Glass Surface Treatments: Commercial Processes Used in Glass Manufacture

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Outline

- Applications > Glass Containers and Float Glass
- Purpose of Surface Treatments

  > weathering and corrosion resistance/ scratch resistance
- Process Technologies
- Testing and Evaluation

  > surface and in-depth analysis

- Other Surface Treatments (often secondary processing)
- **functional coatings > 2/26, 3/03**
- **polishing > 3/5**
- **silanization and sizing of fiberglass > 3/17**
- **ion exchange strengthening** > 4/30
- acid etching, acid polishing, fire polishing

Float Glass > soda-lime-silicate

Application	Purposes
• top and bottom surfaces • annealing lehr rollers	• weathering/corrosion resistance • optical properties • electrical properties • resistance to roller damage
• treatment for stacked float glass sheets	• weathering resistance in storage and transport

Glass Containers > soda-lime-silicate

Application	Purposes
• inside surface of beverage containers • inside surface of pharma vials and ampules	• weathering/corrosion resistance • minimize leaching and contamination of the product • strengthening?
• outside surface of beverage and other containers intended for high-speed filling lines	• scratch resistance • lubricity

Float Glass > soda-lime-silicate

<table>
<tr><th>Application</th><th>Treatments</th></tr>
<tr><td>

- top and bottom surfaces
- annealing lehr rollers

</td><td>

- 'sulfur' ; SO_2 ; sulfur dioxide

>> de-alkalization

> lower surface reflectivity

> lower surface conductivity

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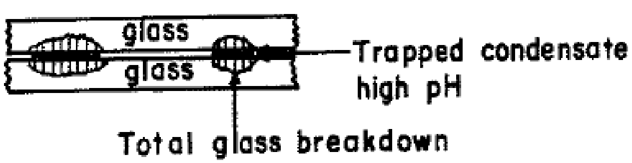
<tr><td>

- interleave treatment for stacked glass sheets



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- acidic liquid or powdered coating
- inert polymer bead spacers

>> acidify and minimize condensed water on and between stacked glass sheets

</td></tr>
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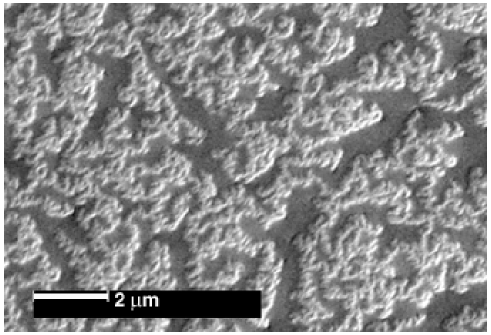
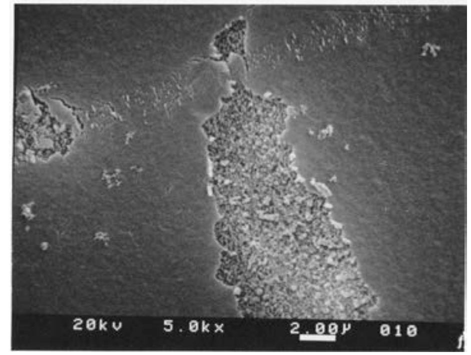
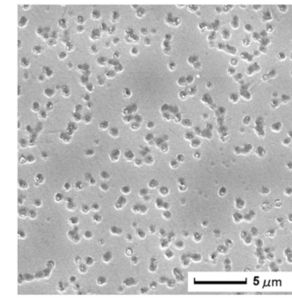
Glass Containers > soda-lime-silicate

Application	Treatments
• inside surface of beverage containers • inside surface of pharma vials and ampules	• 'sulfur' ; SO_2 ; sulfur dioxide • 'fluorine' ; fluorocarbon • ammonium bifluoride/ sulfuric acid **>> de-alkalization**
• outside surface of beverage and other containers intended for high-speed filling lines	• hot-end coating • cold-end coating **>> strength retention**





<u>Effects of Glass Corrosion</u>



- dissolution/etching/weight loss
- leaching/ion-exchange/surface layer formation
- hazing/ dimming/ pitting, staining/ <u>VISUAL EFFECTS</u>
- roughening/microporosity/ <u>REACTIVITY</u>
- increased susceptibility to soiling/difficulty cleaning
- <u>STRENGTH and FATIGUE</u>

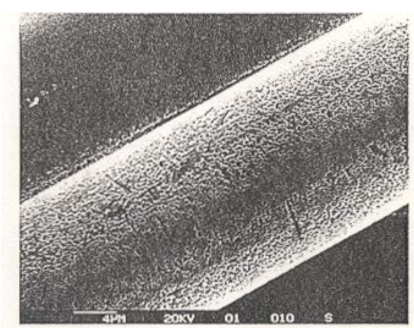
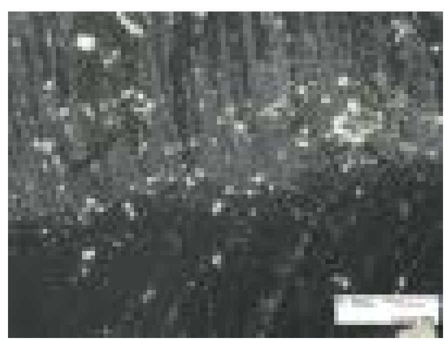
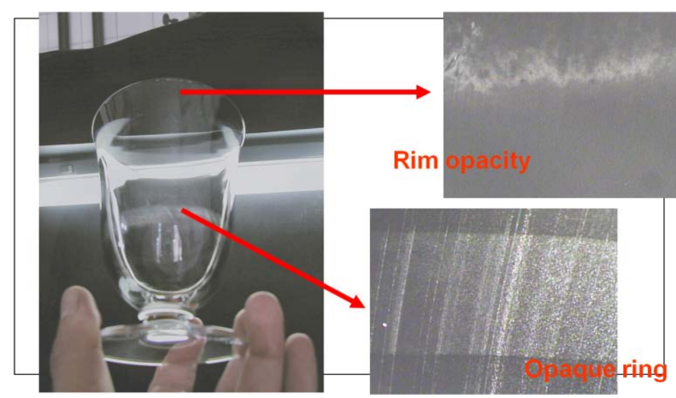


Fig. 3 – *Fiber No. 10 after 28 days corrosion.*





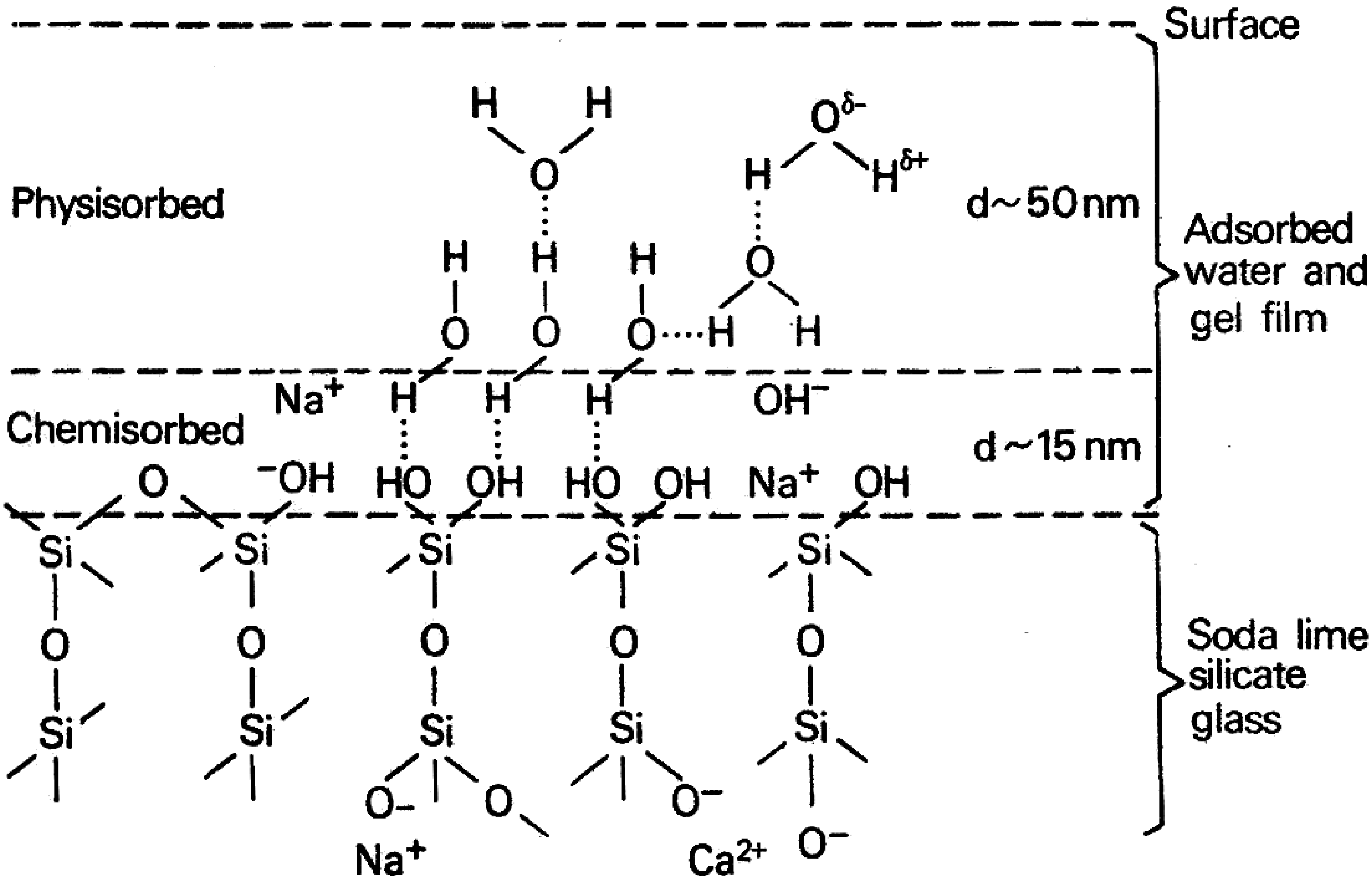
water reaction

$$\equiv Si - O^{-}Na^{+} + H_2O \rightarrow \equiv Si - OH + Na^{+} + OH^{-}$$

initially, neutral pH ∅ later

- in general, a two-stage attach (sometimes three-stage)
- kinetics = f (interdiffusion, solubility, local pH, solution volume.....)

Interaction glass-water vapor



Schematic representation of the formation of a water film on glass by adsorption of water vapour.

Weathering (leaching and corrosion by HUMIDITY)

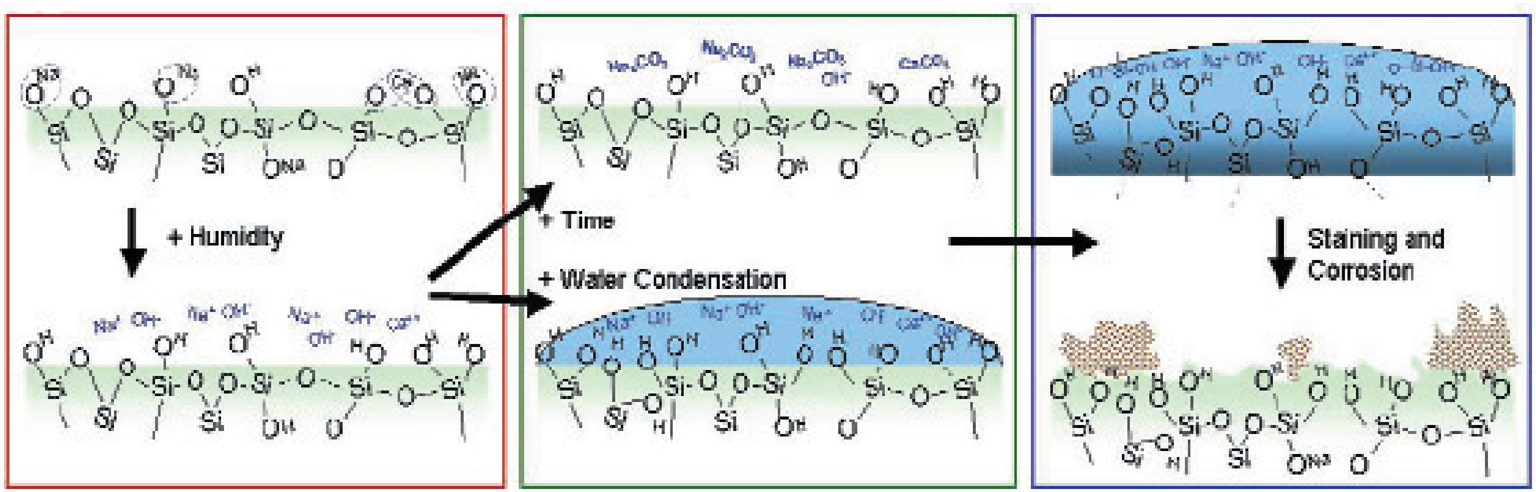
$$Na^{+} + 2H_2O \rightarrow H_3O^{+} + NaOH$$

These hydroxides then react with carbon dioxide from the atmosphere to form carbonates, as in the reaction

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

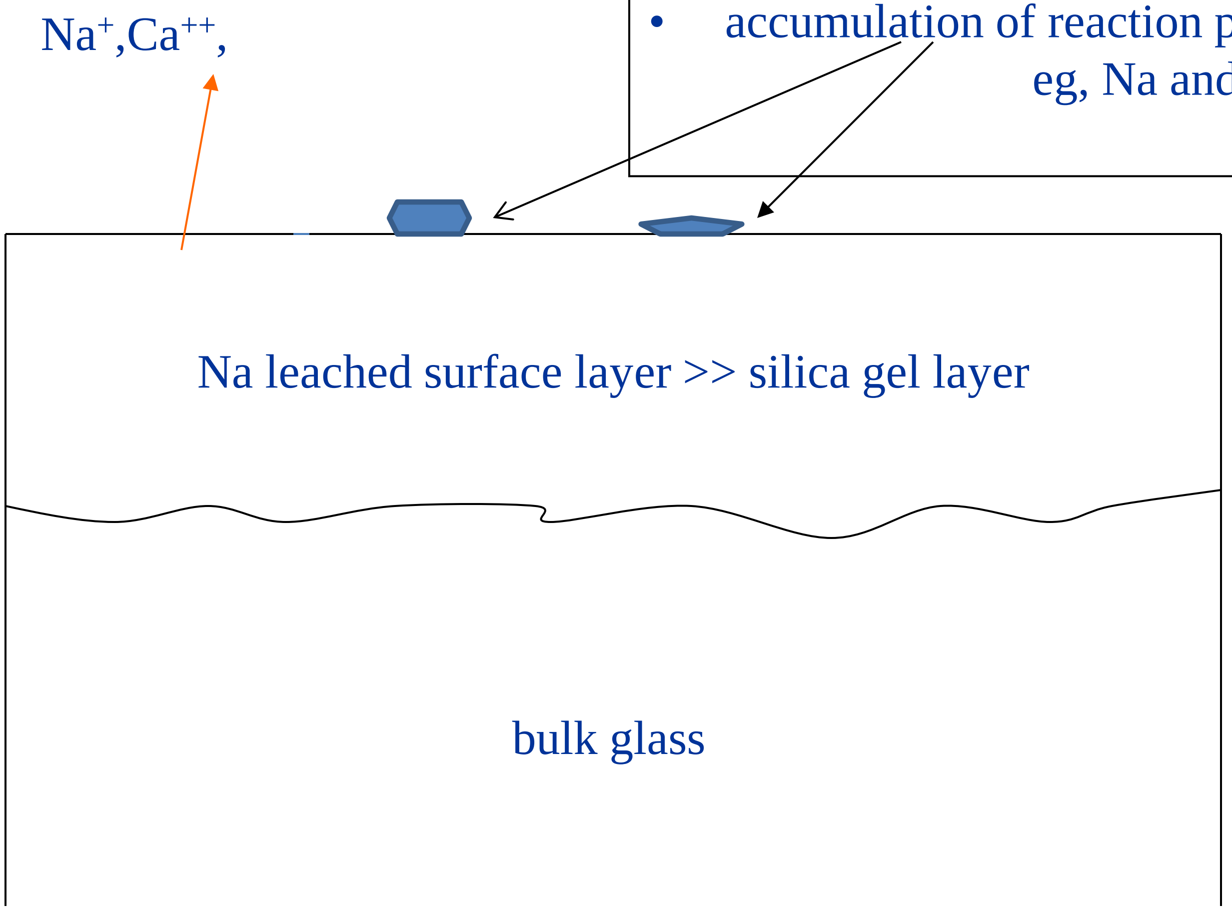
and the reaction

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$



Surface Layer Formation by Humidity

- water adsorption and condensation on the surface
- hydroxylation and leaching ion exchange and water reaction
- accumulation of reaction products on the surface
  eg, Na and Ca hydroxides and carbonates



<< hazy surface

<< delamination of the gel layer

Glass Containers > soda-lime-silicate

Application	**Treatments**
• inside surface of beverage containers • inside surface of pharma vials and ampules	• ‘sulfur’ ; SO_2 ; sulfur dioxide • ‘fluorine’ ; fluorocarbon • ammonium bifluoride/ sulfuric acid **>> de-alkalization**
• outside surface of beverage and other containers intended for high-speed filling lines	• hot-end coating • cold-end coating **>> strength retention**

SO_2 surface treatment

$$Na_2O + SO_3 \longrightarrow Na_2SO_4$$

SO_2 surface treatment

For H_2O present in SO_2 gas:

$$2Na^+ \text{(glass)} + SO_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2H^+ \text{(glass)} + Na_2SO_4$$

For dry SO_2 gas:

$$Na_2O \text{(glass surface)} + SO_2 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \text{(glass surface)}$$

