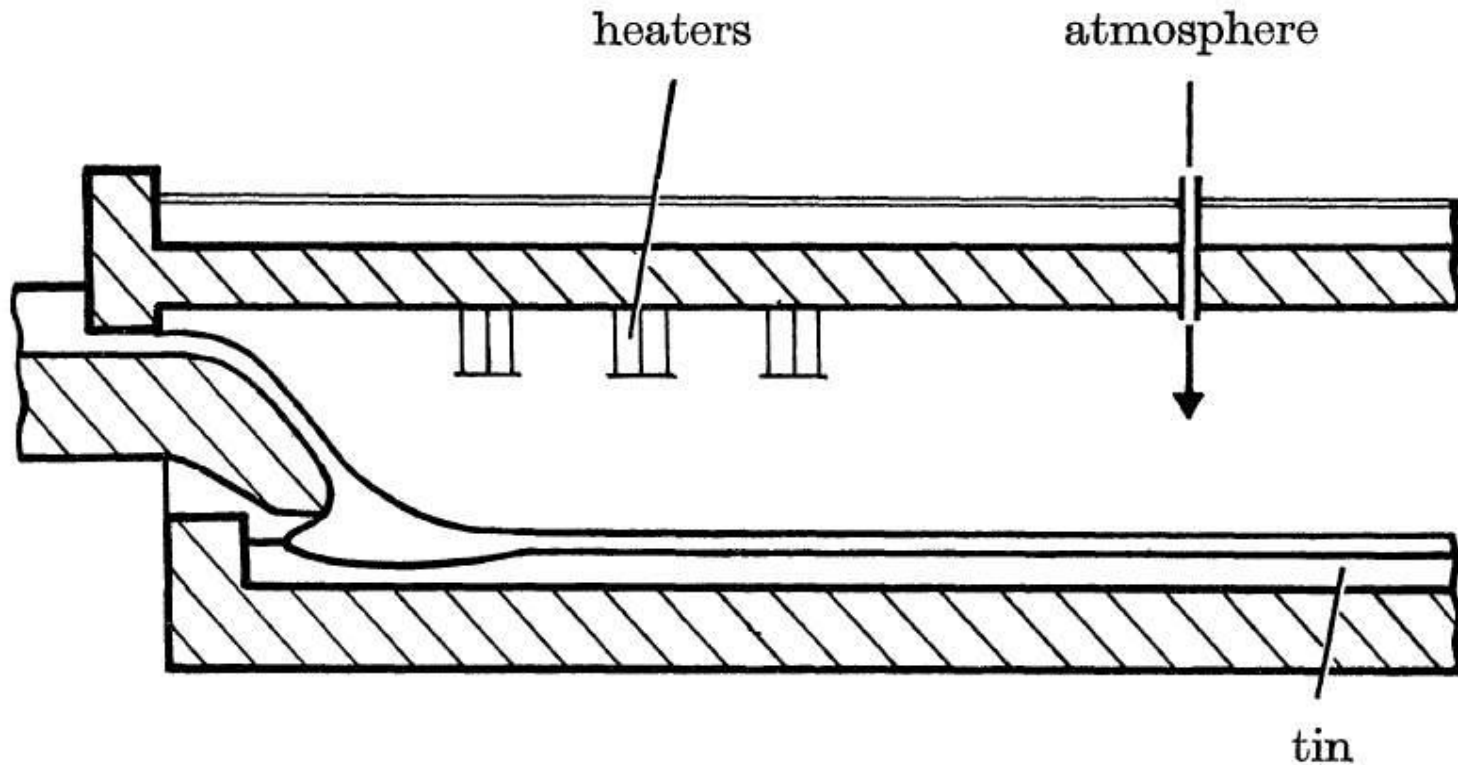
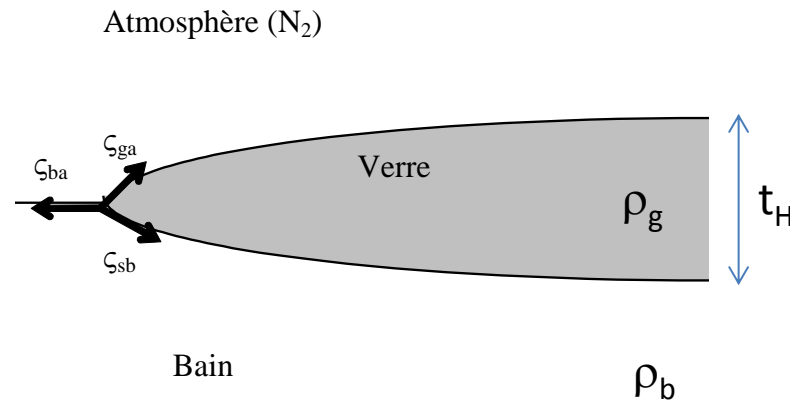


FIGURE 13. Finally a spout was fitted which did not dip into the tin. It allowed a free fall of glass.

Troisième tentative: verre versé avec l'outil surplombant le bain

- attaque du réfractaire limitée à l'interface verre/réfractaire
- contrôle des surfaces formées

Épaisseur d'équilibre du ruban



$$\frac{gt_H^2\rho_g}{2}\left(1 - \frac{\rho_g}{\rho_b}\right) = \zeta_{ga} + \zeta_{gb} - \zeta_{ba}$$

Verre SSC: $\rho_g = 2500 \text{ kg.m}^{-3}$, $\rho_b = 6500 \text{ kg.m}^{-3}$, $\zeta_{ba} = \zeta_{gb} = 0.5 \text{ J.m}^{-2}$, $\zeta_{ga} = 0.35 \text{ J.m}^{-2}$,

$t_H = 6.8 \text{ mm}$

(dépend du verre ex borofloat $\rho_g = 2220 \text{ kg.m}^{-3}$).

→ Top roll: 2-18 mm

Le float aujourd'hui

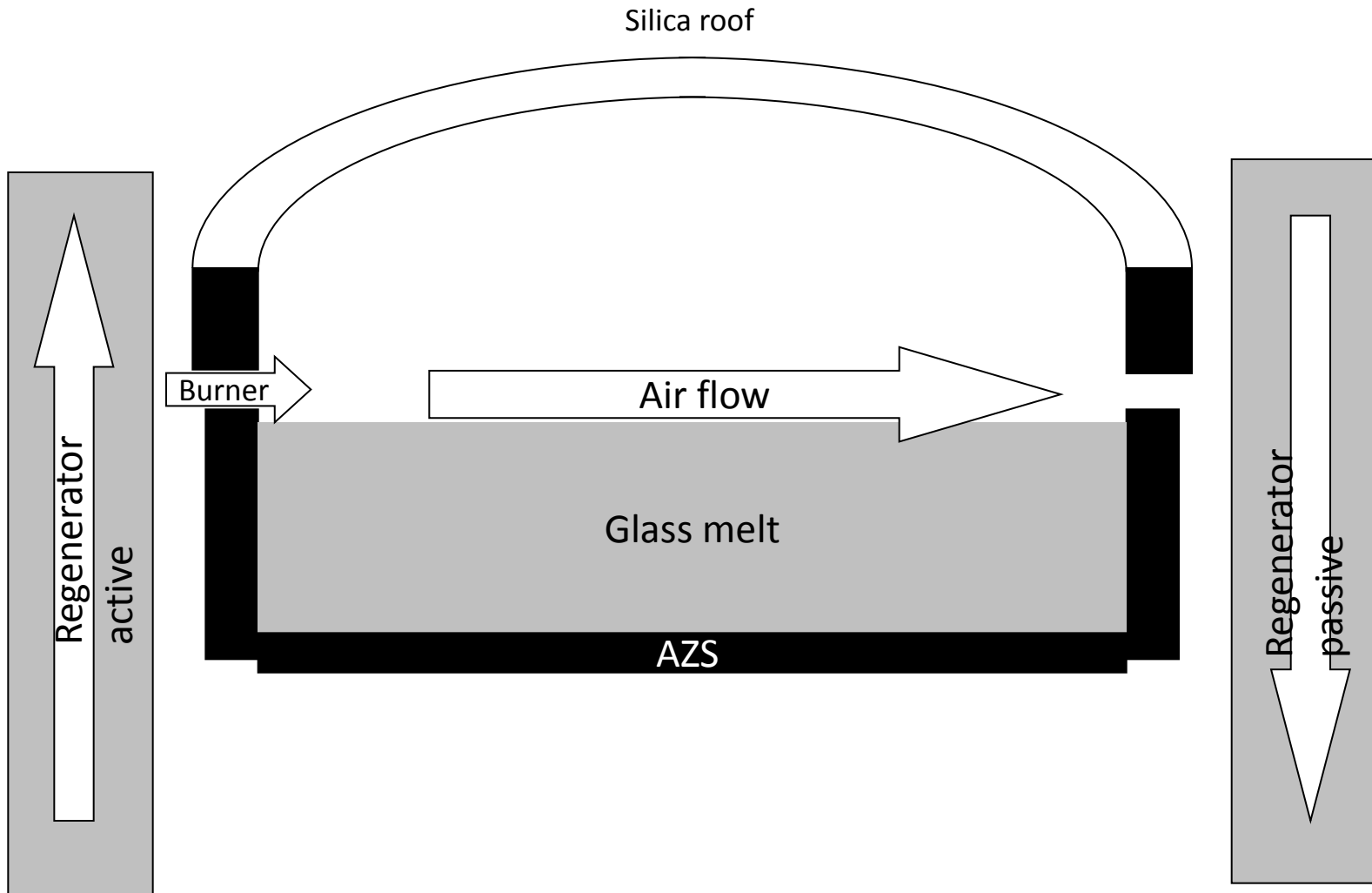


Usine Float de Chennai (Saint-Gobain)