SO_2 surface treatment

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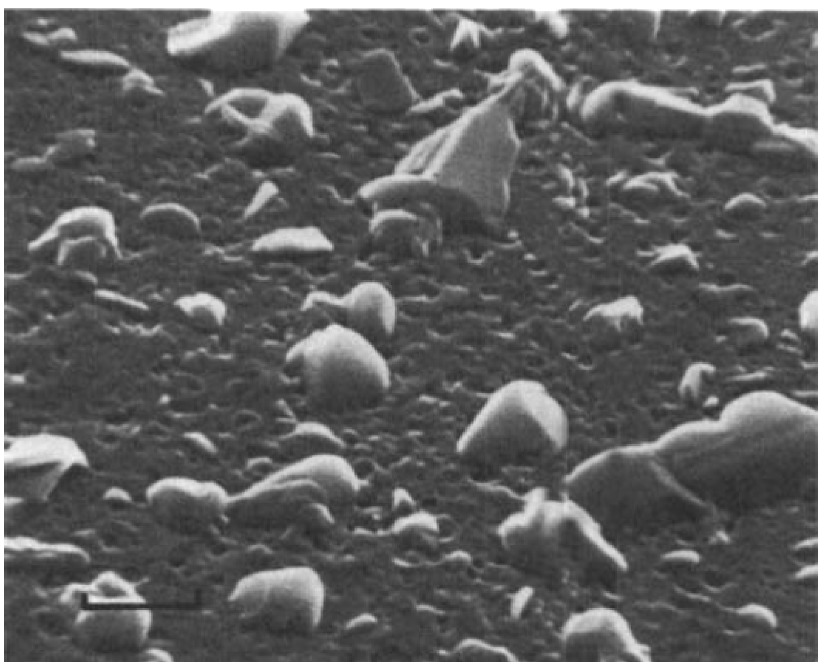
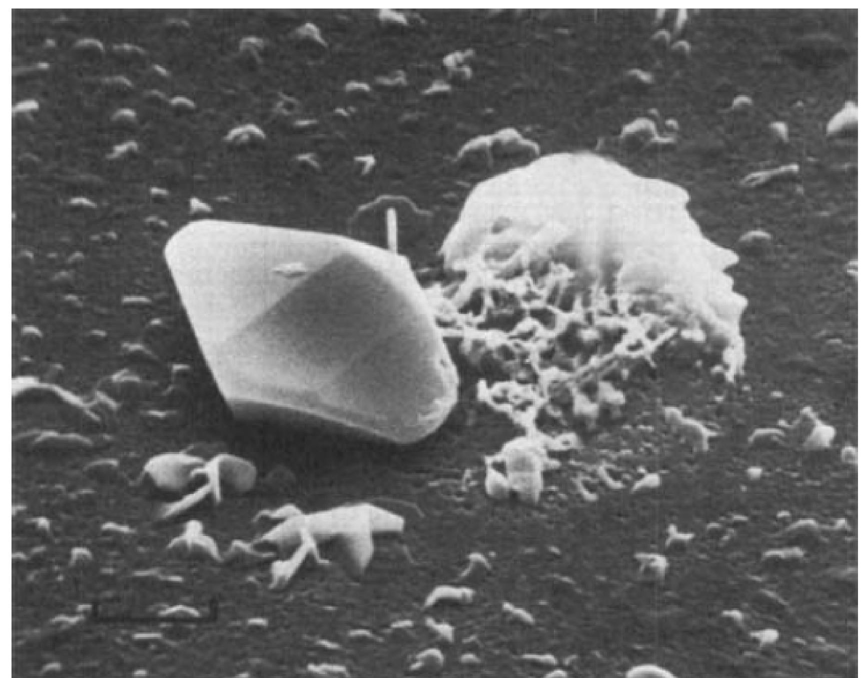


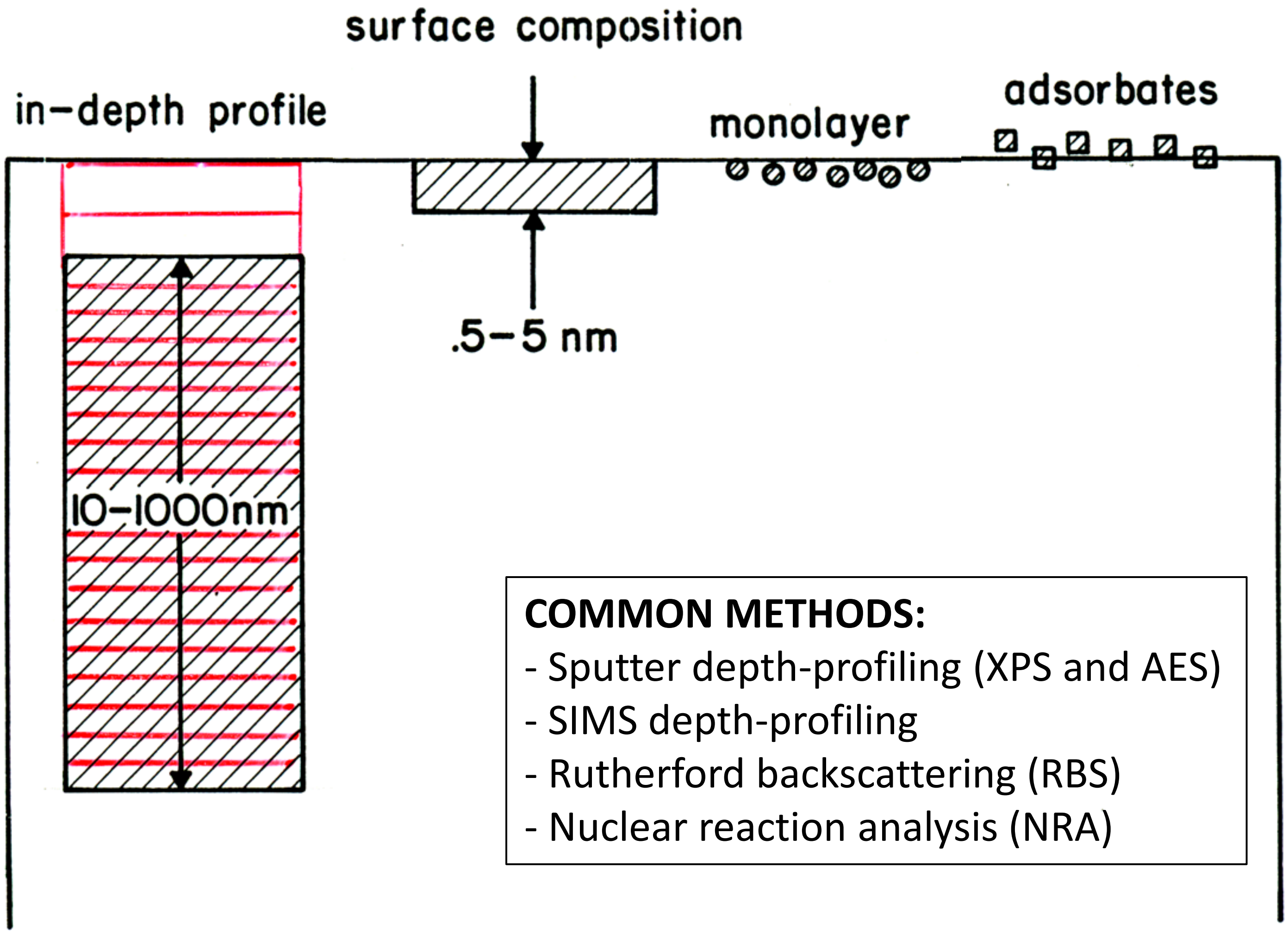


SO_3 is more reactive than SO_2 and increases the reaction kinetics

$$2SO_2 + O_2 \xrightarrow[\text{ashestos}]{\text{Pt on}} 2SO_3$$

$$SO_3 + \text{glass} \begin{array}{l} Na^{1+} \\ Si^{4+} \\ O^{2-} \\ \text{etc.} \end{array} + H_2O \rightarrow Na_2SO_4 + \text{glass} \begin{array}{l} Si^{4+} \\ O^{2-} \\ H^{1+} \\ H_2O \\ \text{etc.} \end{array}$$

SURFACE AND IN-DEPTH ANALYSIS



COMMON METHODS:
- Sputter depth-profiling (XPS and AES)
- SIMS depth-profiling
- Rutherford backscattering (RBS)
- Nuclear reaction analysis (NRA)

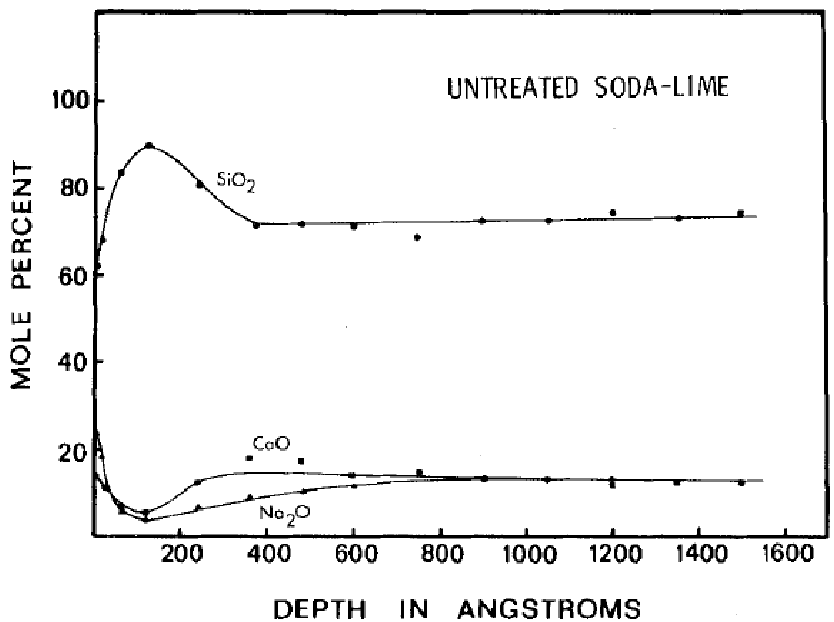


Figure 1

Concentration Depth Profiles of Untreated Soda-Lime Glass.

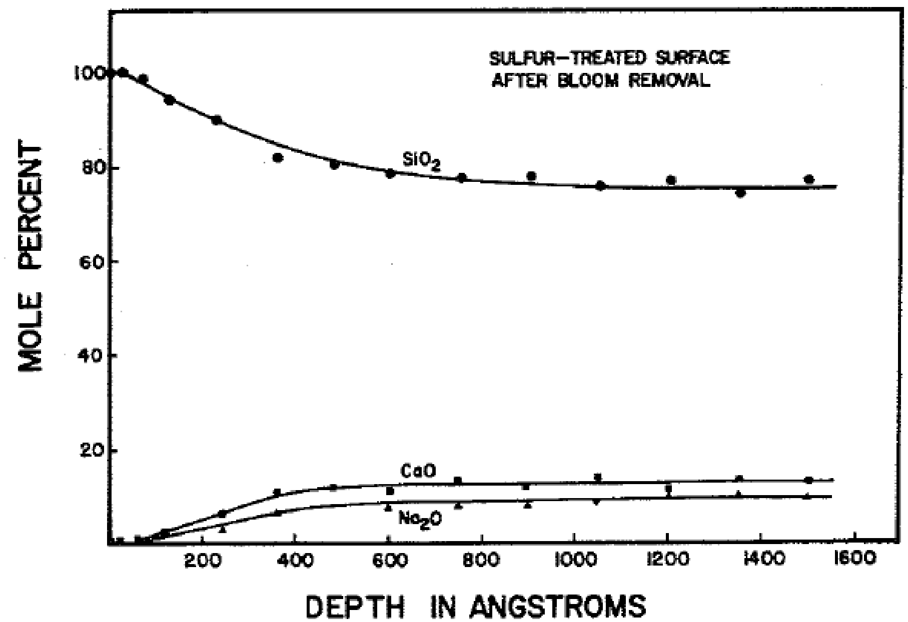


***Figure 73.** Depth compositional profile of sulfur-treated surface after rinsing in water*

Fluorocarbon Surface Treatment

$$2 \equiv Si-O^{-}Na^{+} + Freon(eg, CH_3CHF_2) \rightarrow 2 \equiv Si-F + Na_2O + xCO_2 + H_2O$$

Analysis does not support

(US Patent 3,314,772)

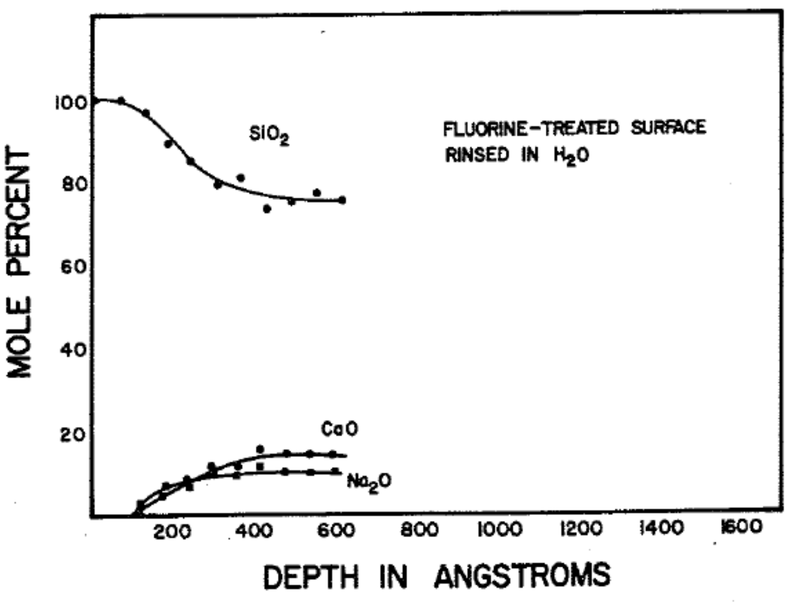


Figure 76. Depth compositional profile for a fluorine-treated surface after rinsing in water

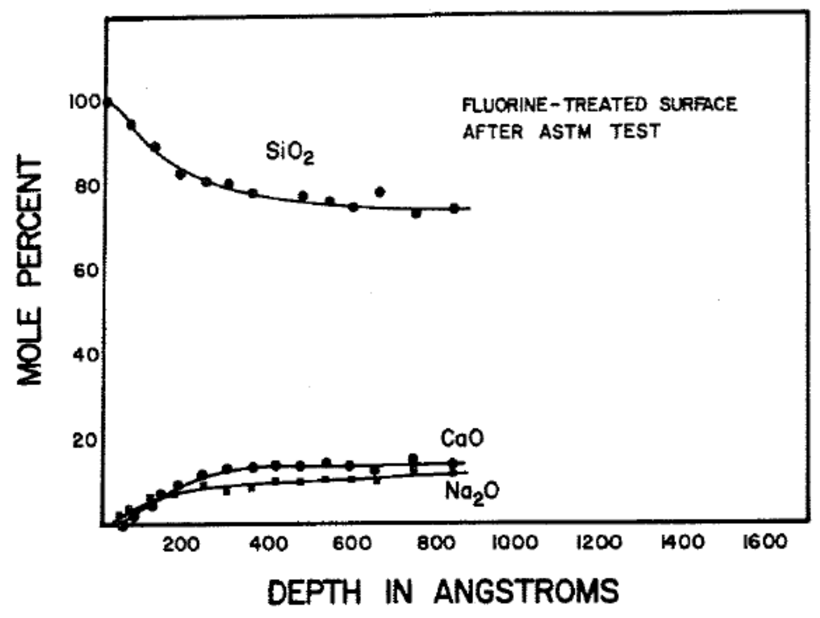


Figure 77. Depth compositional profile for a fluorine-treated surface after the ASTM durability test

Fluorocarbon Surface Treatment

$$2 \equiv Si - O^{-}Na^{+} + Freon(eg, CH_3CHF_2) \rightarrow \equiv Si - O - Si \equiv + 2NaF(volatile) + xCO_2 + yH_2O$$

alternate mechanism

JAmCerSoc, C124, 1983

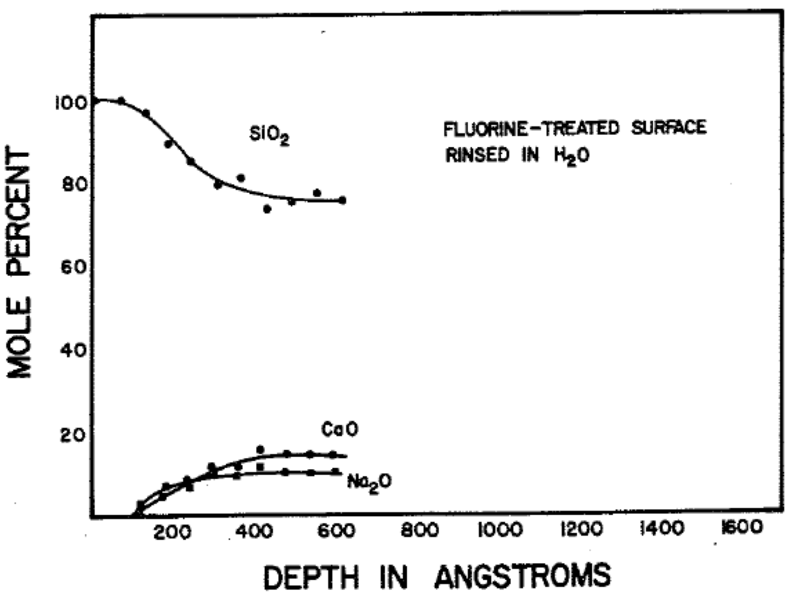


Figure 76. Depth compositional profile for a fluorine-treated surface after rinsing in water

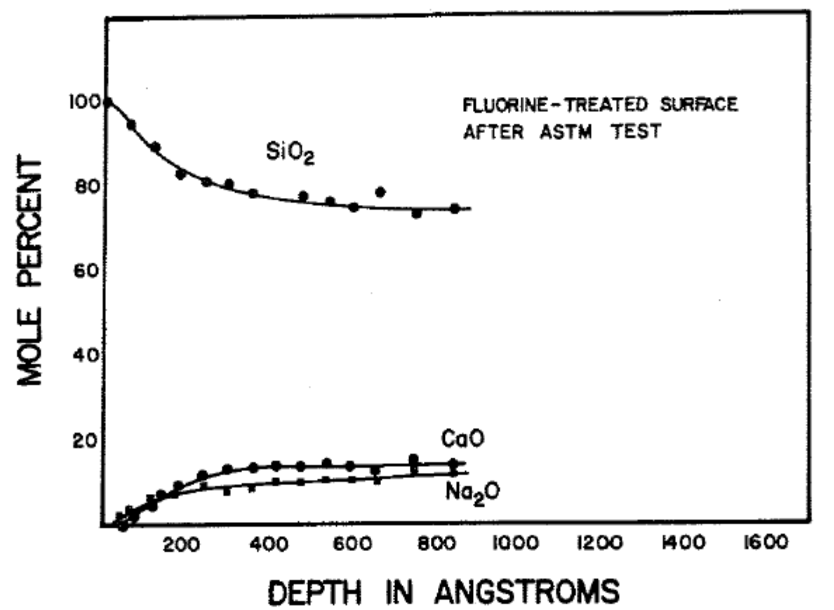
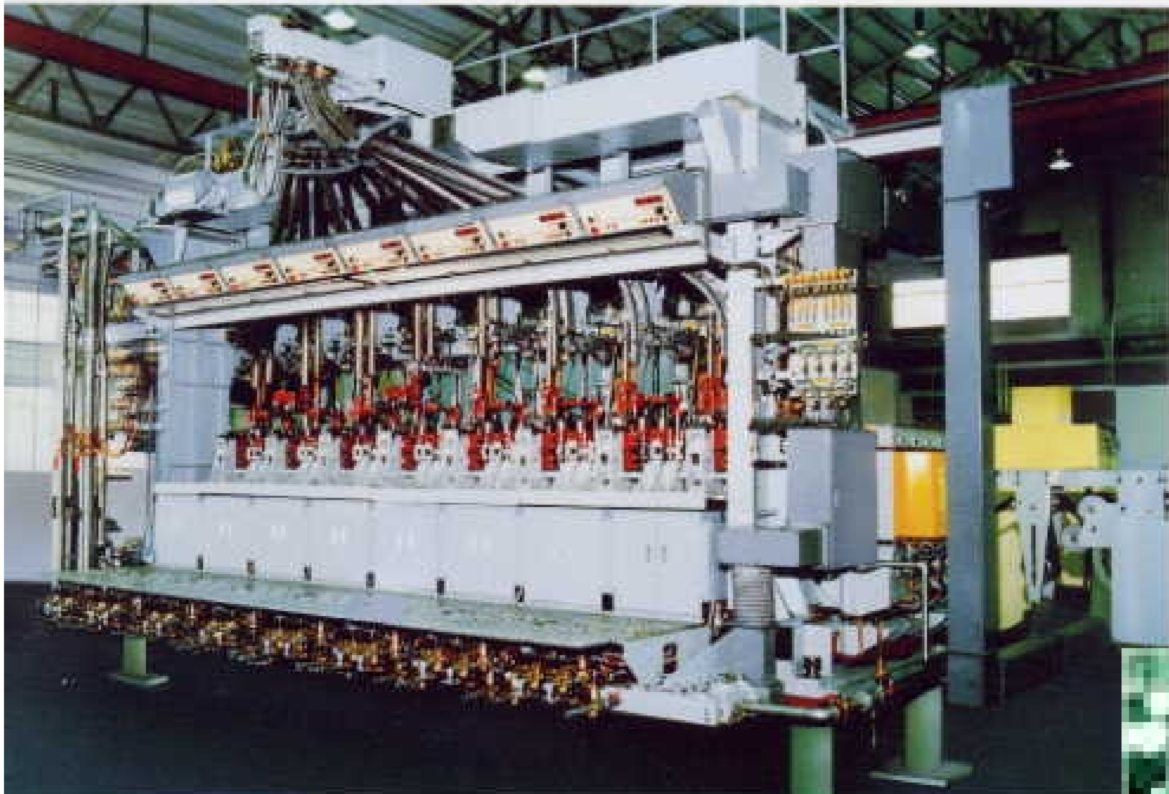
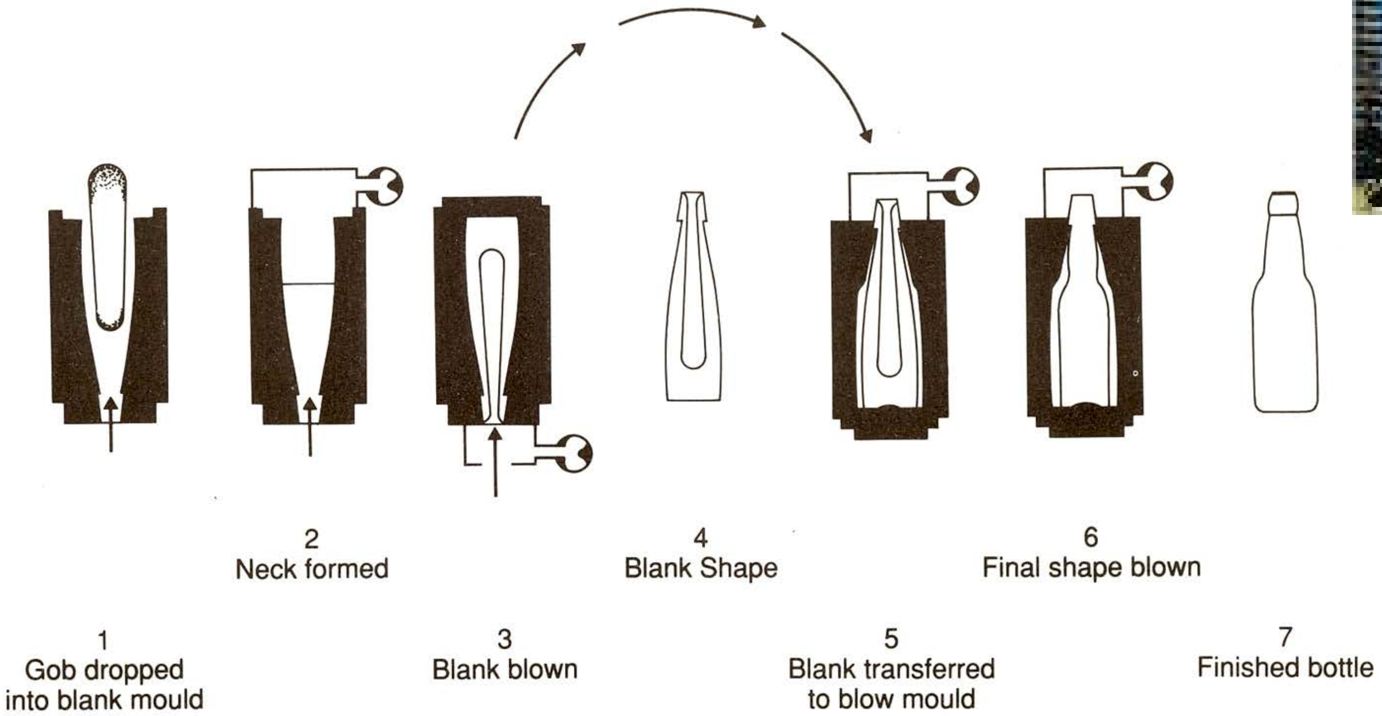


Figure 77. Depth compositional profile for a fluorine-treated surface after the ASTM durability test





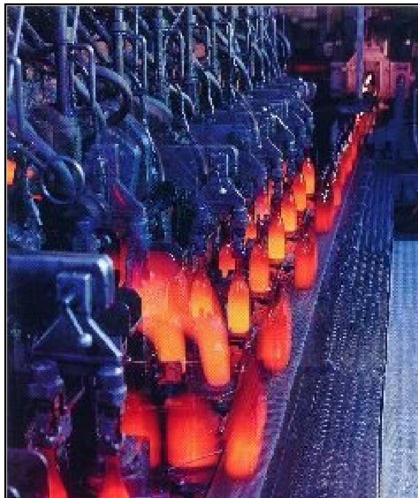


Figure 60. The blow-blow process (Moody 1977)

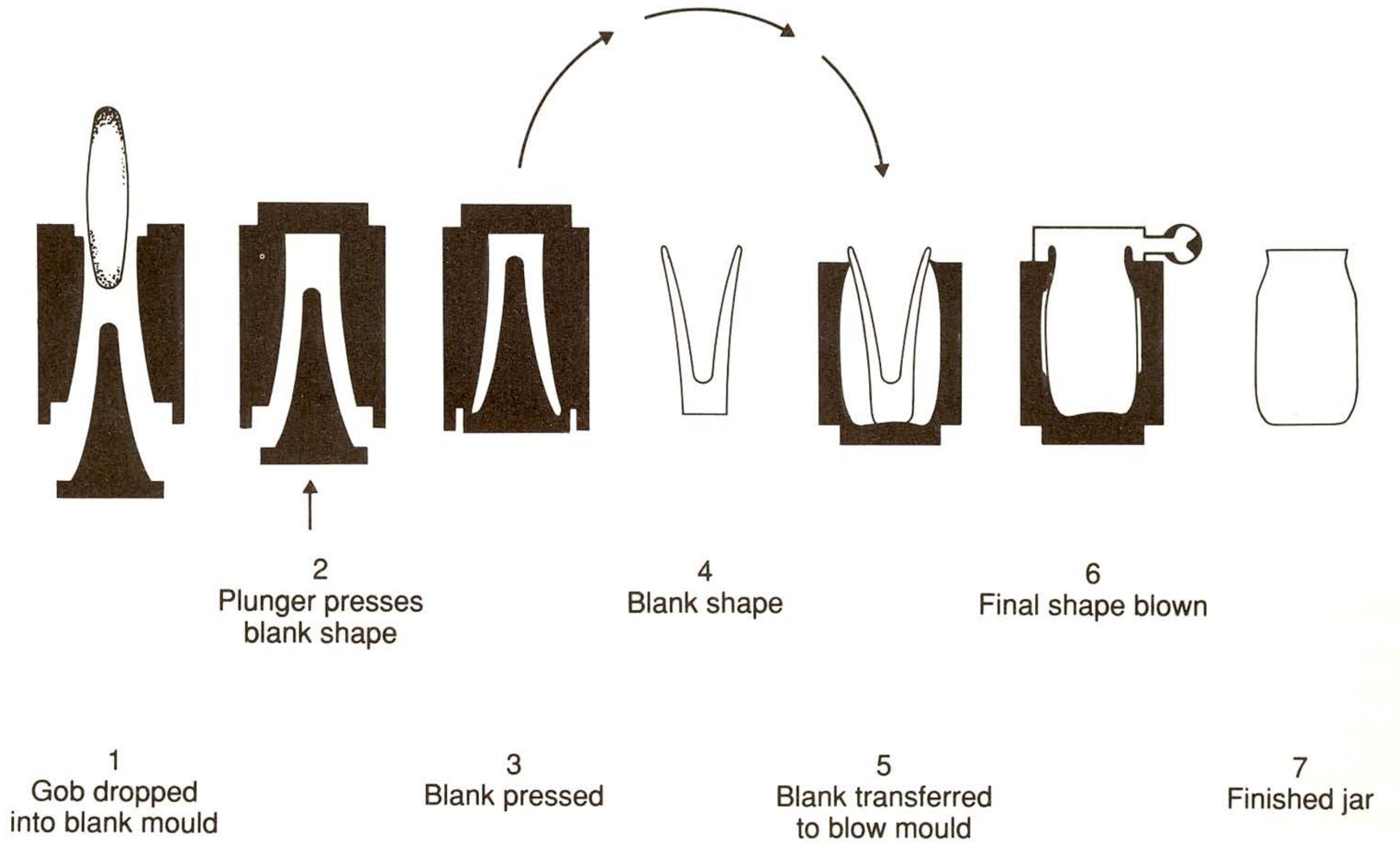


Figure 59. The press-blow process (Moody 1977).

ASTM C225-73 Chemical Durability Test

1 HOUR at 121.5C
-water (or relevant test solutions*)

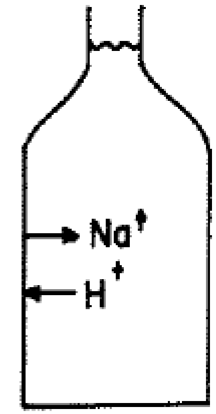


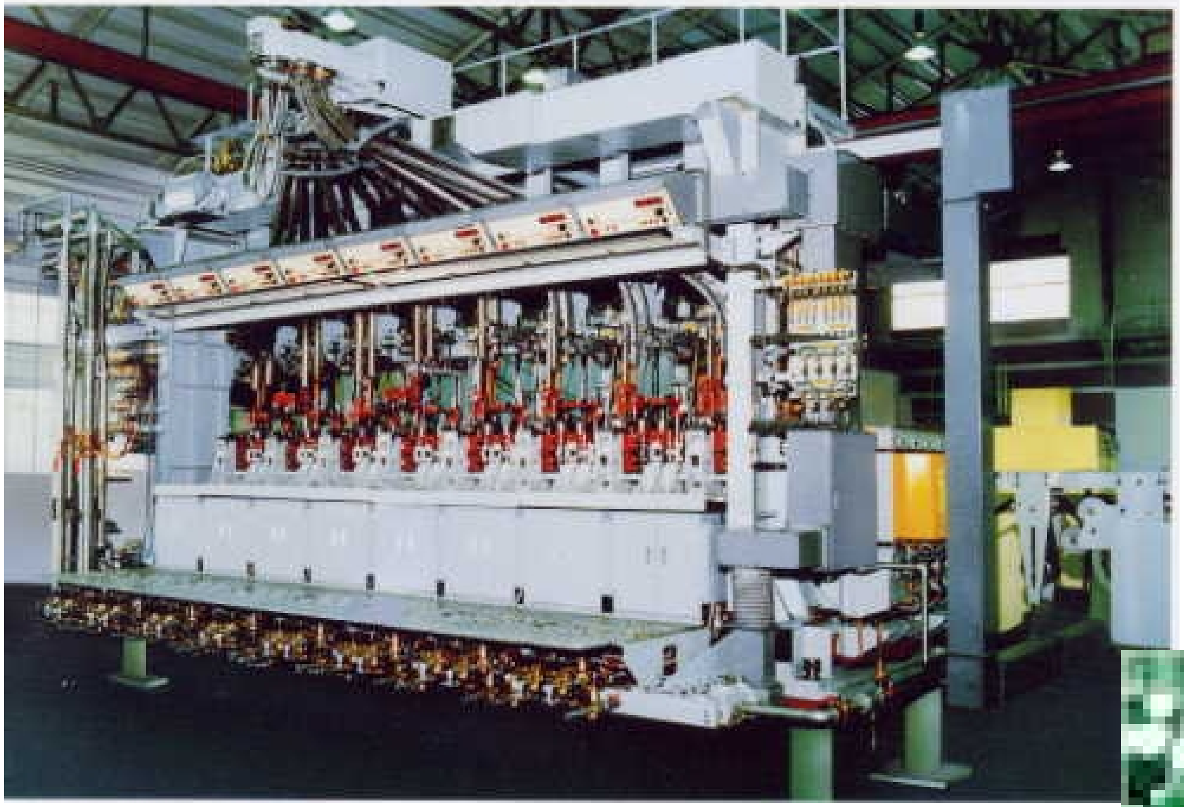
Table 1
Water extraction (C225-73, method B-W) titration results. The alkaline material having an influence in the titration includes CaO, MgO, Na_2O and K_2O.

Bottle	ml 0.02 N H_2SO_4/100 ml	Equivalent ppm Na_2O
UNTREATED	1.32, 1.34, 1.42	8.2, 8.3, 8.8
FLUORINE	0.14, 0.28, 0.18	0.9, 1.7, 1.1
SULFUR	0.02, 0.02, 0.02	0.1, 0.1, 0.1

* for example, protein based drugs which are stabilized in high pH solutions

Glass Containers > soda-lime-silicate

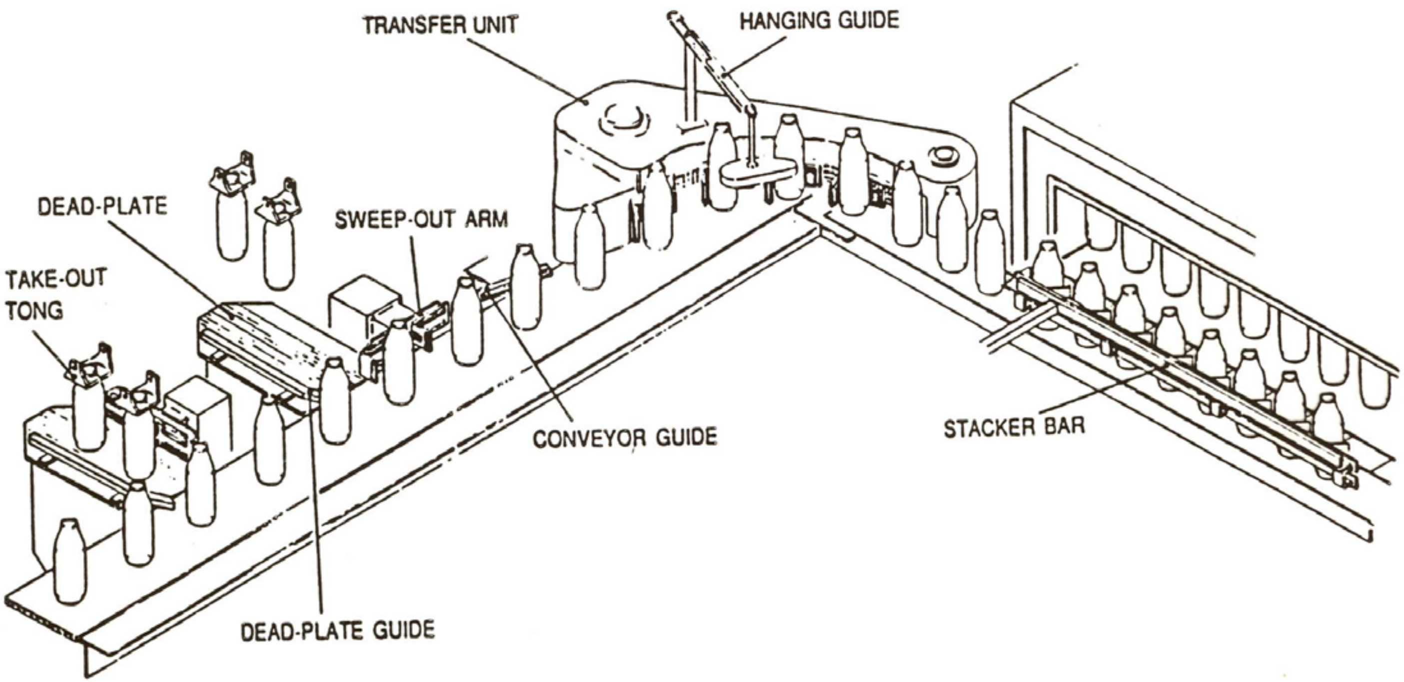
Application	**Treatments**
• inside surface of beverage containers • inside surface of pharma vials and ampules	• 'sulfur' ; SO_2 ; sulfur dioxide • 'fluorine' ; fluorocarbon • ammonium bifluoride/ sulfuric acid **>> de-alkalization**
• outside surface of beverage and other containers intended for high-speed filling lines	• hot-end coating • cold-end coating **>> strength retention**