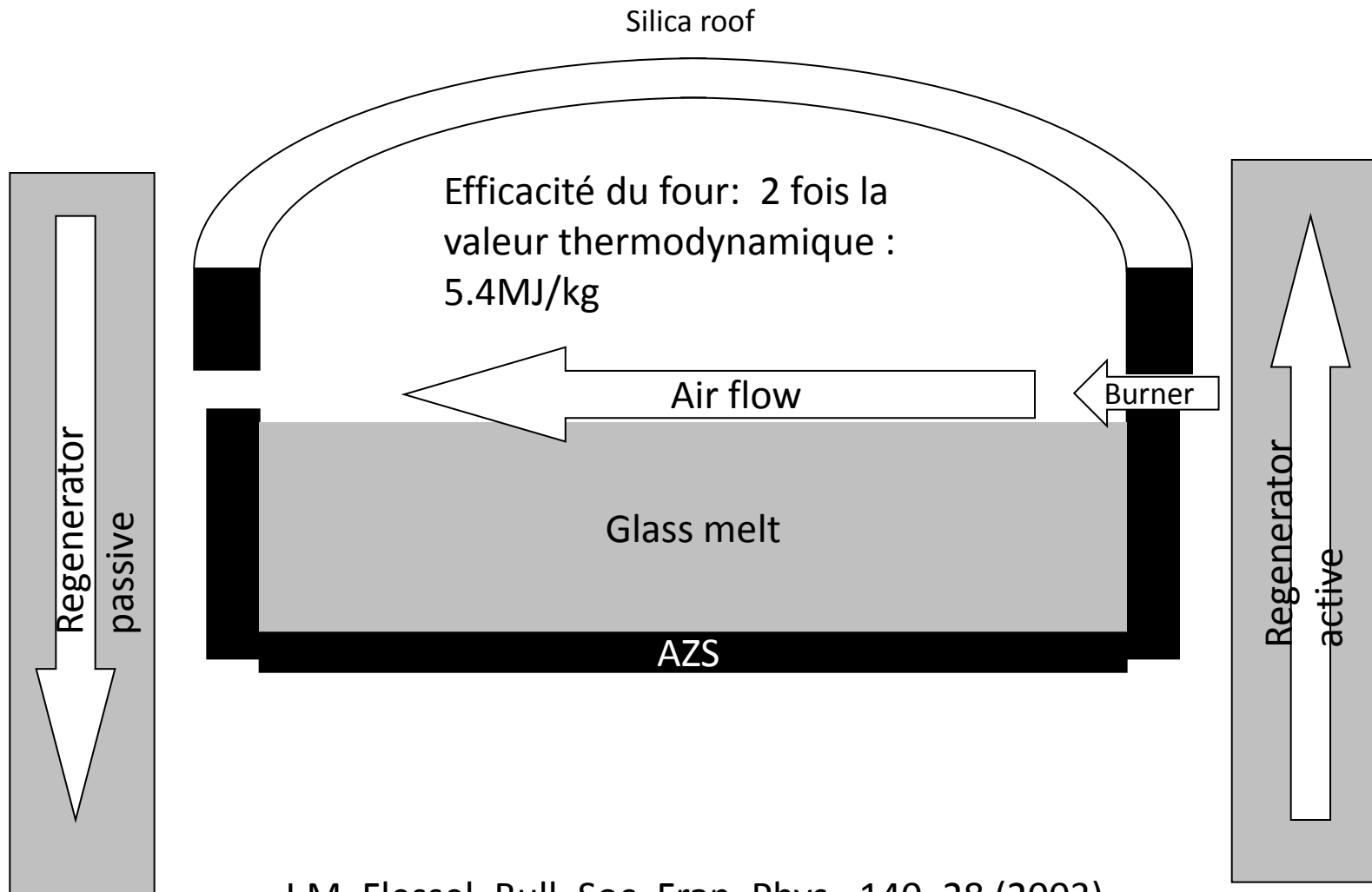


Un outil efficace: 500 t/j, 24h/24
Majorité du verre plat: 2-18 mm

Le float aujourd'hui

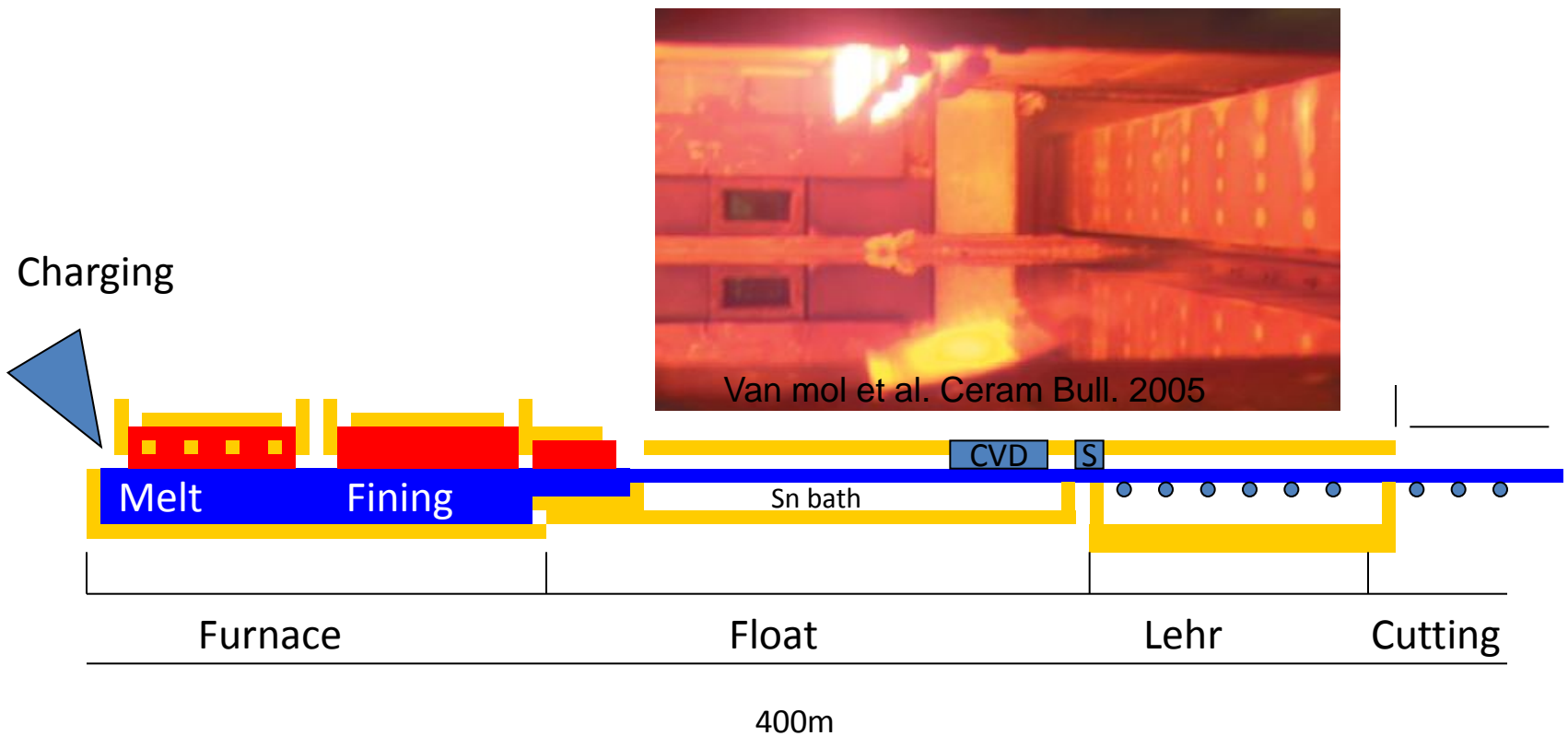


Le float aujourd'hui



J.M. Flessel, Bull. Soc. Fran. Phys., 140, 28 (2003)

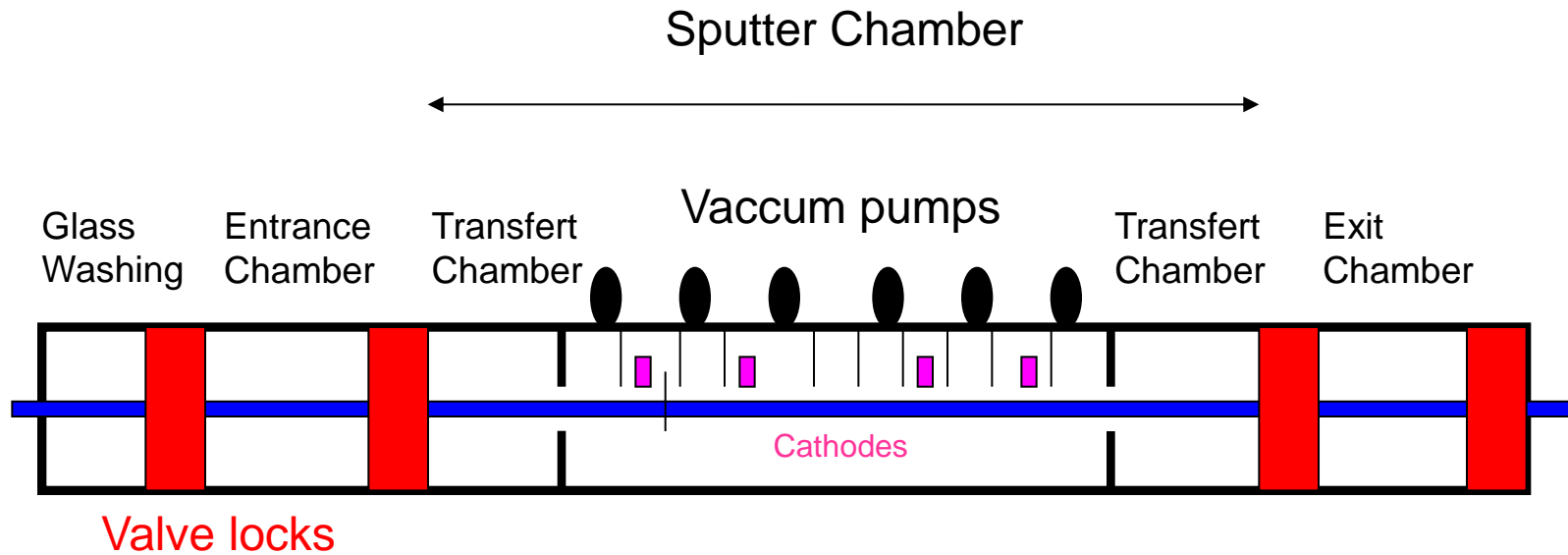
E. Le Bourhis, Glass : mechanics and technology, 2nd Edition, Wiley-VCH, 2014