Hot End and Cold End Coatings to Provide Damage Resistance

- Tin oxide at the hot end
- Lubricious polyethylene at the cold end

*** the surface of clean, dry, freshly-made glass exhibits high friction***



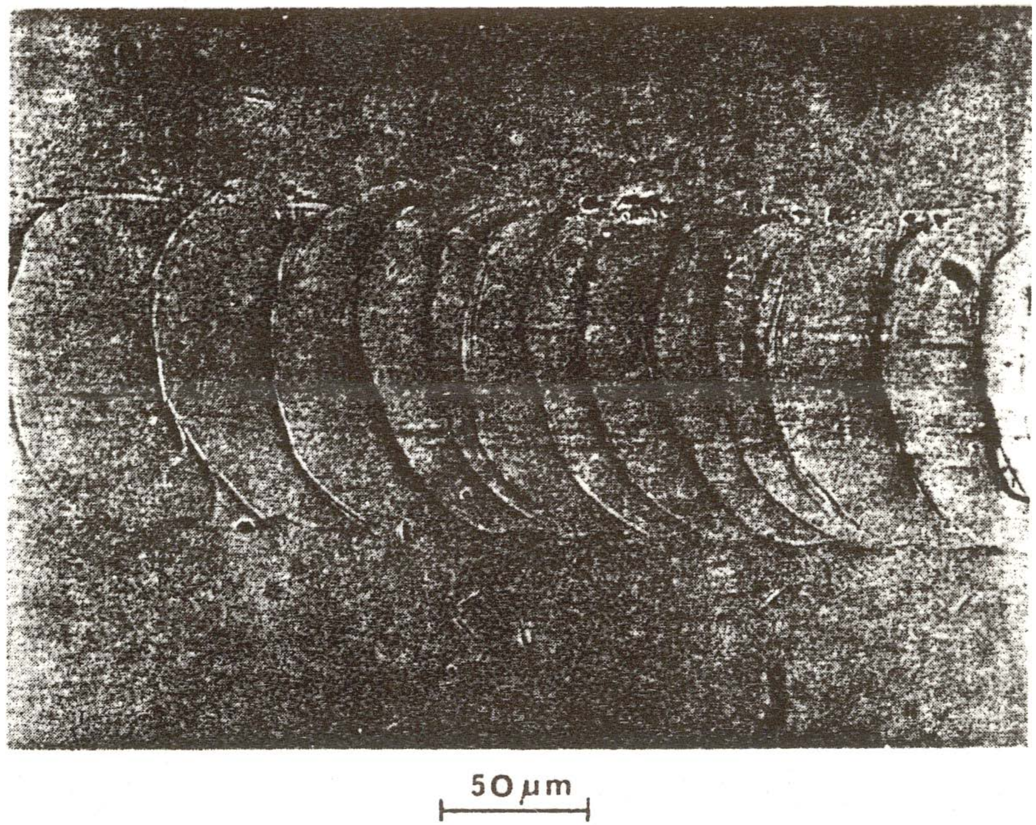


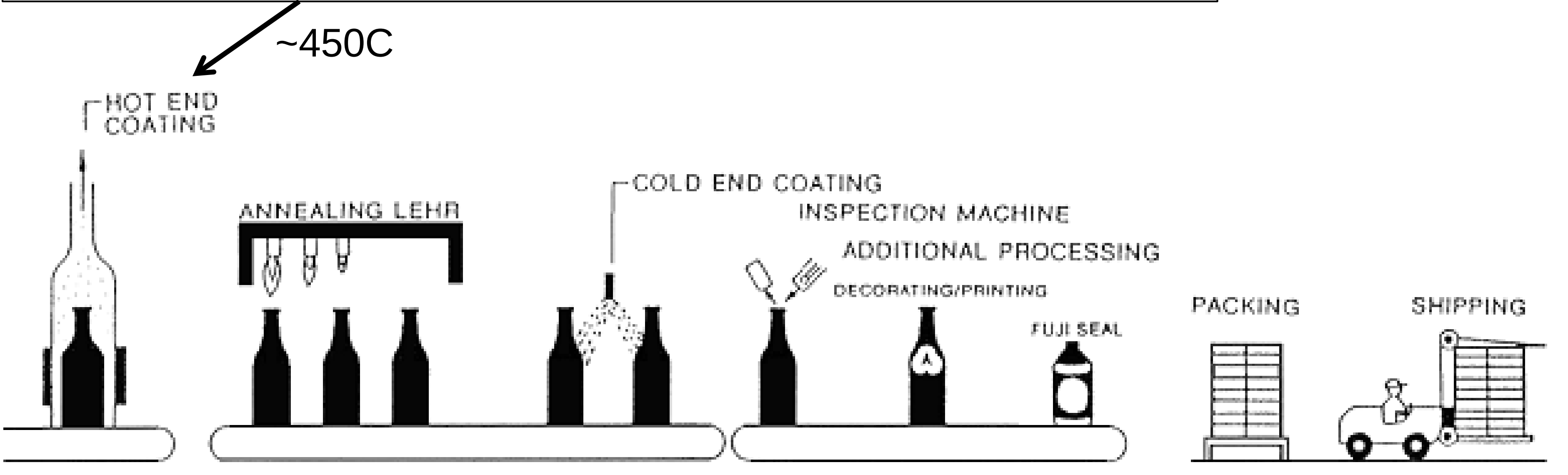
Figure 5.15. Horse-shoe shaped cracks in the surface of glass produced by a small ball, sliding from left to right.

Figure 6.7. (a) Surface damage produced by light abrasion of one glass rod on another

Coatings for Glass Containers

THREE COMMON PRECURSORS for the SnO_2 Hot-End Coating

- anhydrous stannic chloride >> SnO_2 + x HCl
- dimethyl tin dichloride >> SnO_2 + x HCl + y CO_2 + z H_2O
- butyl tin chloride >> SnO_2 + x HCl + y CO_2 + z H_2O

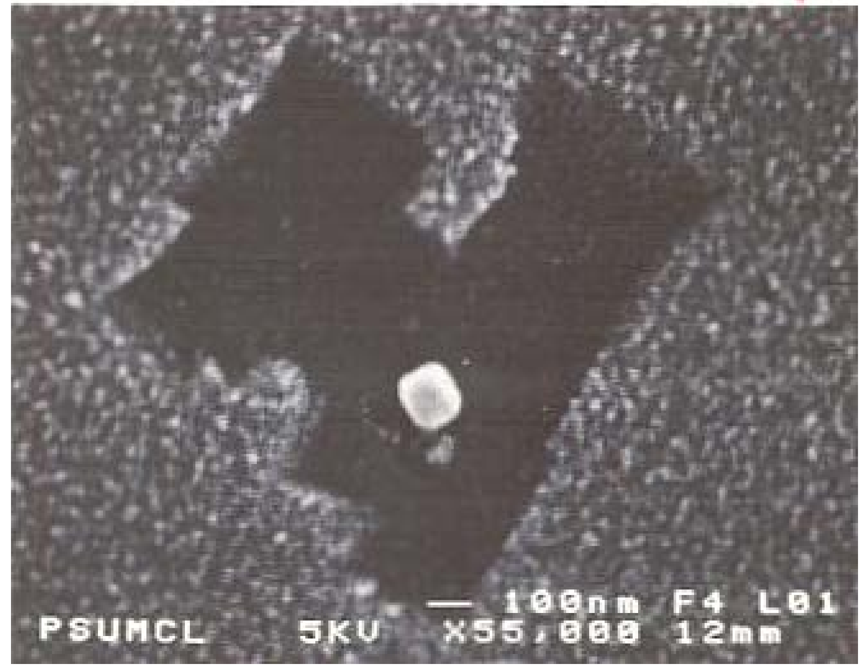


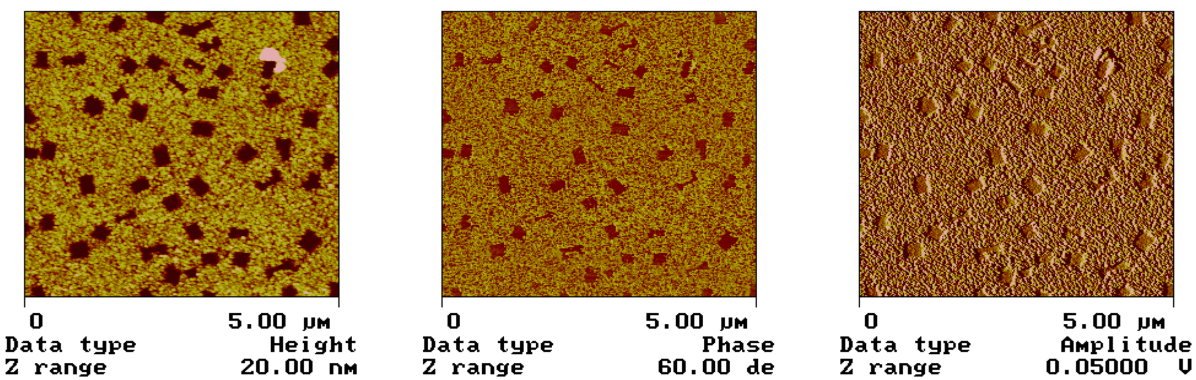
Properties

Property	Soda Lime Silica Glass	Tin Oxide
Hardness (GPa)	6.3	10–14 (Ref. [24])
Young's Modulus (GPa)	72	263 (Ref. [25])†
Poisson's ratio	0.23	0.294 (Ref. [25])
Thermal Expansion Coefficient ($/^0C$)	8.3	4.13* (Ref. [27])
Density (Mg/m^3)	2.53	6.990

PENNSTATE 1855


1µm
PSUMCL 20KV X15,000 13mm

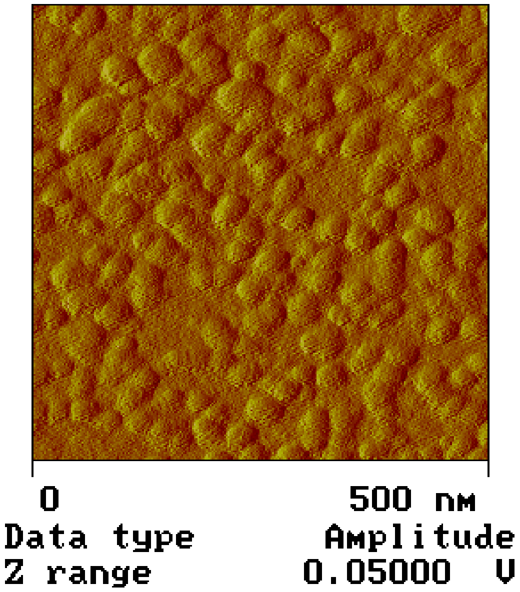

100nm F4 L01
PSUMCL 5KV X55,000 12mm


0 5.00 µm
Data type Height
Z range 20.00 nm
0 5.00 µm
Data type Phase
Z range 60.00 de
0 5.00 µm
Data type Amplitude
Z range 0.05000 V

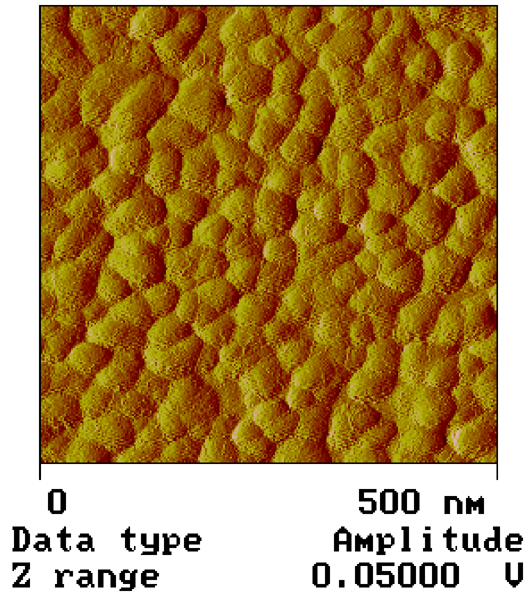
30bp_med.001

tin-oxide (pyrolytic) coatings on glass containers

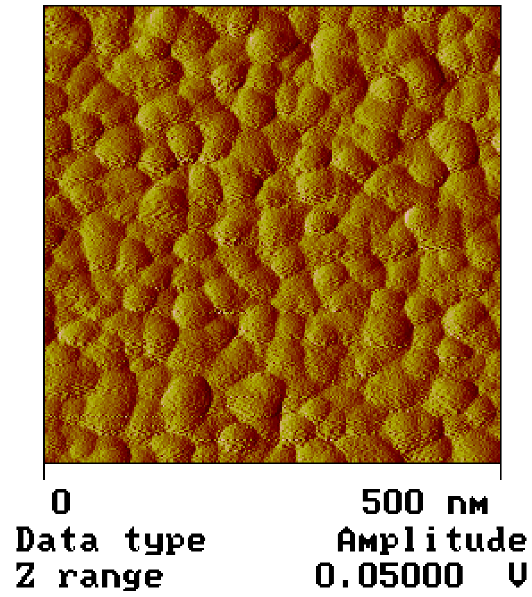
2.0nm



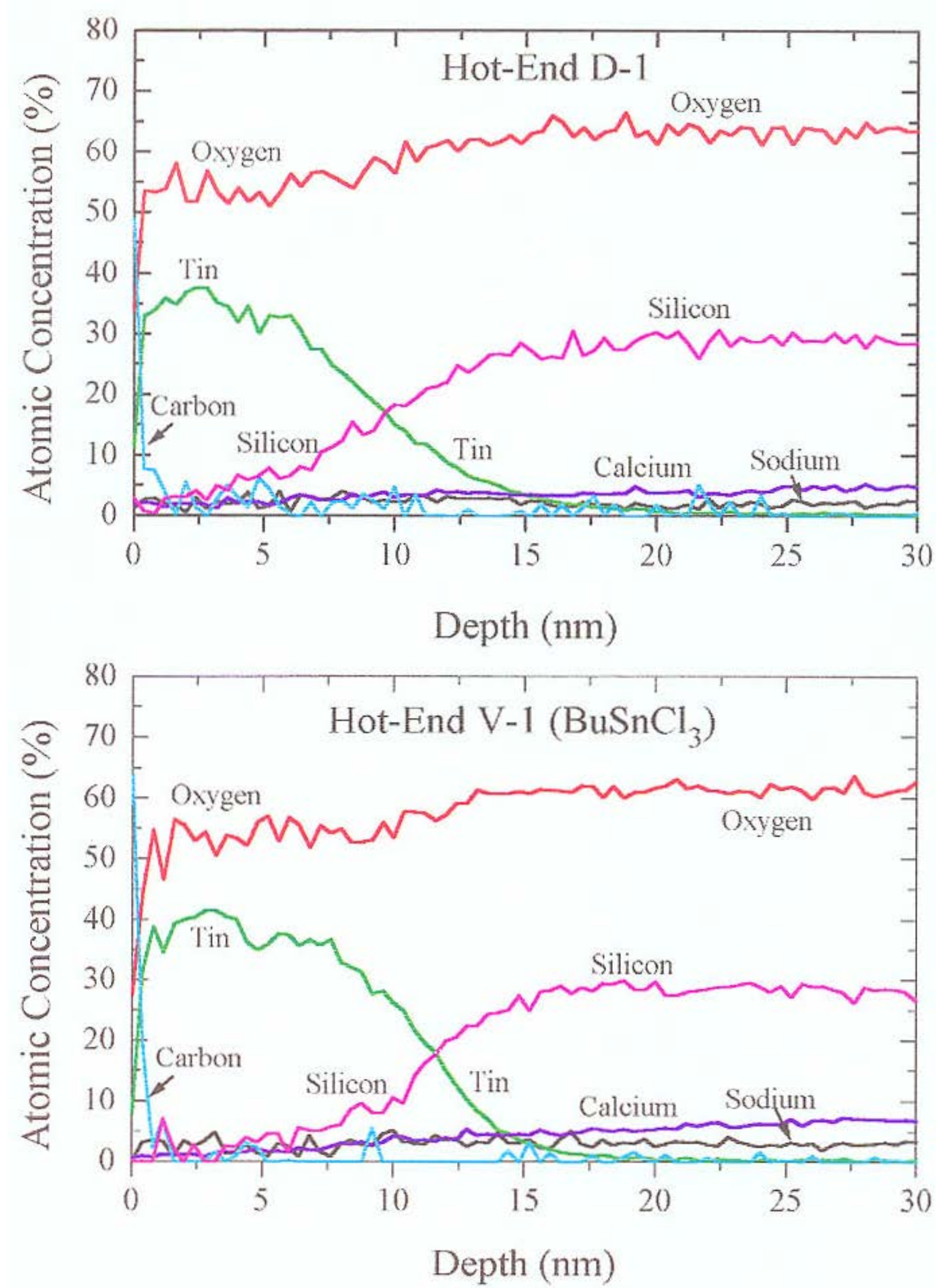
3.0nm



4.0nm




HOT END COATING
MEASUREMENT
SYSTEM
Agr

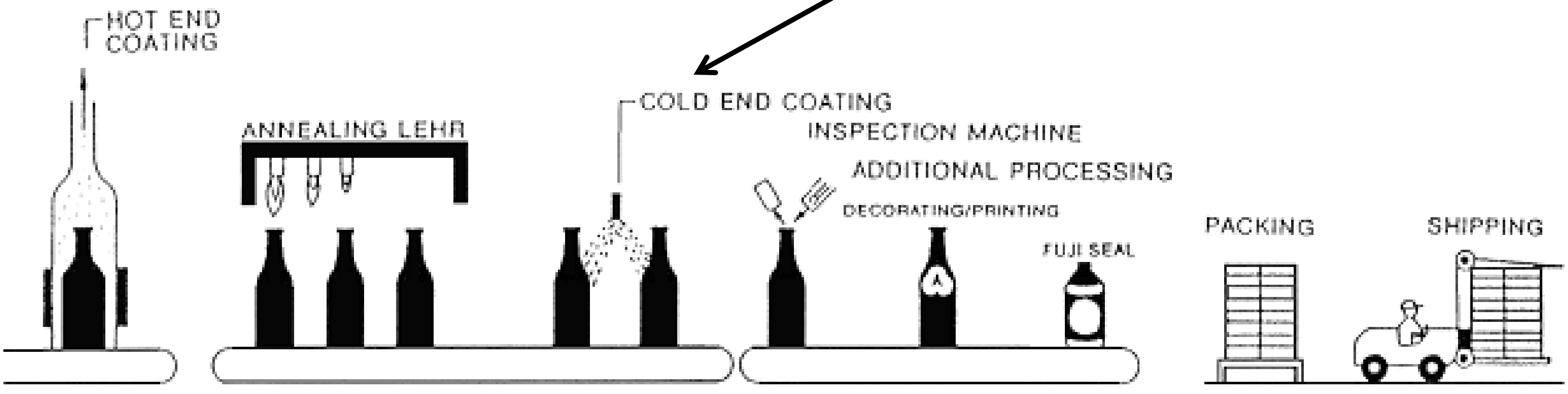

Hot-End D-1
Atomic Concentration (%)
Depth (nm)
Oxygen
Oxygen
Tin
Silicon
Carbon
Silicon
Tin
Calcium
Sodium
Hot-End V-1 ($BuSnCl_3$)
Atomic Concentration (%)
Depth (nm)
Oxygen
Oxygen
Tin
Silicon
Carbon
Silicon
Tin
Calcium
Sodium

Coatings for Glass Containers

COMMON Materials for Cold-End Coatings

- stearates, silicones, glycerides, **oleic acid**, **polyethylene emulsions**
- thickness ~100 nm ± 50%
- ~12.5 ug/cm$_2$

~65-180C



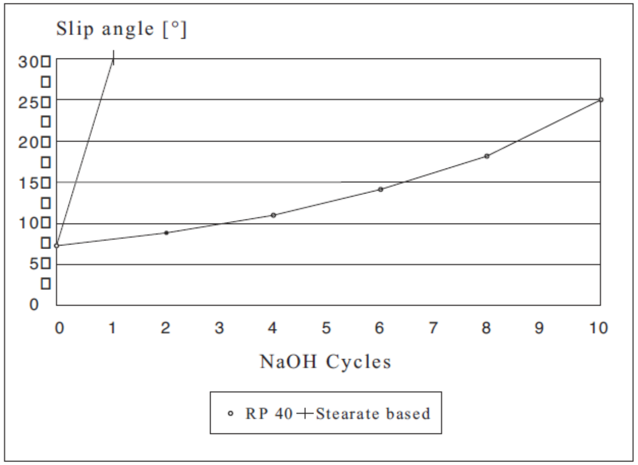


Figure 2. Lubricity comparison.