Un outil efficace: 500 t/j, 24h/24

mais peu flexible → fonctionnalisation de surface: CVD, spray en ligne
 → microfloat

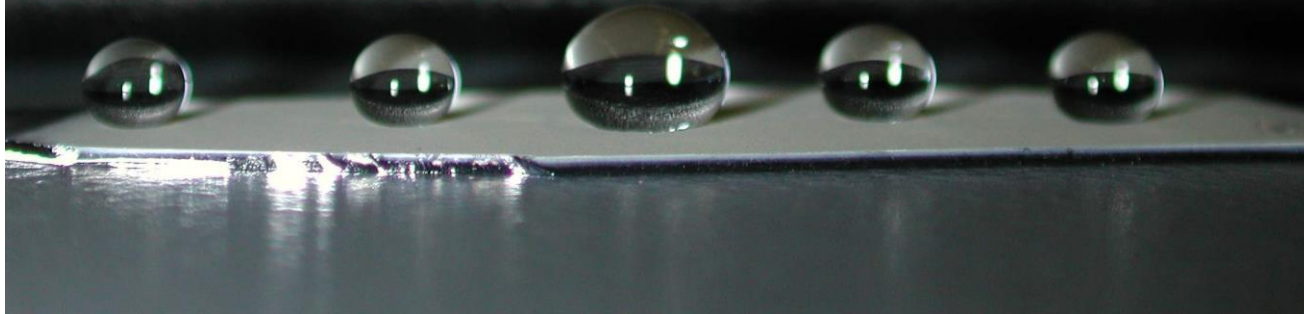
PVD en reprise: améliorer la performance des empilements



Glass transport direction →



Fonctionnalisation des surfaces



Function	Product
Anti-abrasion	Fiber, containers
Low-Emissivity	Energy-conserving windows
Solar control + Low-E	Windows in large building
FDP	TV, computers
Anti-reflection	TV, pictures frames
Defogging	Supermarket freezers, windows in vehicles
Anti-reflexion	TV, pictures frames
Electrocromics	Automatic rear-view mirrors
Water repellence	Plane windscreen
Self cleaning	Self cleaning windows

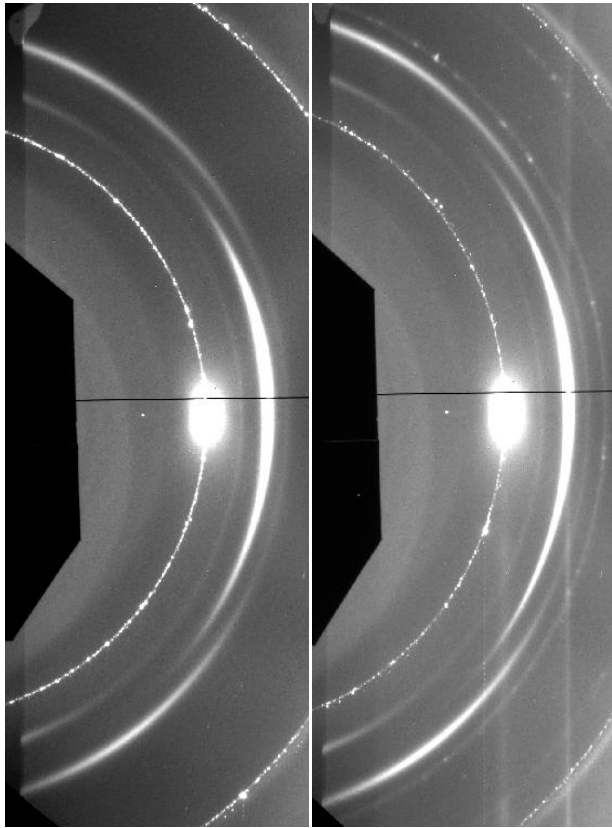
Enjeux

- Fonctionnalisation des surfaces → amélioration des tenues mécaniques
 - thermomécanique : PVD vs CVD
 - sous contact: Sol-gel
- Développement de substrats minces résistants et/ou stables vis-à-vis des procédés électroniques (température)

Résistance thermomécanique de Revêtements bas émissif (PVD)

ZnO (100nm)
Si (sub.)

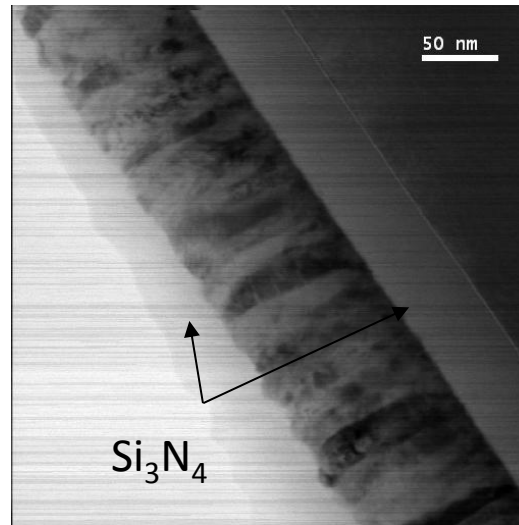
Si₃N₄ (50nm)
ZnO (100nm)
Si₃N₄ (50nm)
Si (sub.)



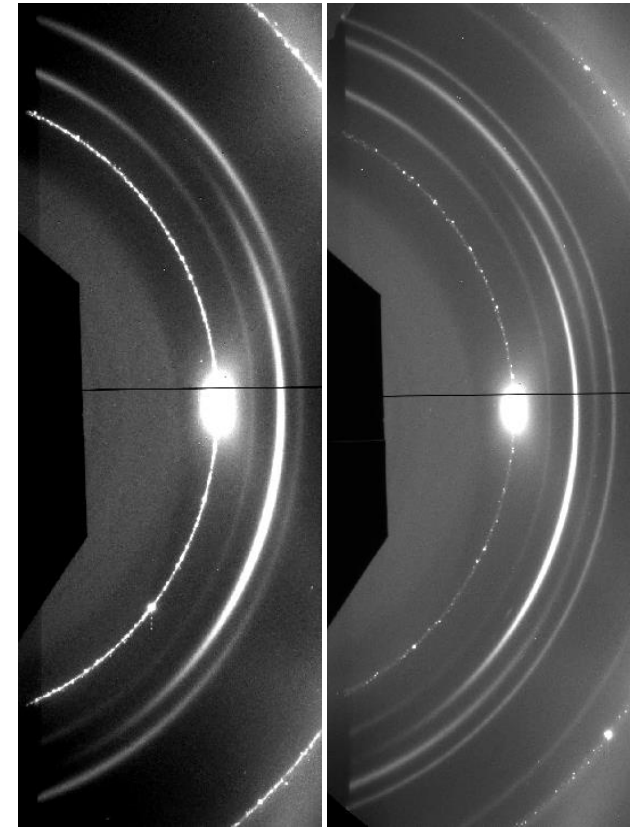
Before

After annealing

Ring discontinuities
<=>
ZnO texture
different!



Columnar texture :
20nm in size



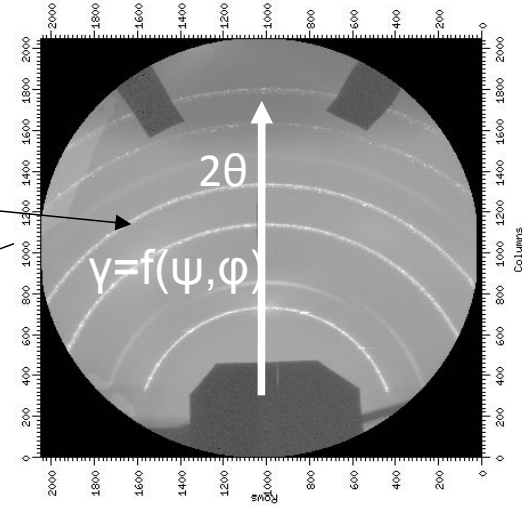
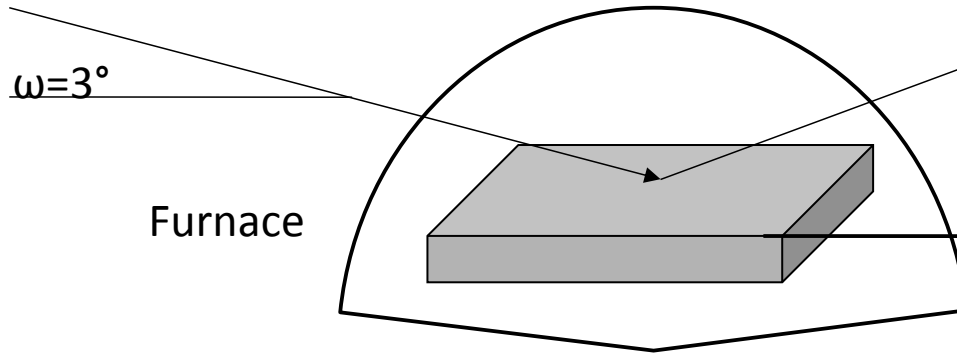
Before

After

Set-up

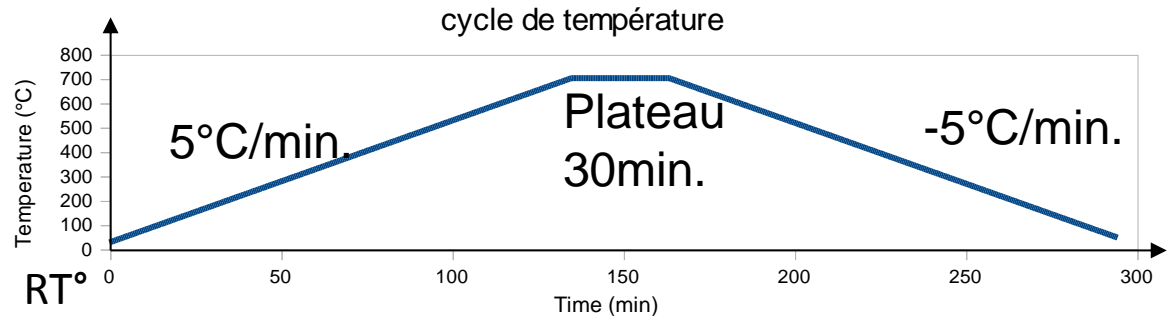
Configuration: XRD-
Synchrotron
 $\lambda=0.68962\text{\AA}$

Debye-Scherrer rings



- Annealing:

25°C à 700°C \ 5°C/min.
700°C \ 30min.
700°C à 25°C \ 5°C/min.

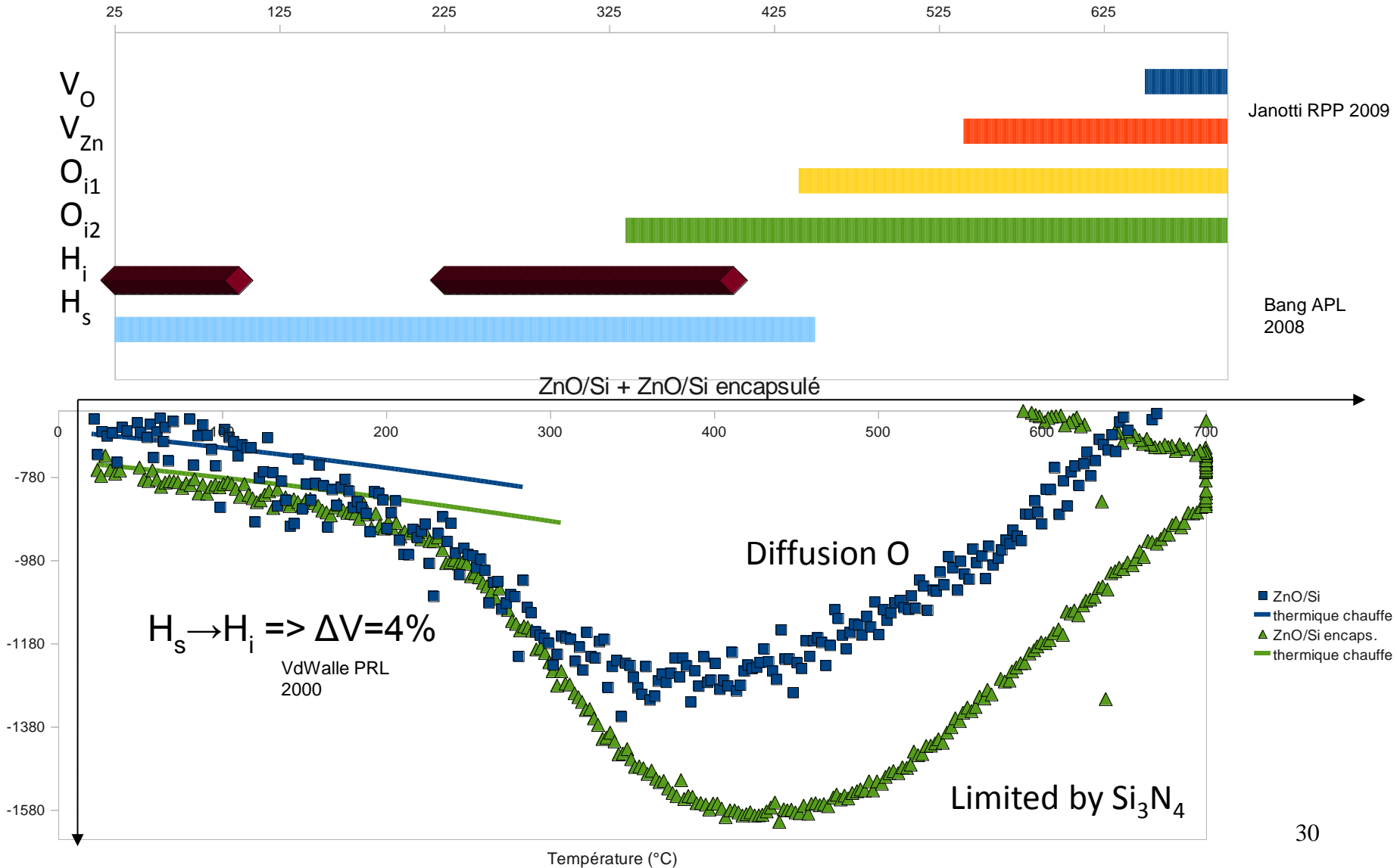


Thermal drift: along z axis

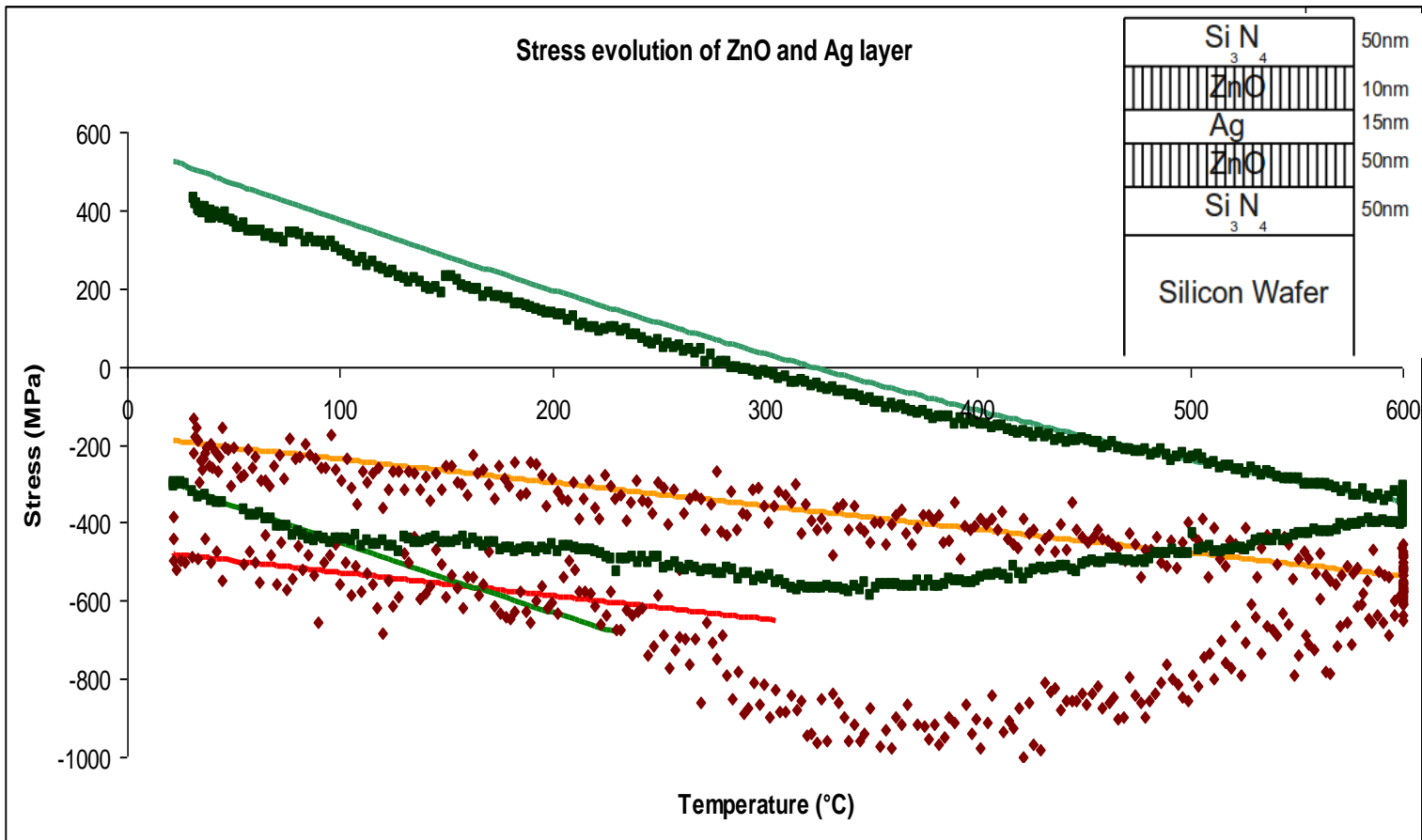
Adjustment along Z axis in order to maintain the geometry: minimal displacement: 50µm.

Mécanisme: Détail

Phenomena expected to play in:



ZnO/Ag stack



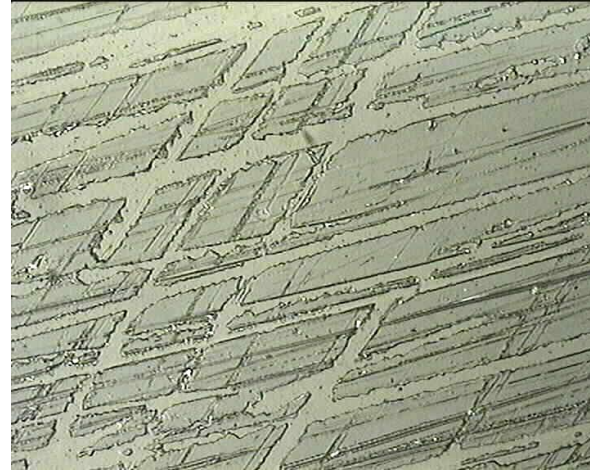
☒ Co deformation : Ag relaxation

☒ Less uncertainty on Ag (15 nm vs 50+10 nm) !