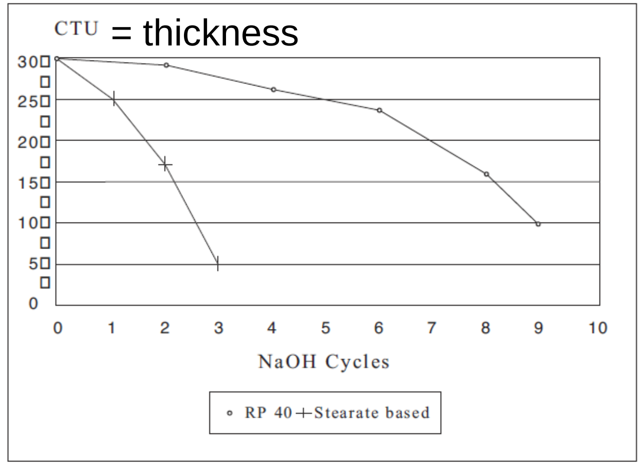


Figure 3. hot-end coating protection by cold-end coating.

~450-500N force

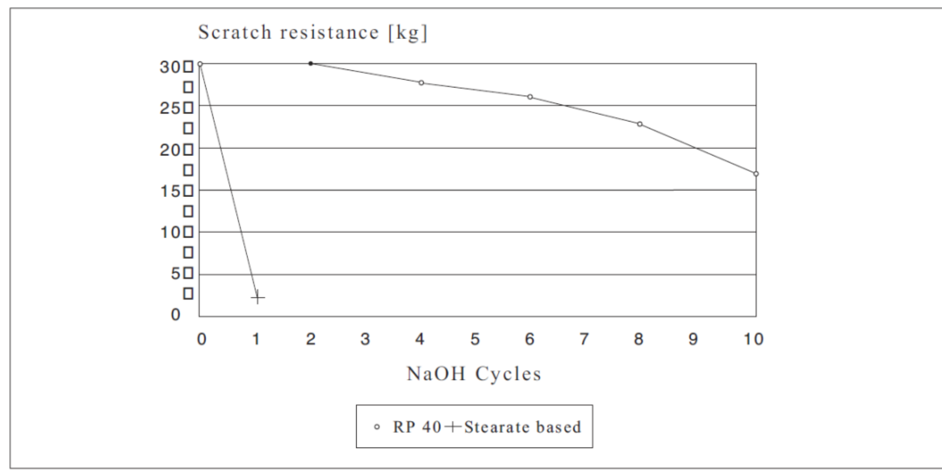


Figure 1. Scratch resistance comparison.

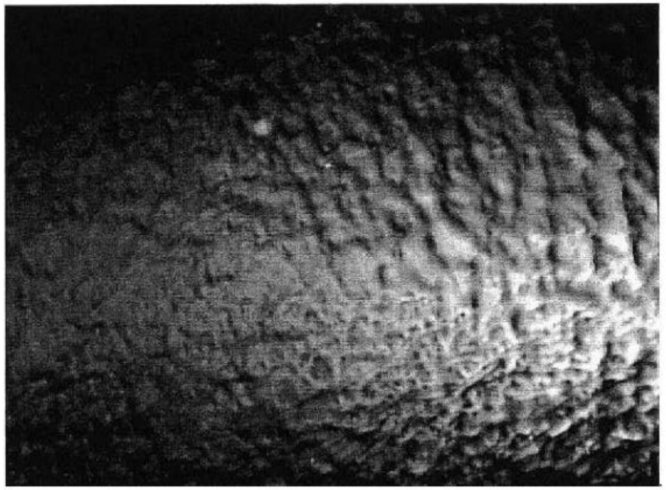


Figure 1. *Optical micrograph (24×). Surface roughness of container glass*

Figure 2. *Optical micrograph (385×). Section of the surface of a container cold end coated with RP 40 LT showing roughly circular deposits*

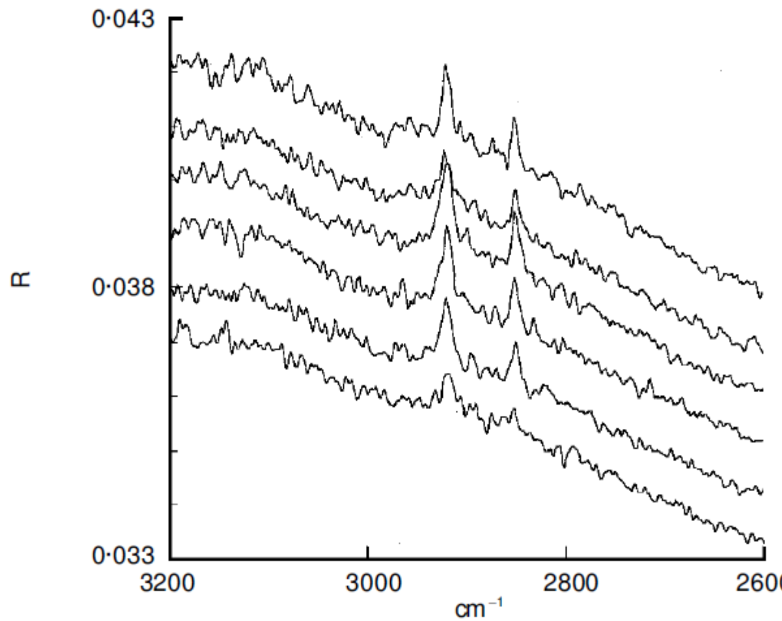


Figure 5. *Micro infrared reflectance spectra obtained at regular 0·1 mm intervals, scanning a selected area of the sidewall of a liqueur bottle cold end coated with RP 40 LT. The microscope image of the scanned area features a ring shaped deposit similar to those shown in Figure 2. As the ring area is scanned (from top to bottom curve), the C–H band intensity (ranging between 0·0006 and 0·0016) goes through a maximum*

High Speed Filling-Line Simulator

... subject container surfaces to abrasive contact

Pressure Tester

....puts the outside surface in tension.

Table 12

Strength of coated containers after abrasion

	Relative Bursting Pressure
Uncoated	1.0
Heavy hot end coating only	2.44
Cold end coating only	2.88
Heavy hot end and cold end coating	2.53
Medium hot end and cold end coating	3.00

Strength retention >>> NOT strengthening
…. light-weighting the container is an outcome.

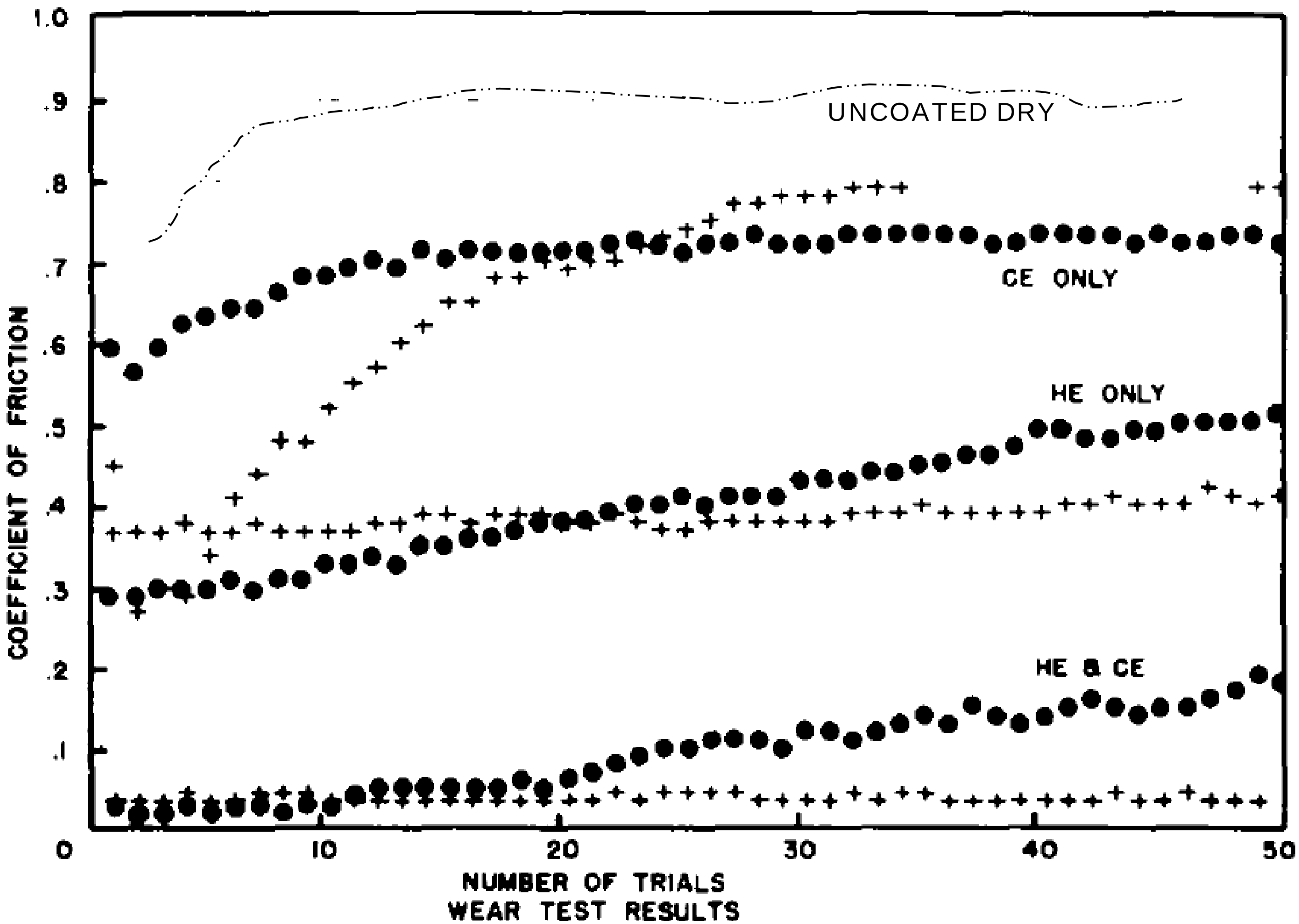


Fig. 6. Coefficient of friction wear data obtained on bottle friction analyzer: +, tested dry; ●, tested wet. The broken lines indicate the range of μ values for uncoated glass tested dry.

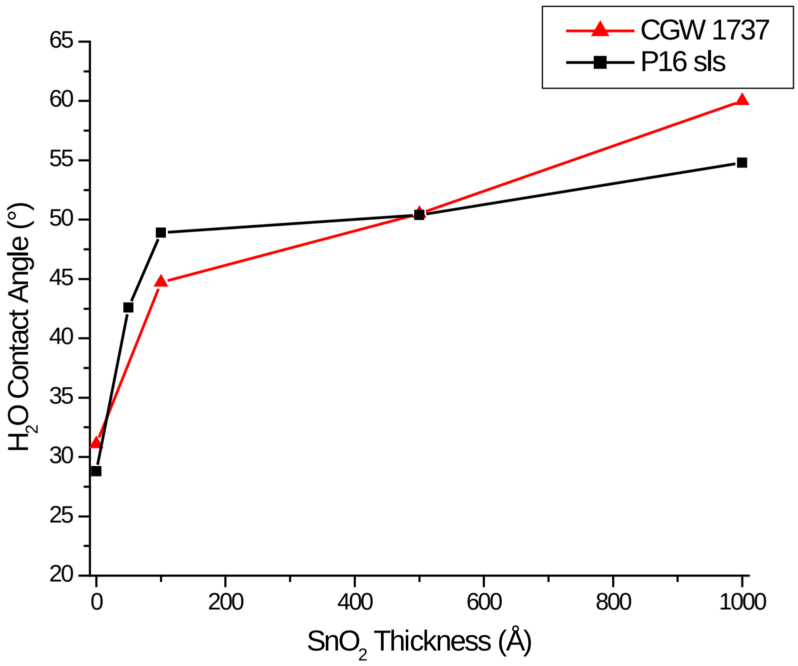
Thin Solid Films, 77(1981)41-50

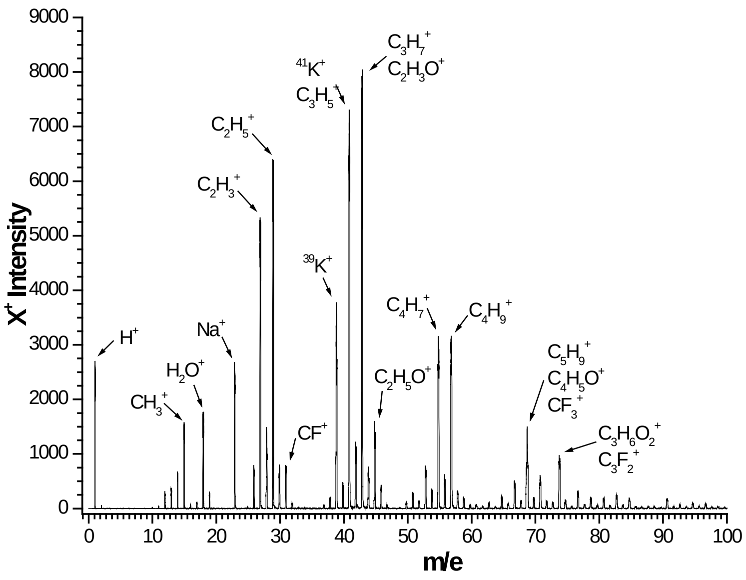
Damage resistance of dual-end coated glass containers

- **Mechanical effects**
  - abrasion/sliding → friction = f (roughness, chemistry)
  - contact/Hertzian → E_{film} vs $E_{substrate}$, thickness
  - impact → E, H, thickness

- **Chemical effects**
  - tin oxide is an adhesion promoter for the CE-coating
  - aqueous attack of the glass is reduced (diffusion barriers)
  - Sn diffusion modifies the glass properties (Si-O-Sn) ?

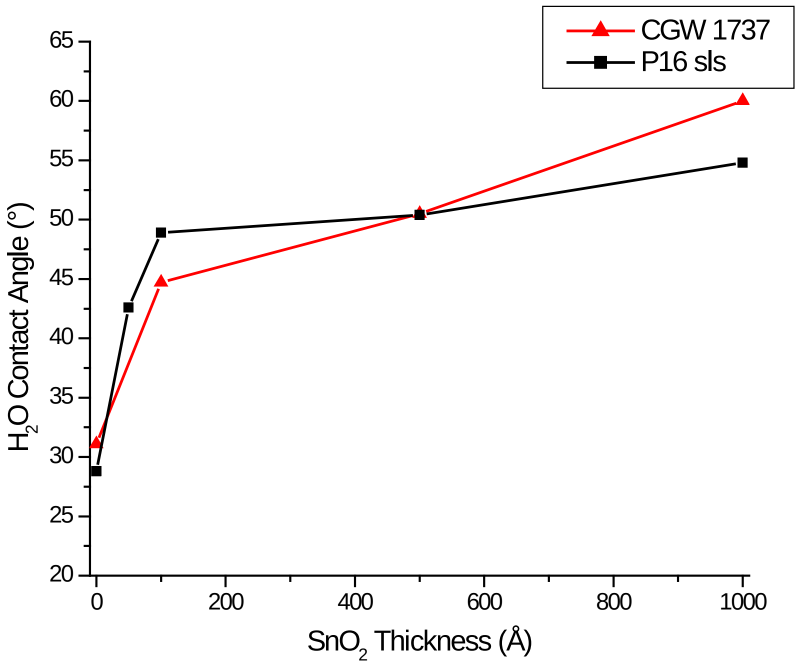
H_2O Contact Angle vs SnO_2



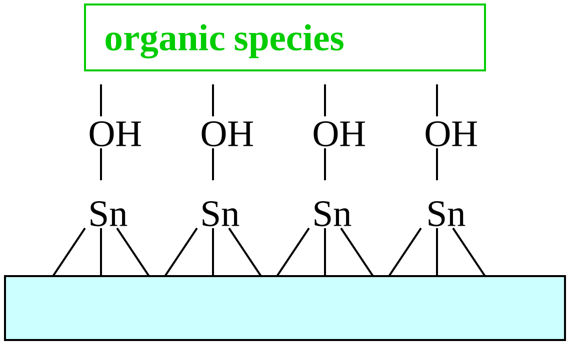


TOF-SIMS spectra shows corresponding hydrocarbon adsorption

H_2O Contact Angle vs SnO_2



….. suggests that the SnO_2 surface is more hydrophobic than the glass, and thereby provides strong adhesion of the organic (cold-end) coating.