Résistance sous contact de revêtements hybrides sol-gel glass



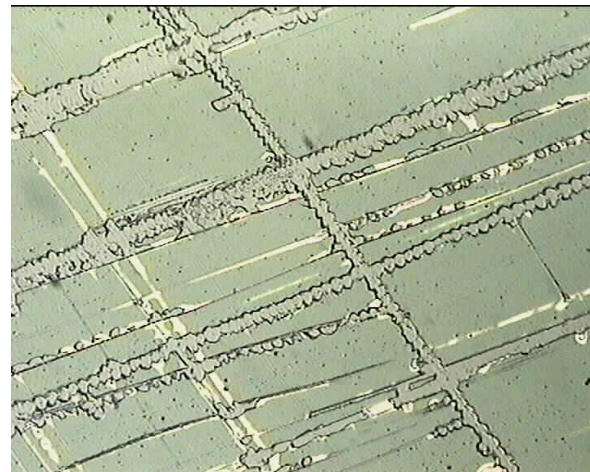
PMMA (before test)



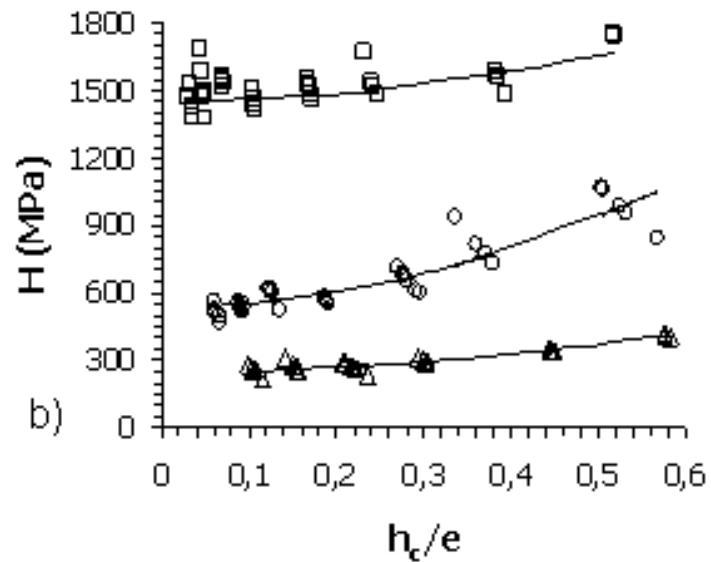
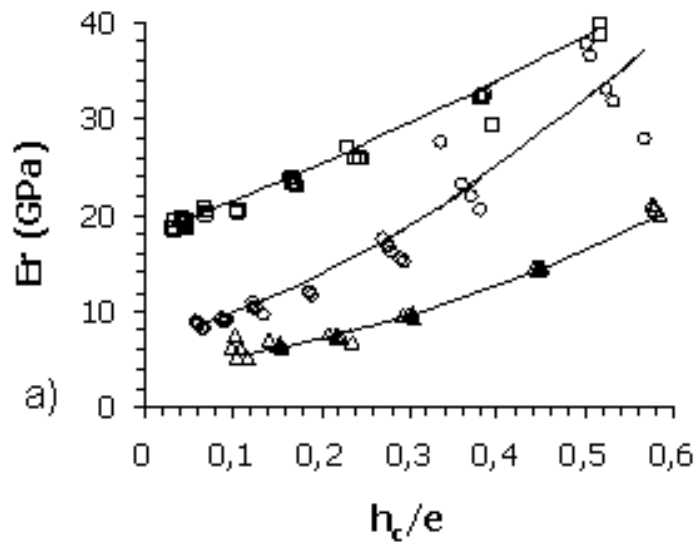
PMMA (After test)



PMMA-silica (before) test)

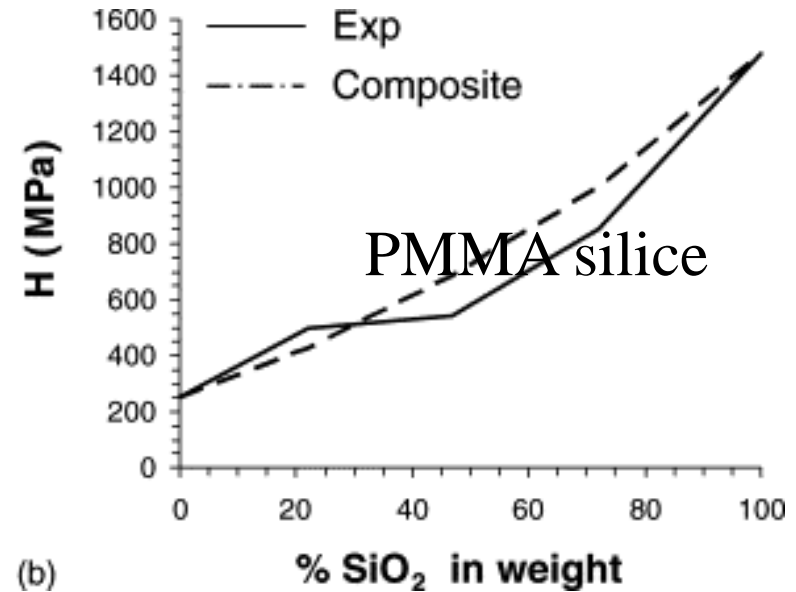
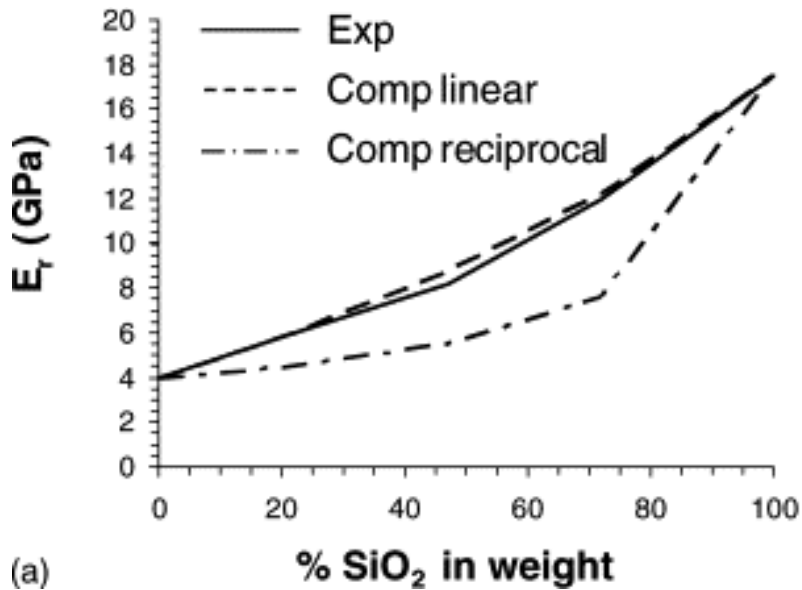


PMMA-silica (before)



Echantillon	Epaisseur (nm)	E (GPa)	H (GPa)	H^3/E^2 (MPa)
f-PMMA	1790	4.1	0.25	1
PMMA75	1680	7.6	0.496	2
PMMA50	2030	6.6	0.538	4
PMMA25	1890	9.5	0.846	7
Sol-gel silica	2190	17.5	1.488	11

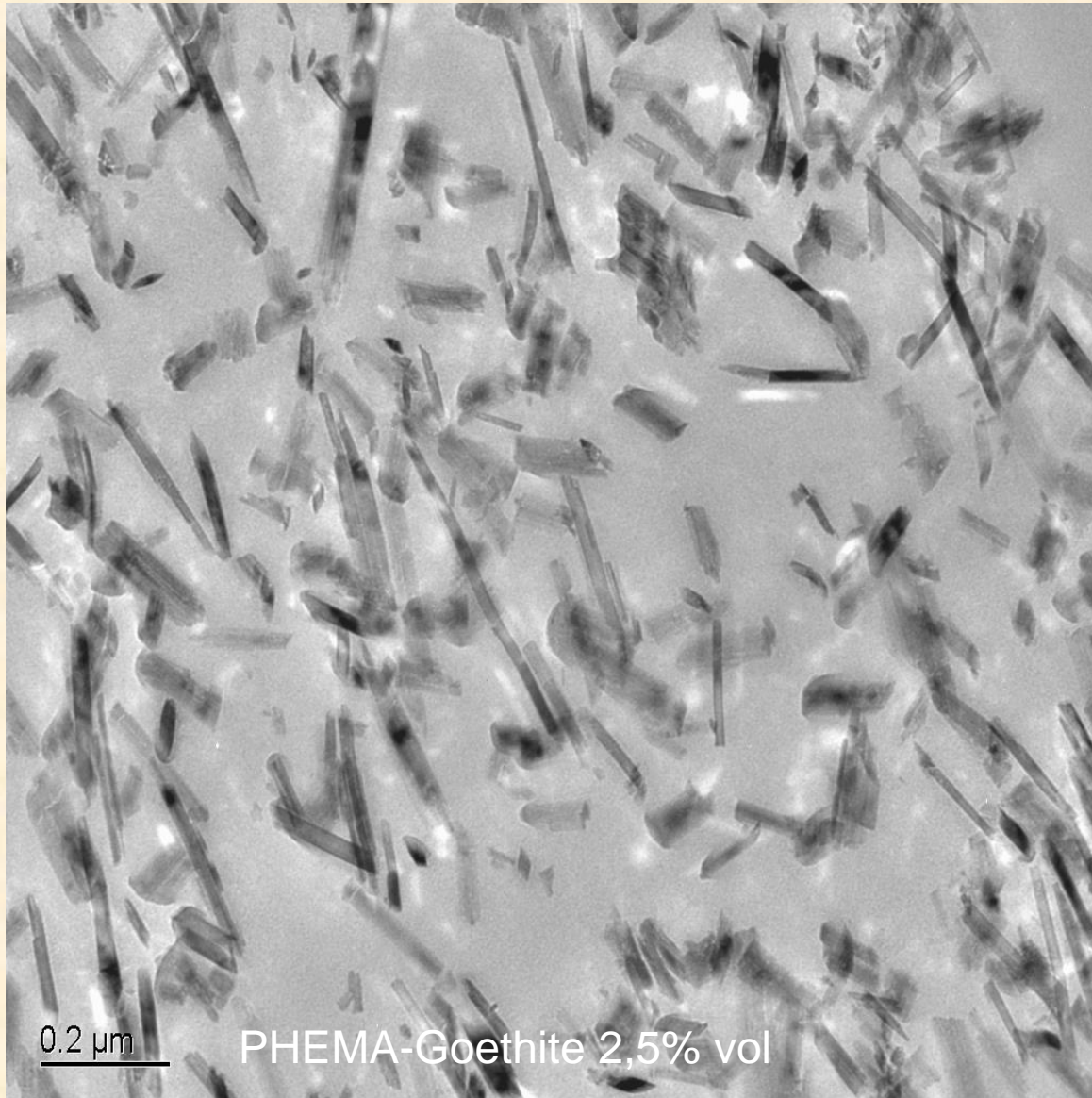
Maîtrise des performances tribologiques par des hybrides I/O hybrids (H^3/E^2)