WEAR RESISTANCE OF TIN-OXIDE ON GLASS

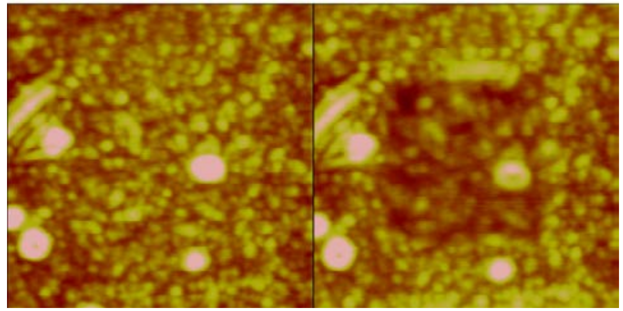


Figure 6. Wear test on SnO_2 films on P16 SLS before and after 2 passes at 20μN normal force
.

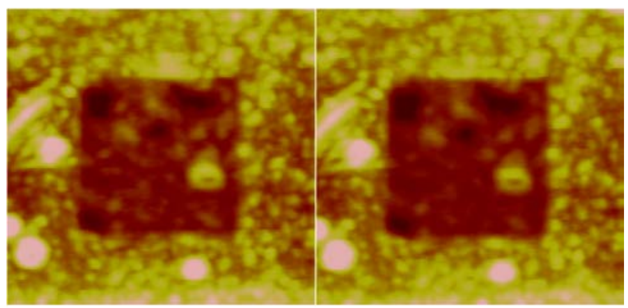
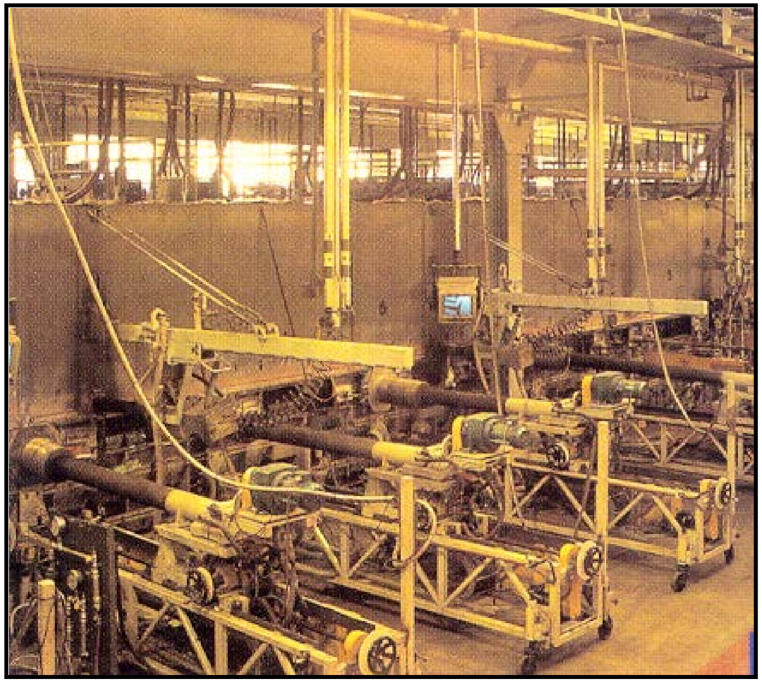
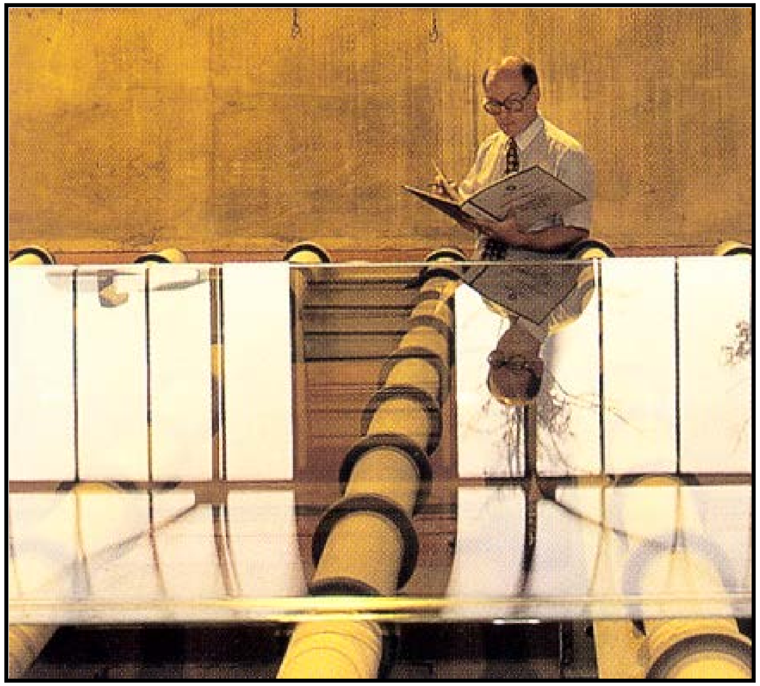
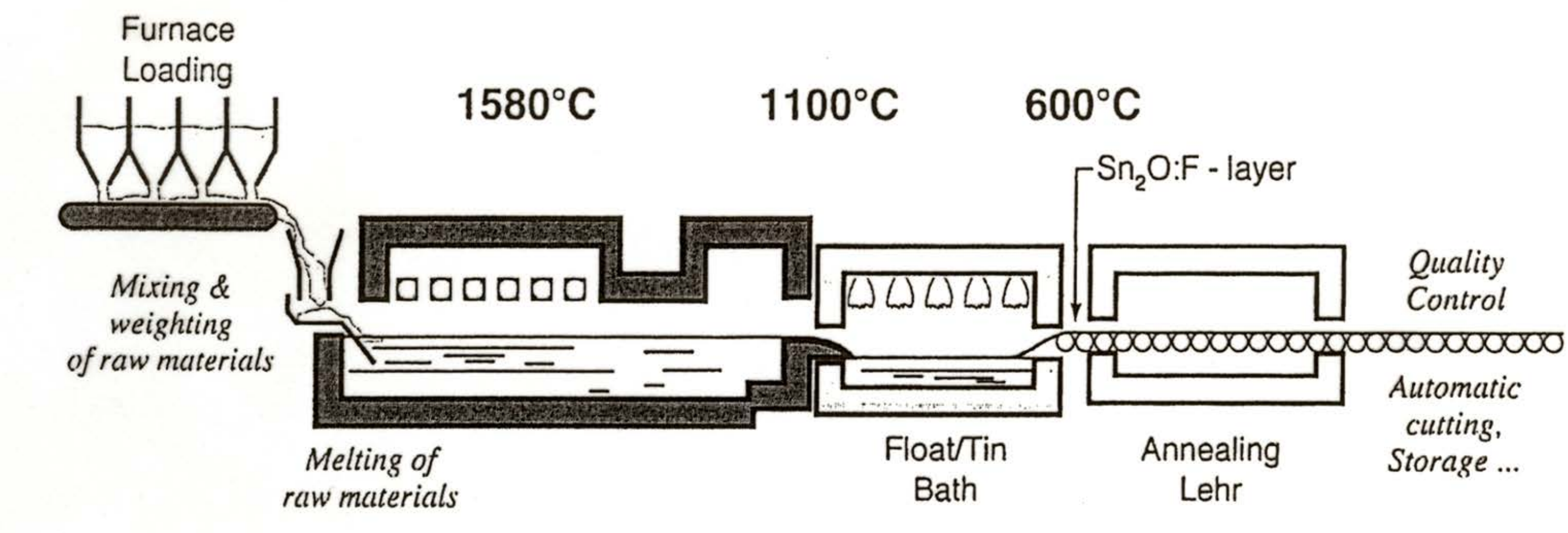


Figure 7. Wear test on SnO_2 films on P16 SLS after 2 and 4 passes at 50μN.

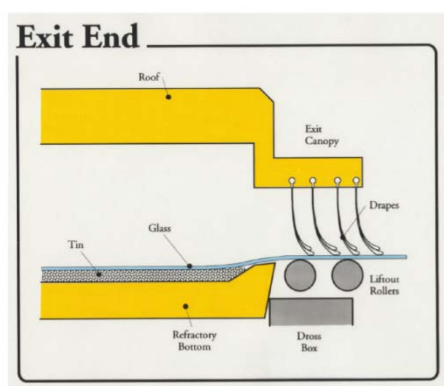


Float Glass





Ribbon Removal from Float Bath



‘sulfur treatment for surface DEALKALIZATION’

$$2Na^{+} + SO_2 + H_2O + \frac{1}{2} O_2 >> Na_2SO_4 + 2H^{+}$$

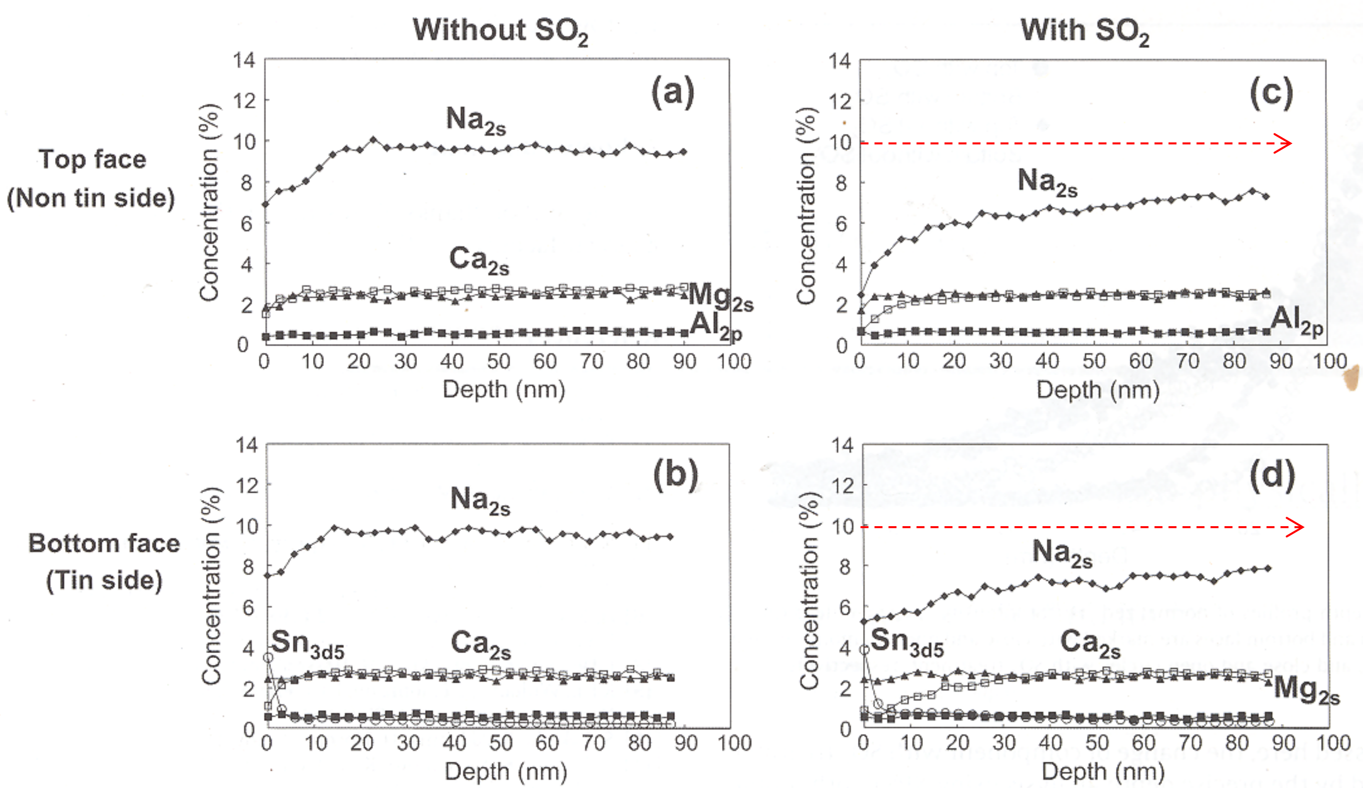


Fig. 2. XPS depth profiles using C_{60} ion beam on (a, c) top and (b, d) bottom face on soda–lime–silica float glass (24.6Si, 0.6Al, 2.5 Mg, 2.7Ca, 9.5Na, 60.1O in mol%) (a, b) without and (c, d) with SO_2 treatment, respectively. The vertical scale is expanded for the comparison of mobile ions. The concentration of Na, Ca, Mg, Al, Sn are monitored with the signals of Na_{2s} (close diamonds), Ca_{2s} (open squares), Mg_{2s} (close triangles), Al_{2p} (close squares) and Sn_{3d5} (open circles). C_{1s} is eliminated from the calculation for the detailed comparison on the glass component.

Hydrogen in-depth profiles before and after SO2 treatment

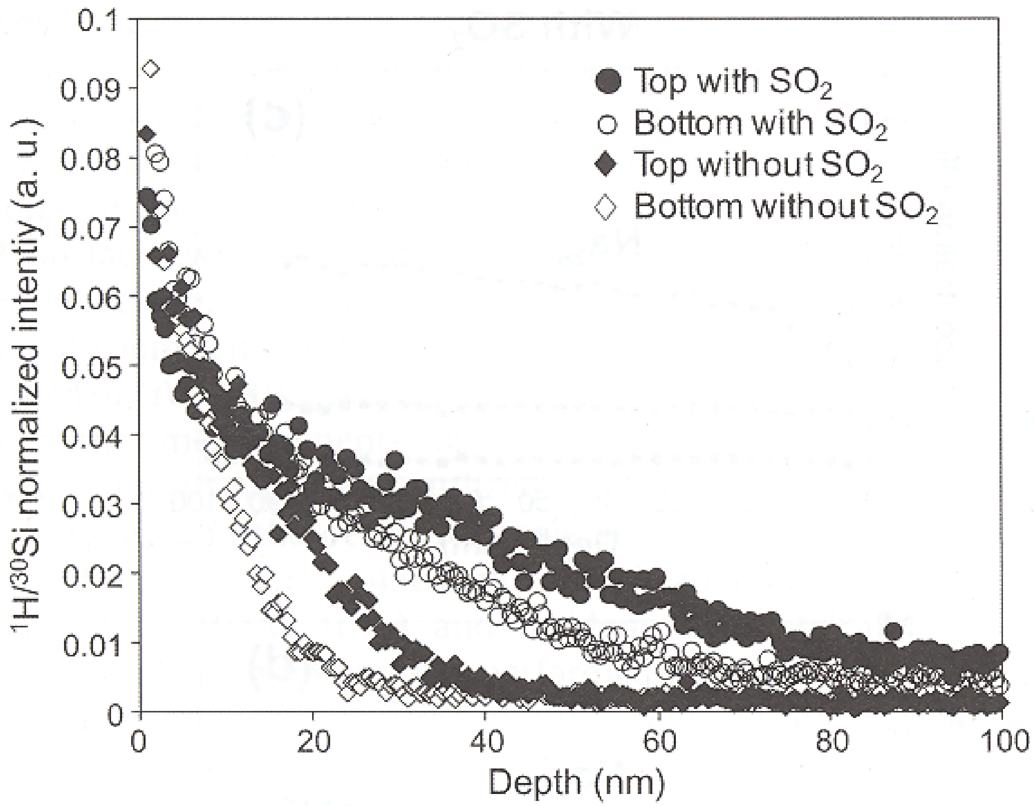
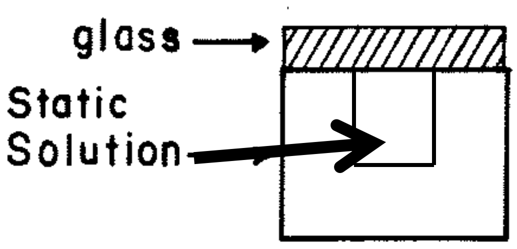
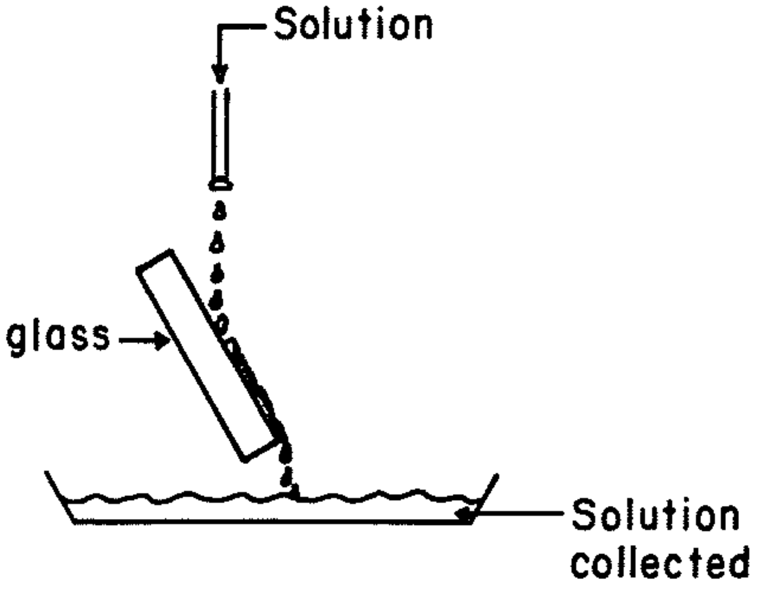


Fig. 4. SIMS depth profiles of normalized $^1H/^{30}Si$ intensity (negative detection) in float glass. Top and bottom faces are marked with close and open diamonds without SO_2 treatment, and close and open circles with SO_2 treatment, respectively.