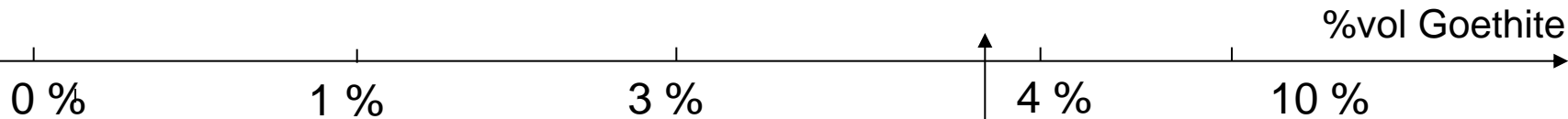
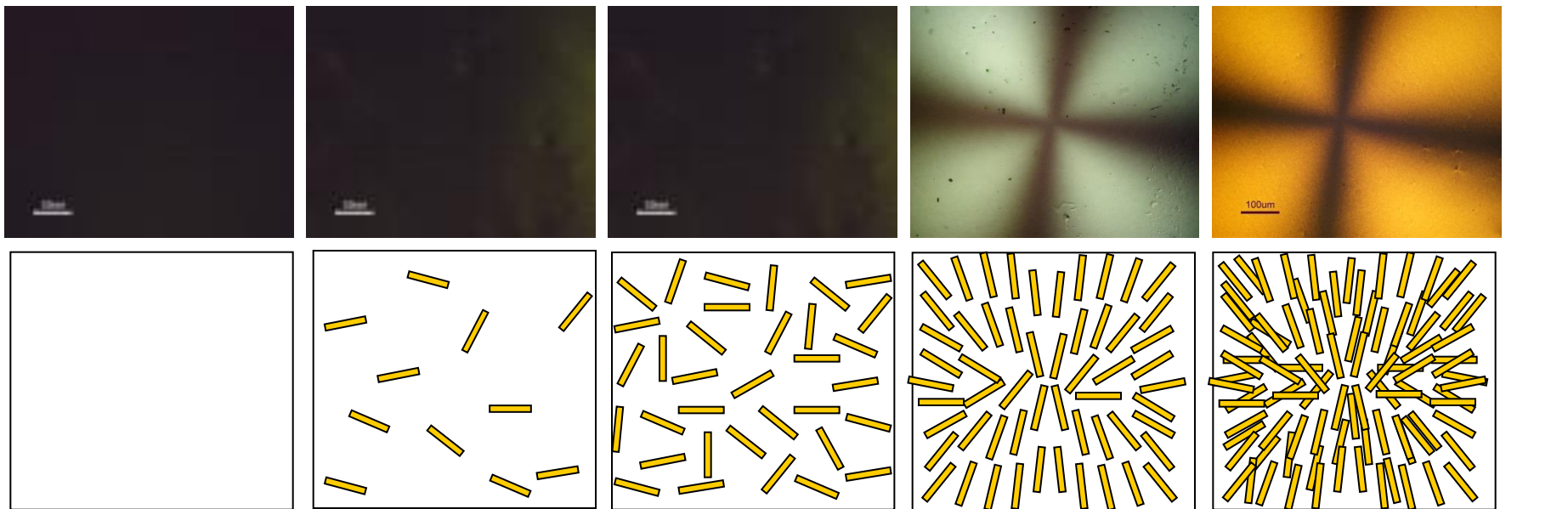


- Rôle des interfaces
- Morphologie
- Classe I/II

Mammeri et al. J. Mater. Chem. 2005, JECS 2006

PHEMA-Goethite FeOOH





Distribution aléatoire

Réorganisation
Interactions max

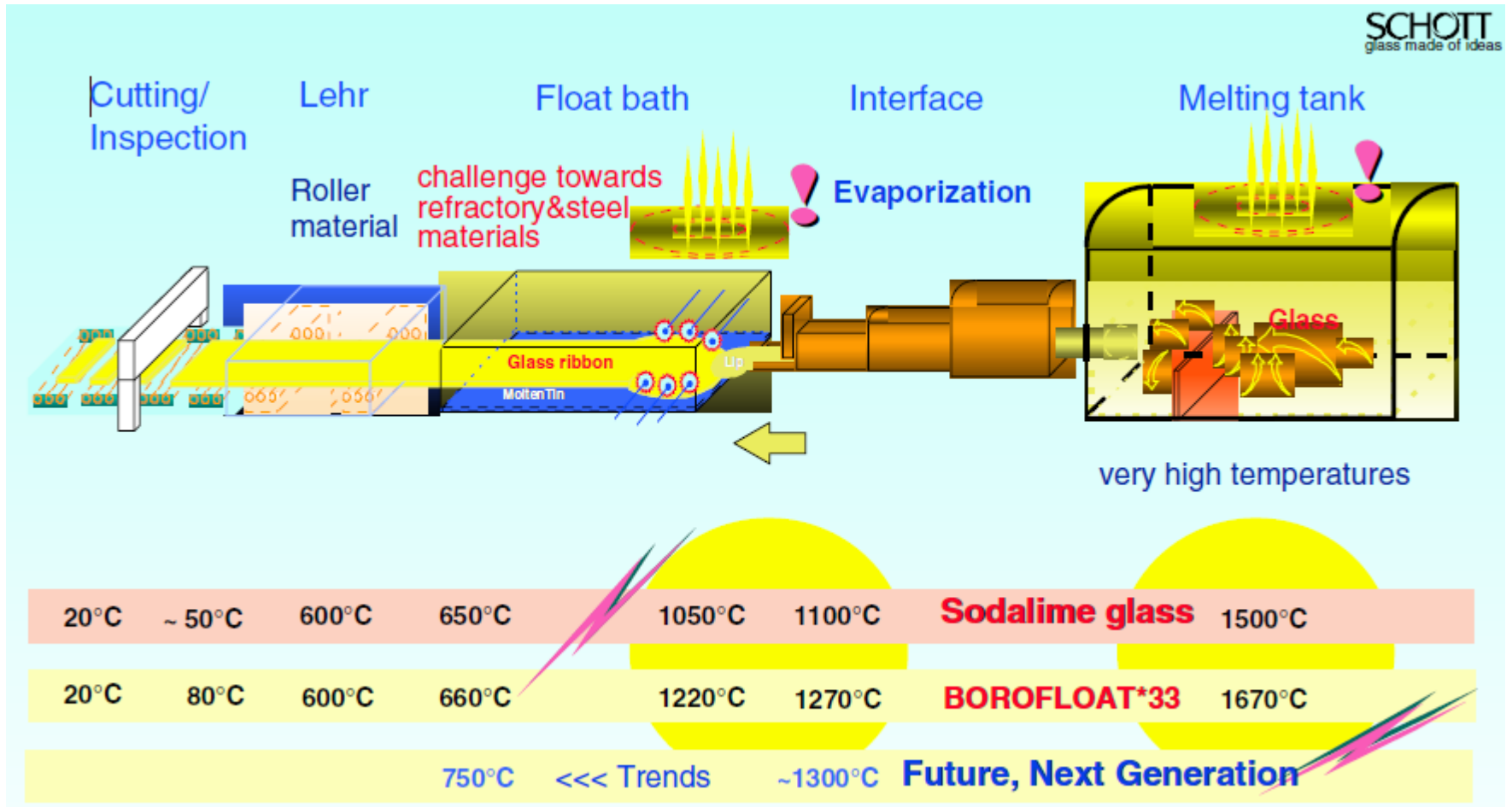
Début
d'agrégation

Phase d'augmentation du module

Phase de plateau

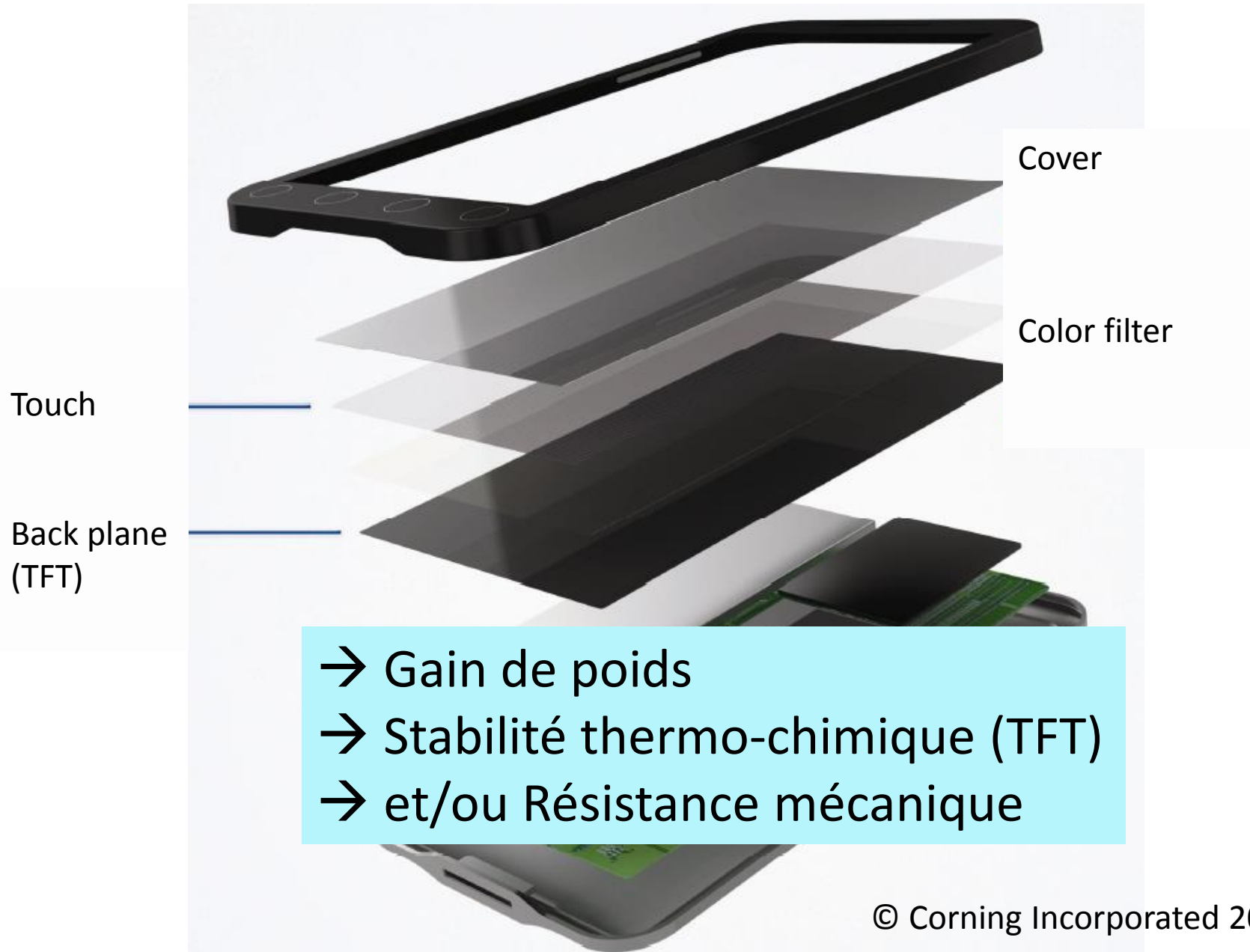
Réorganisation de la Goethite et de sa dispersion
 ⇒ ↗ interactions entre Goethite et PHEMA
 ⇒ ↗ propriétés mécaniques

Nouvelles formulations: Microfloat



500t/j → 50t/j

Demande de verres minces



- Gain de poids
- Stabilité thermo-chimique (TFT)
- et/ou Résistance mécanique

Mince (fusion draw) vs large (microfloat)

Gen Size		Substrate Thickness (mm)						
		≤ 0.1	0.2	0.3	0.4	0.5	0.6	0.7
0.3m	1	Flex display & electronics E-Paper, Continuous Roll-to-Roll Manufacture	Portable LCD panels & touch sensor plates	LCD panels, covers glass, touch sensor plates for notebooks, net-books & mobile internet devices	Notebook monitors & TV Smaller touch & cover glass	TV & desktop monitors Larger size cover glass & sensor plates		
	2							
0.5m	3							
	4							
1m	5							
	6							
1.5m	7							
	8 & 10							

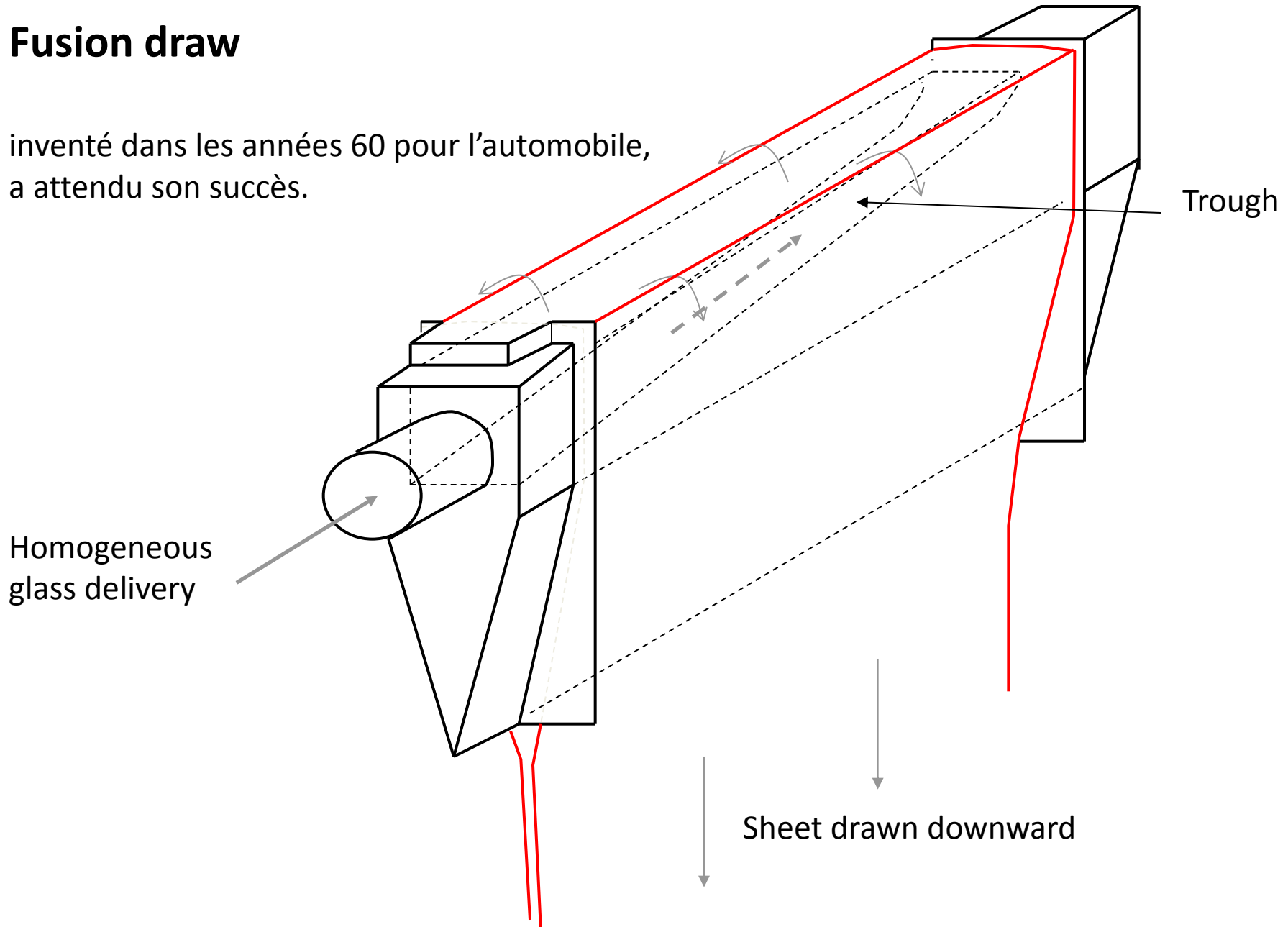
= In Development
 = Commercial availability
 = Currently Supported via chemical thinning of panels

P.L. Bocko, SID 2012 Digest, p989

M.Y.M. Lee, "Glass Part 2: Thin-film Deposition on Glass for Advanced Displays," Gases & Instrumentation (January/February 2013) pp. 25–31.

Fusion draw

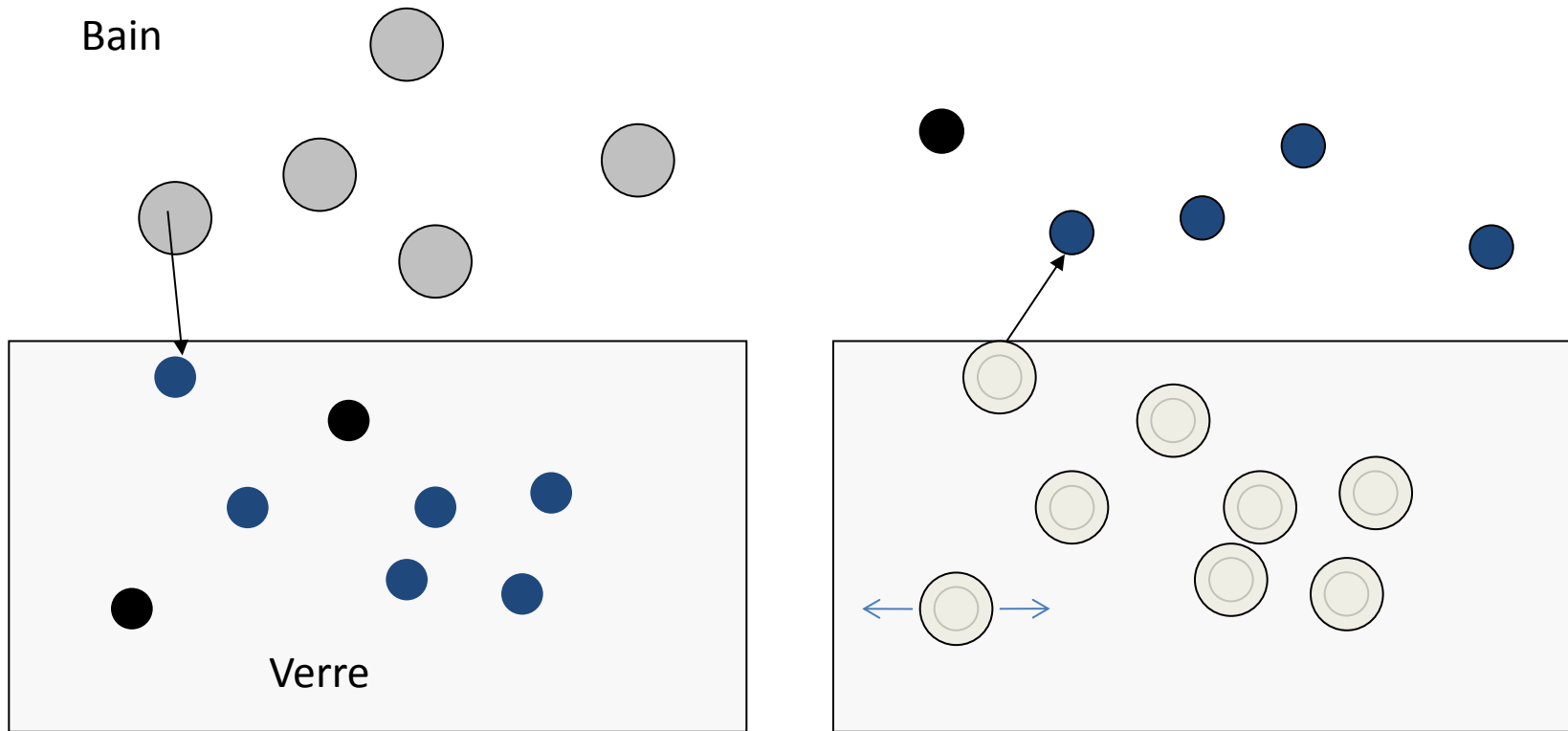
inventé dans les années 60 pour l'automobile,
a attendu son succès.