Chemical Evaluation of Leachable Sodium



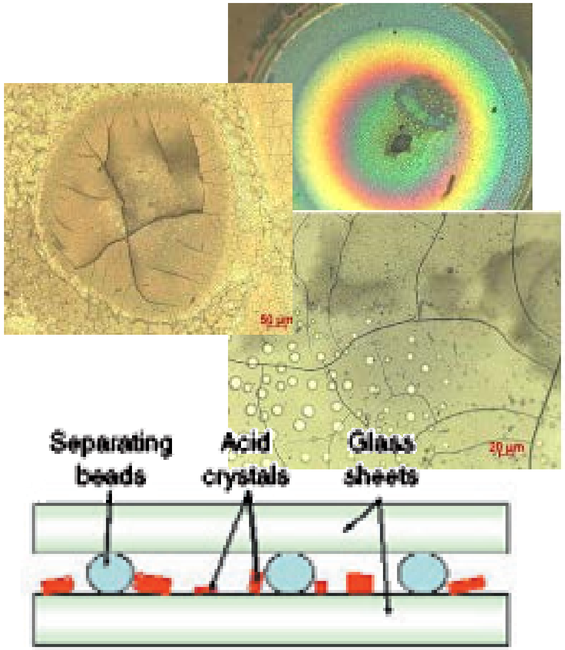
(c) Static corrosion of bulk glass



(d) Dynamic corrosion of bulk glass

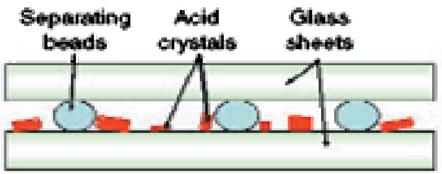
Acid Interleave Coatings

- Acid interleave coatings are widely used in float glass industry to separate sheets and protect from damage in transit & storage
  - ***Physical damage***: glass-to-glass contact, trapped particulate
  - ***Chemical damage***: corrosion, weathering, "stain"
- Applied to surfaces of fresh float glass after final inspection but before stacking
- Most common is a blend of powdered adipic acid and polymer beads; new products recently introduced

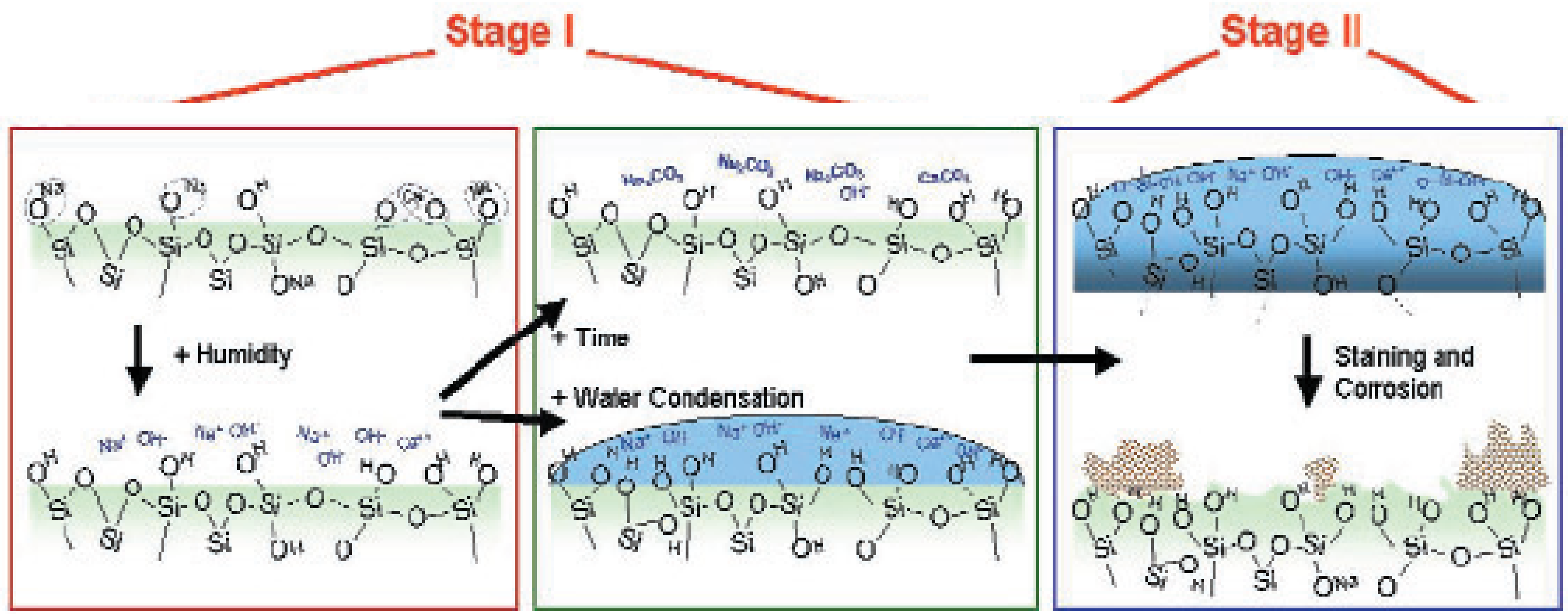


❖ New and emerging applications of glass require control of **glass surface properties at the nanoscale** for optical coating, display electronics and bio-substrates.

Weathering

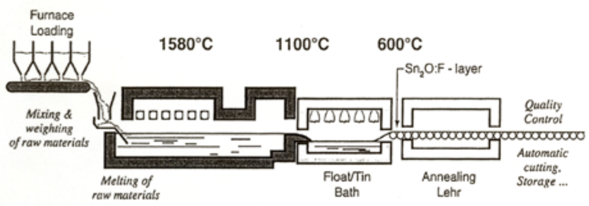


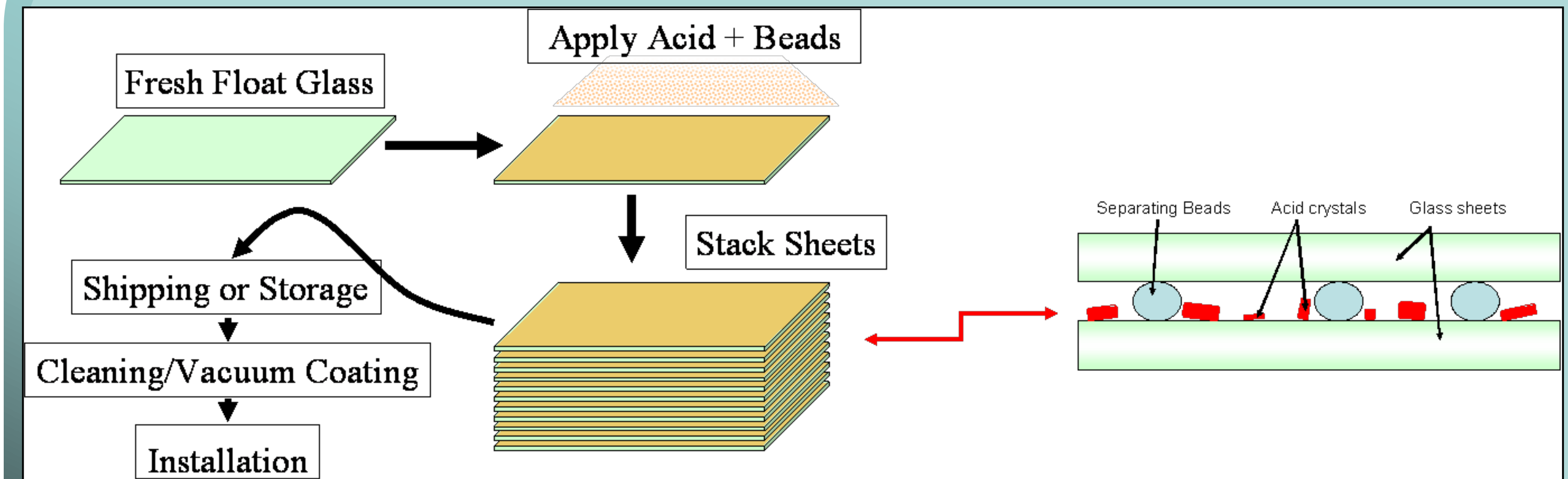
- glass corrosion often described by two primary stages:
  - "Stage I": Ion-exchange (leaching) of mobile alkali with H^+/H_3O^+, forming SiO_2-rich layer (with potential for static pH rise)
  - "Stage II": Dissolution of silica network at pH >9 with degradation of surface, formation of insoluble precipitates



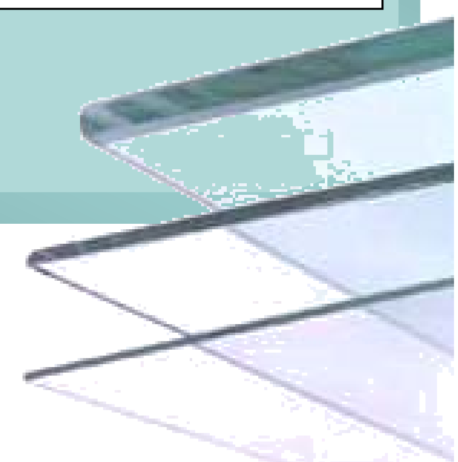
R. A. Schaut, Pantano C.G., The Glass Researcher (2005)

Application Process





- PMMA beads
- typically, 200 mg/m2 of acid powder



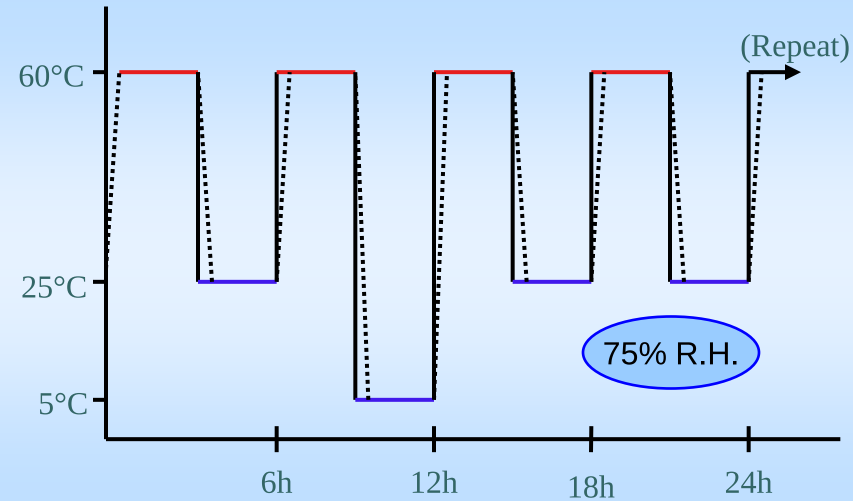
Testing and Evaluation
-Laboratory and Field-

CYCLIC weathering conditions:

- 60°C/25°C/5°C cycles
- 75% R.H. constant
- 0, 4, 12, 30, 60, 90 day samples

❖ Based on conditions experienced during overseas transport

❖ Visible periods of condensation

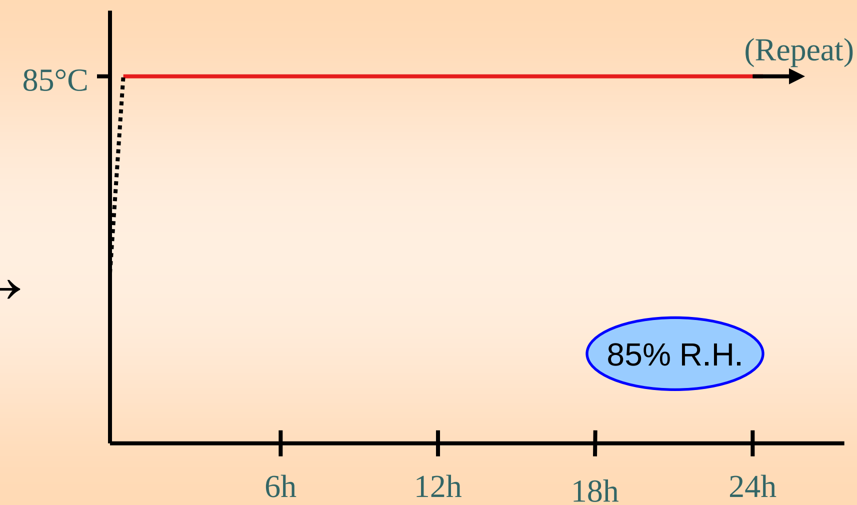


STATIC weathering conditions:

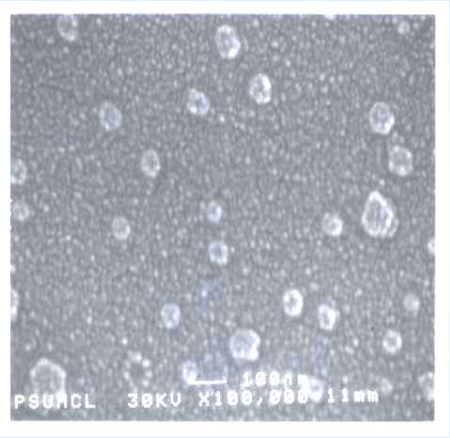
- Constant 85°C, 85% R.H.
- 0, 1, 2, 3, 4 day samples