S. M. Dockerty and G. C. Shay, "Downflow Sheet Drawing Method and Apparatus," U.S. Patent No. 3149949, 1964.

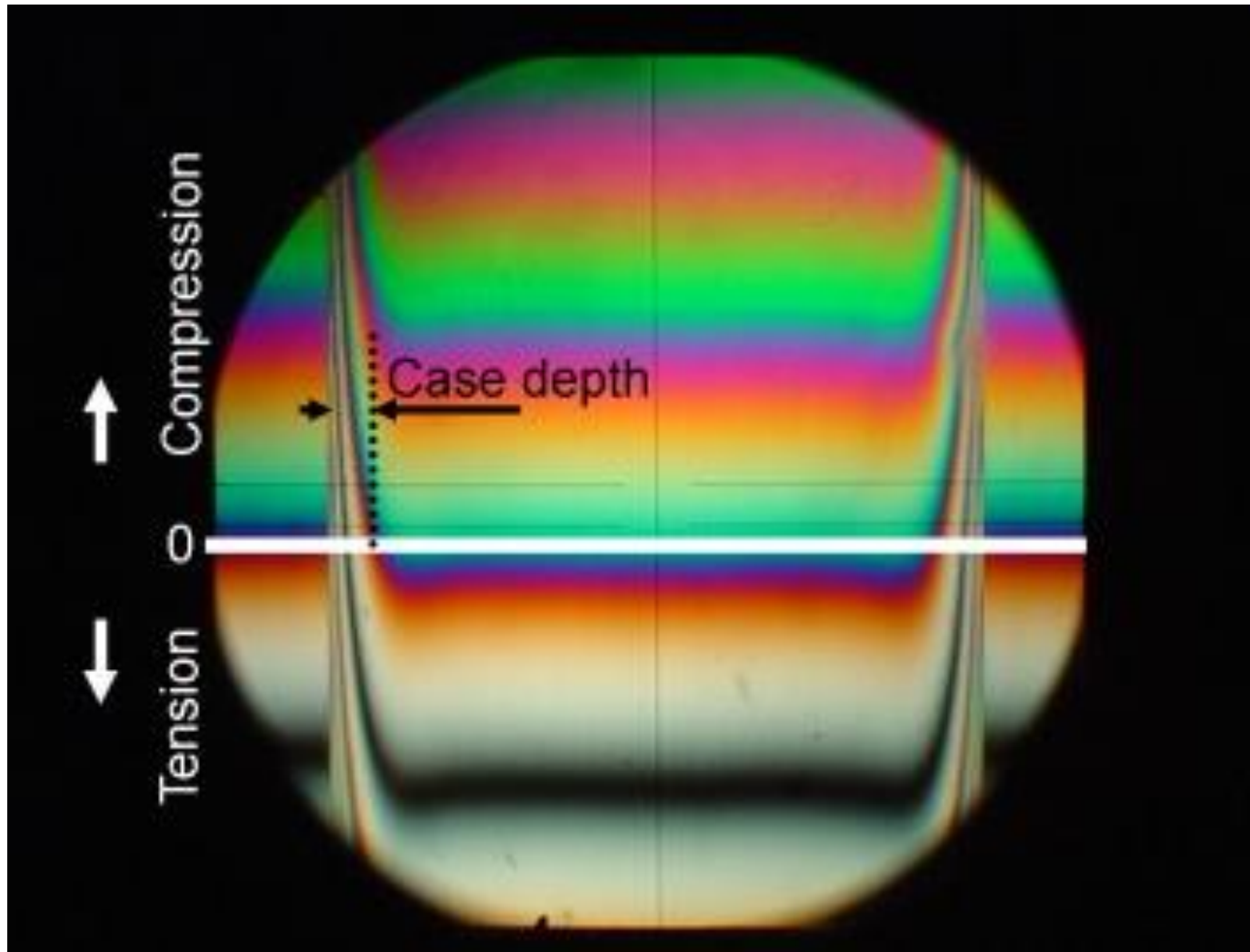
S. M. Dockerty, "Sheet Forming Apparatus," U.S. Patent No. 3338696, 1967.

Redécouverte de la trempe chimique: intérêt pour les verres minces



Echange \bullet Na^+ \rightarrow Contrainte de compression
 \circ K^+

Redécouverte de la trempe chimique: intérêt pour les verres minces



Stress pattern in a chemically tempered glass: side view in a polariscope equipped with a Babinet compensator

		Chemical tempering			
		Corning ^{2,4,14}	Asahi ^{4,17}	Nippon Electric Glass ⁴	Schott ^{7,8,9}
	Thermal tempering ¹³	Gorilla Glass Gorilla Glass 2 Gorilla Glass 3 Concore (Ion-exchanged full sheet IOX-FS) for touch screens and one-glass-solution applications	Dragontrail 0.28-mm substrate for touch screens	CX-01 CX-01P CX-01T	Xensation Cover Xensation Cover 3D Xensation Cover AG
Compressive stress built up in glass after strengthening	Low (95–150 MPa)	High (300–900 MPa)			
		Capable \geq 800 MPa \geq 1000 MPa @40 μ m DOL \geq 950 MPa @50 μ m DOL \geq 950 MPa @ 50 μ m DOL Capable $>$ 550 MPa	Capable $>$ 845 MPa @20 μ m —	750 MPa @45 μ m Capable $>$ 850 MPa Capable $>$ 900 MPa —	Capable $>$ 900 MPa Capable $>$ 700 MPa Capable $>$ 900 MPa
Depth of compressive stress layer (DOL)	Thick (approx. 1/6 of plate thickness)	Thin (10–300 μ m)			
		Capable \geq 40 μ m Capable \geq 50 μ m Capable \geq 50 μ m Up to 40 μ m for 0.7-mm thick glass	Capable $>$ 90 μ m	Capable $>$ 70 μ m Capable $>$ 75 μ m —	Capable $>$ 50 μ m Capable $>$ 120 μ m Capable $>$ 50 μ m
Young's modulus	High (approx. 1/2 of the compressive stress)	Low			
		71.7 GPa 71.5 GPa 69.3 GPa 71.7 GPa	74 GPa —	75 GPa 75 GPa —	74 GPa 83 GPa 74 GPa
Time required	Short (5–10 minutes)	Long (30 minutes to a few hours; up to one week for special applications)			
Tempered glass thickness and format	Limited	Unlimited except for ultra-thin material			
		Thickness range: 0.5–2.0 mm Sheet size: Available in GEN 5 (1250 mm \times 900 mm) Thickness range: 0.5–2.0 mm Thickness range: 0.5–2.0 mm Concore sheet size: up to GEN 6 (up to 1850 mm \times 1500 mm)	Thickness range: 0.5–5.0 mm Sheet size: 1220 \times 740 mm or 48" \times 29" —	Thickness range: 1.5–4.2 mm Sheet size: 300 \times 500 mm Thickness range: 1.0–1.2 mm Sheet size: 400 \times 500 mm Thickness range: 0.5–0.7 mm Sheet size: GEN 5 (1300 \times 1100 mm)	Thickness Range: 0.5–3.0 mm Sheet Size: 1150 \times 950 mm 575 \times 475 mm Thickness Range: 0.5–2.0 mm Sheet Size: 1150 \times 950 mm Thickness Range: 0.5–3.0 mm Sheet Size: 950 \times 680 mm 575 \times 475 mm
Drawing process	Any	Overflow down-draw (fusion) Overflow down-draw (fusion) Overflow down-draw (fusion) Overflow down-draw (fusion)	Float Float	Roll-out (polishing required) Float (light polishing required) Overflow down-draw	Microfloat Microfloat Microfloat
Glass composition	Most glasses	Alkali-aluminosilicate Alkali-aluminosilicate Alkali-aluminosilicate Alkali-aluminosilicate	Aluminosilicate Soda lime (for touch screens only)	Aluminosilicate Aluminosilicate Aluminosilicate	Sodium aluminosilicate Lithium aluminosilicate Sodium aluminosilicate

Conclusion

- Le float: un procédé en rupture
- Aujourd'hui unanimement adopté
- Fonctionnalisation des surfaces en ligne (CVD, PVD en reprise, sol-gel)
- Microfloat dédié (nouvelles compositions, faibles épaisseurs couplées à de la trempe chimique)