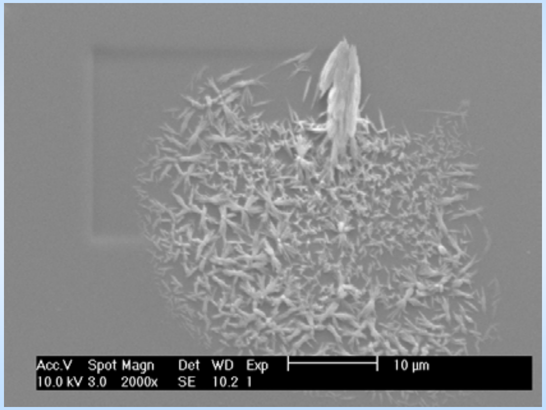
❖ Higher T, humidity more aggressive →

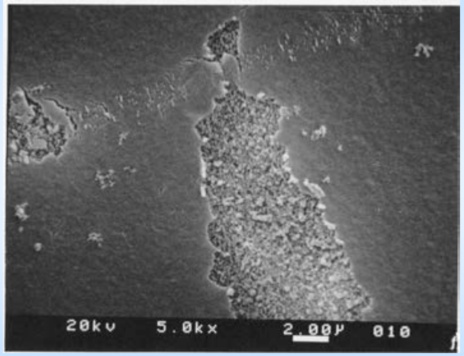
❖ Condensation-runoff unlikely

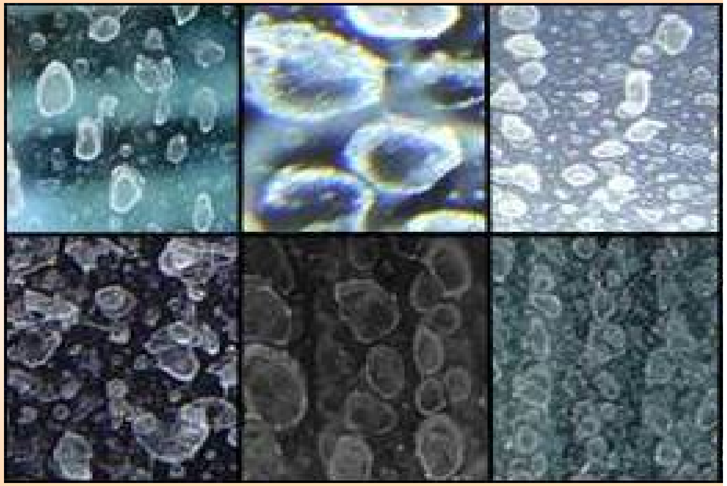


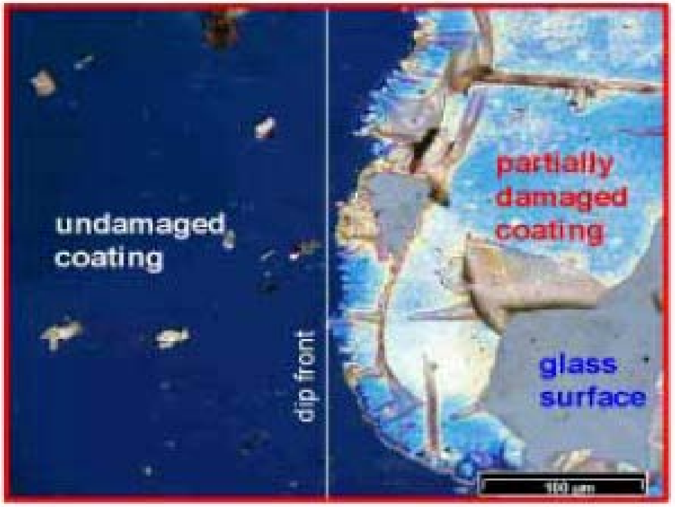
Testing and Evaluation – visual





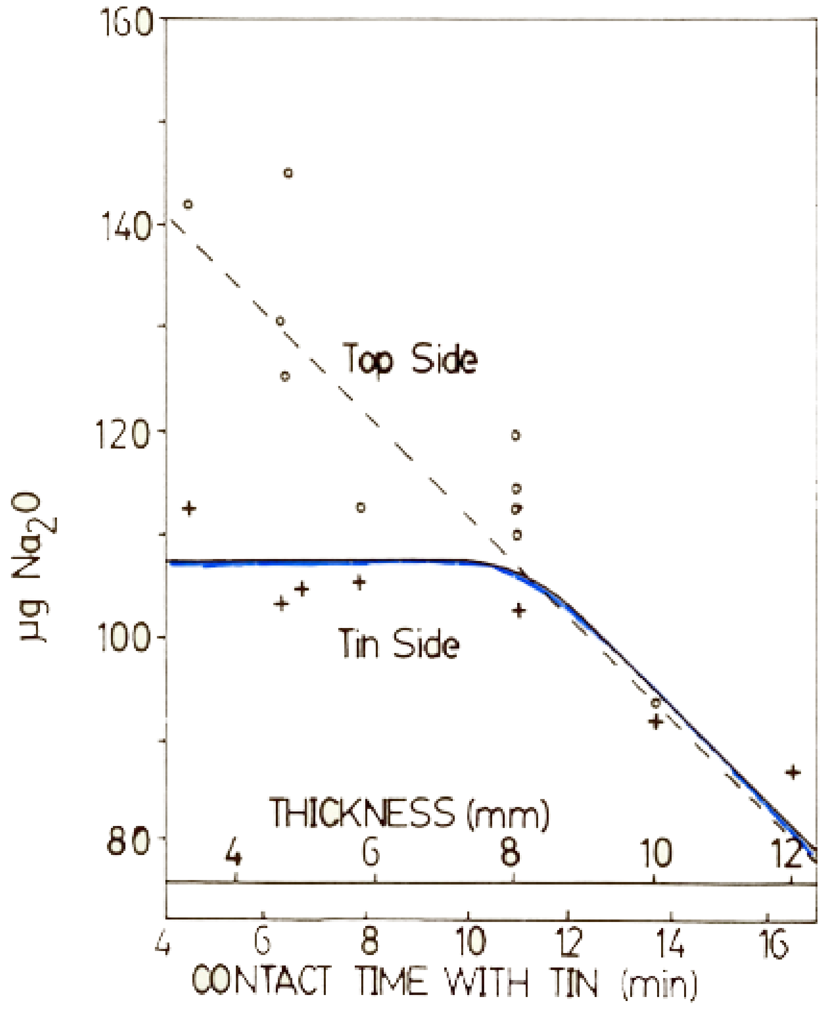




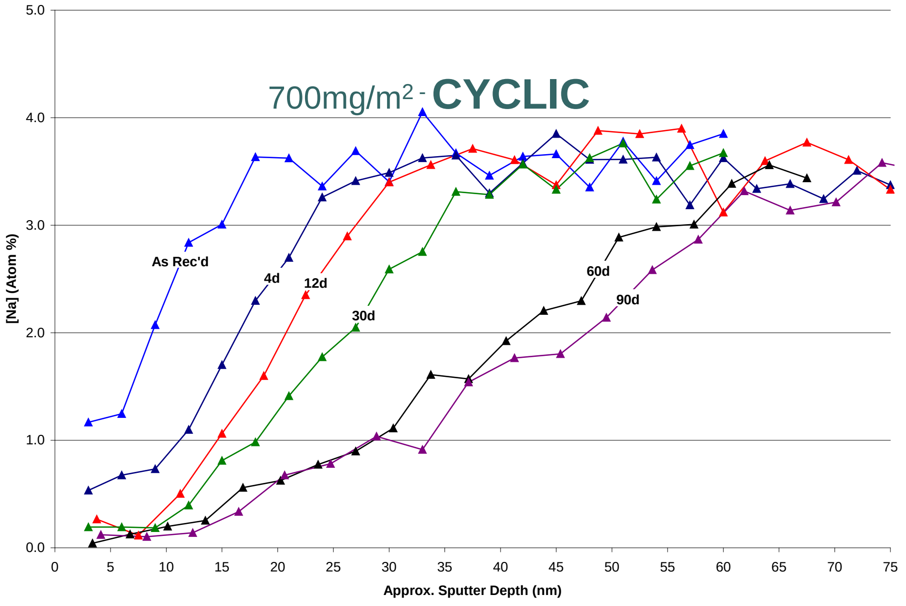


Commercial Float Glass

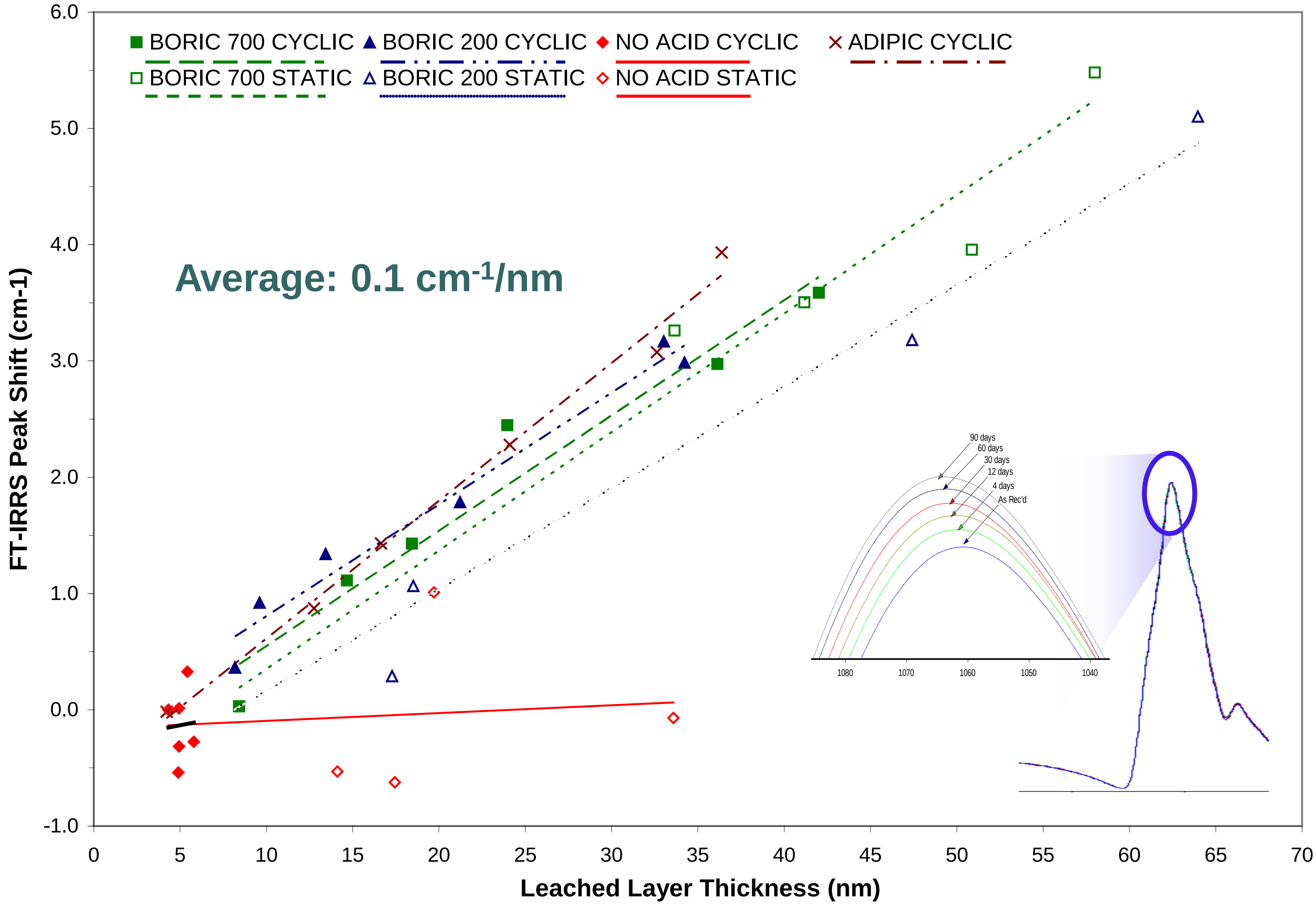
Leached for one hour at 96ºC into 30mL of DI – H_2O



Coating coverage required can depend on the product and its application.

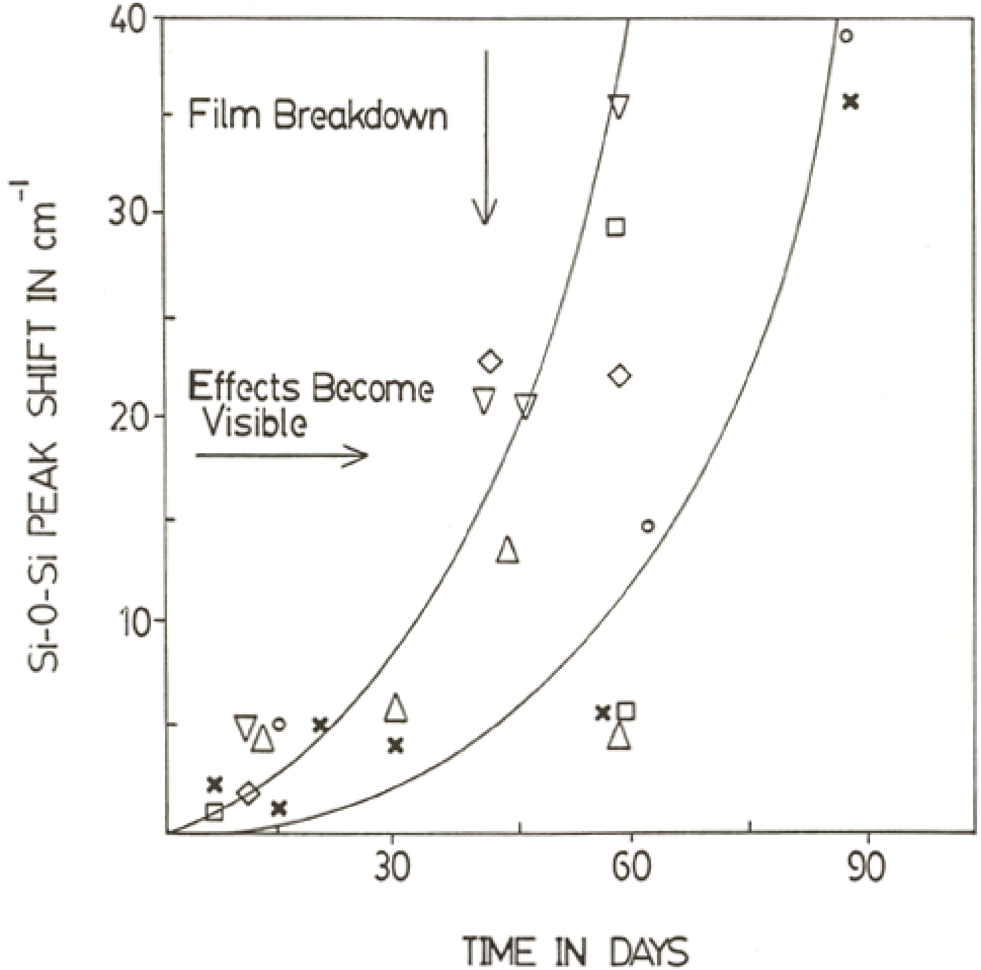


FT-IRRS of Treated Surfaces



Commercial Float Glass

Exposed to 98% RH at 60ºC – Top Side



SUMMARY

- SO_2 and fluorine treatment for the internal surface of glass containers is widely practiced; but it costs the customer extra.
- The visible effects of the 'SO_2 treatment' (ie, before washing off the Na-sulfate crystals can be a plus.
- New drugs are creating renewed interest in SO_2 treatments because some drugs can attack the glass.
- The non-uniformity of the SO_2 dealkalization, especially for float glass, is a factor for some applications.
- The inherent non-uniformity of 'acid interleave coatings' is also a factor for some applications.
- Dual-end coatings on glass containers (ie, hot-end and cold-end) are also widely applied; most products require at least the cold-end coating.

Fluorocarbon Surface Treatment

$$2 \equiv Si - O^{-} Na^{+} + Freon(eg, CH_3CHF_2) \rightarrow 2 \equiv Si - F + Na_2O + xCO_2 + H_2O$$

(US Patent 3,314,772)

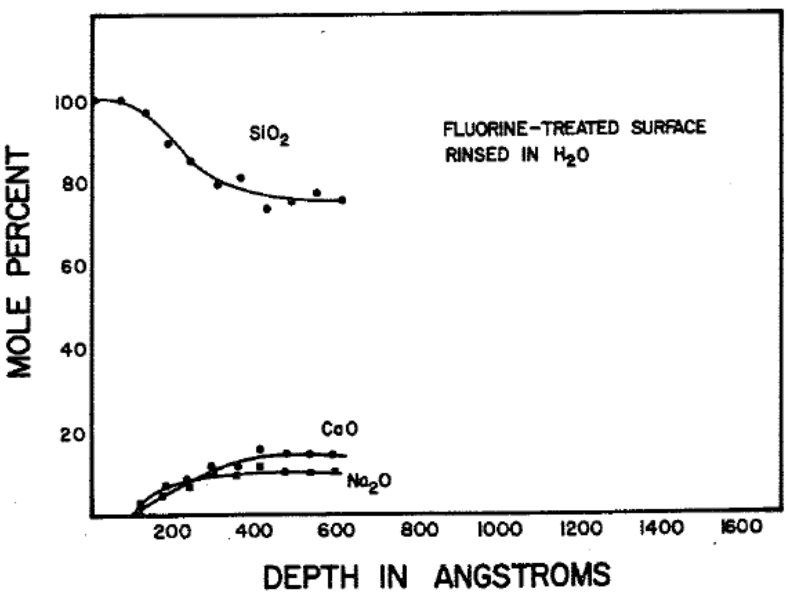


Figure 76. Depth compositional profile for a fluorine-treated surface after rinsing in water

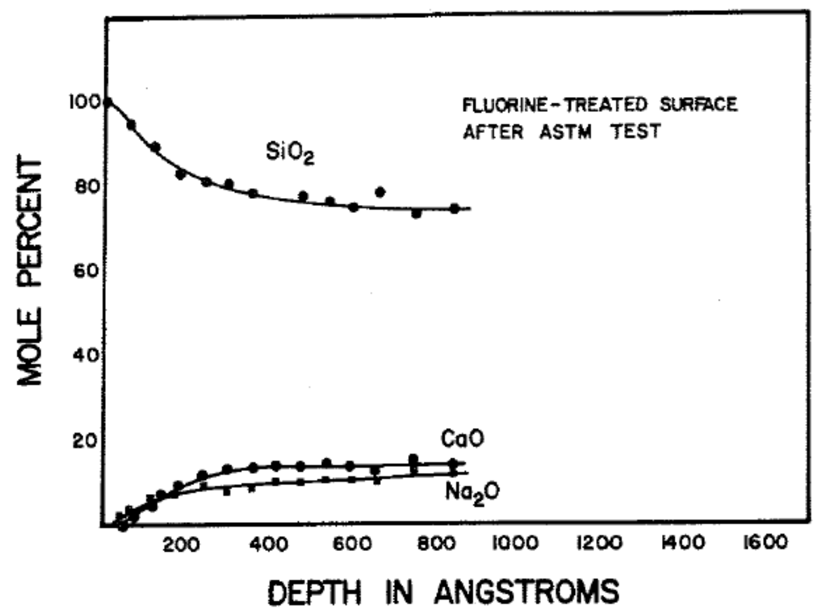


Figure 77. Depth compositional profile for a fluorine-treated surface after the ASTM durability test

High temperature fluorocarbon treatments of glass containers

TABLE I

	S_o $\frac{MN}{(M^2)}$	C	n
internal surface untreated	307	.13	17
internal surface treated	440	.06	35

S_o = instaneous failure stress

C and n = stress corrosion factors

Glass Surfaces, Coatings and Interfaces

A substrate for biomolecules and cell growth

A substrate for electronics… including flexible electronics

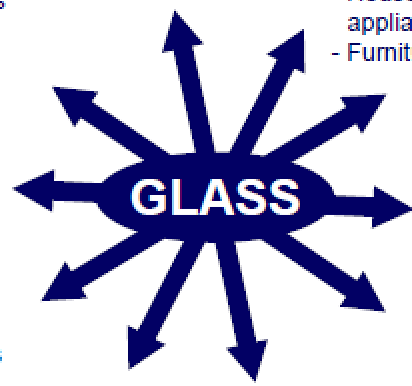
Automotive
- Glazing
- Lighting

Biomedical
- Artificial kidneys
- Prostheses
- Laser operations
- Control release medicines

Household
- Tableware
- Ovenware
- Household appliances
- Furniture

Architecture
- Security glasses
- Safety glasses
- Electrochromic glasses
- City furniture
- Construction materials
- Mirrors
- Photoactive glass surfaces (hygienic and self cleaning surfaces)

Energy
- Solar densifiers
- Solar and heat control glasses
- Fuel cells
- Laser glasses
- Solar cells
- Xenon lightings



Packaging
- Bottles, jars
- Vials, ampoules

Agriculture
- Greenhouses
- Controlled release animal feeds
- Controlled release fertilizers

A substrate for optical coatings…low-E, reflective and anti-reflective

Optics and Optoelectronics
- Optical fibers
- Optical devices
- Lenses/micro lenses
- Photo modulators

Art

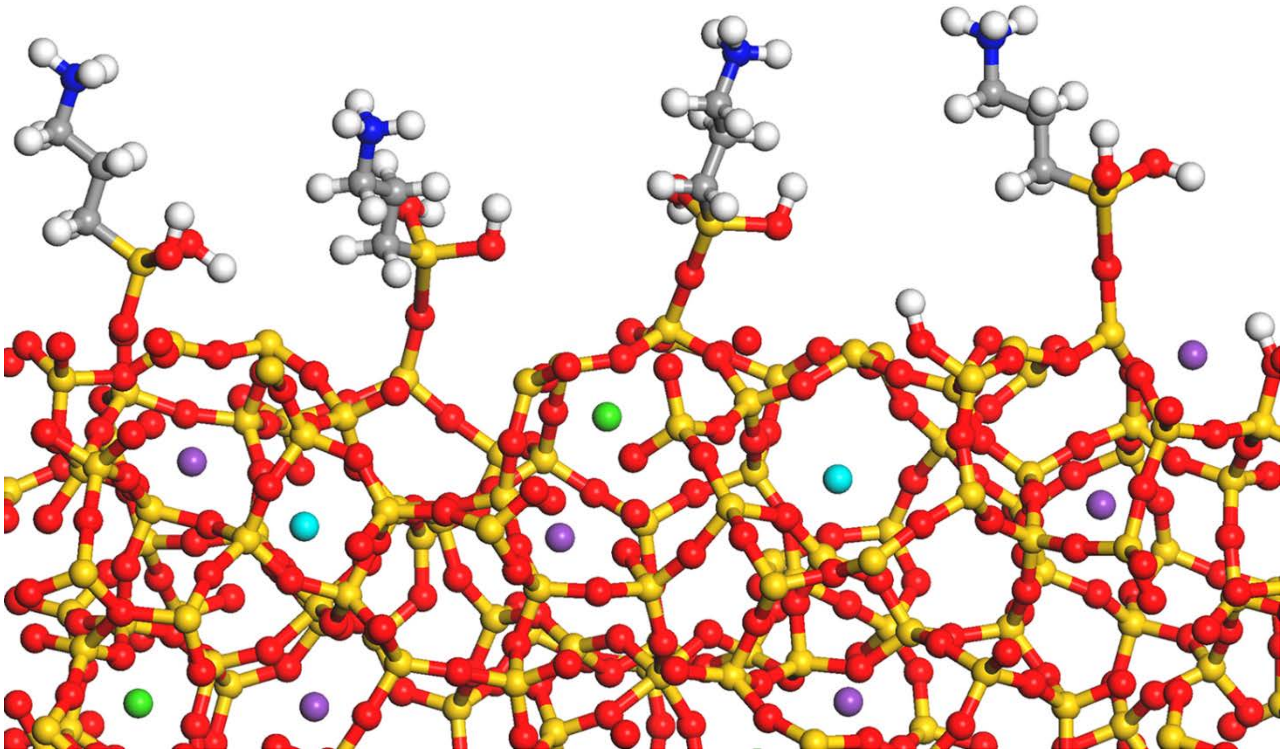
Electronics
- Insulators
- Display panels
- Integrated circuits

Strength determining

Integrated and Interfaced with other materials

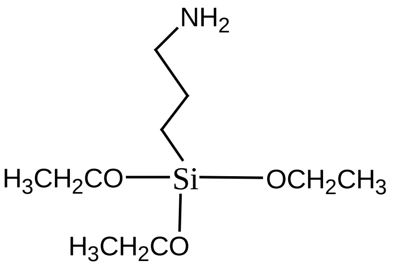
< Stability of the Glass Surface and Glass/Coating Interface>

organo-functionalization of a glass surface

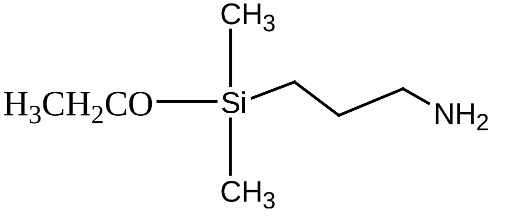


Silanes

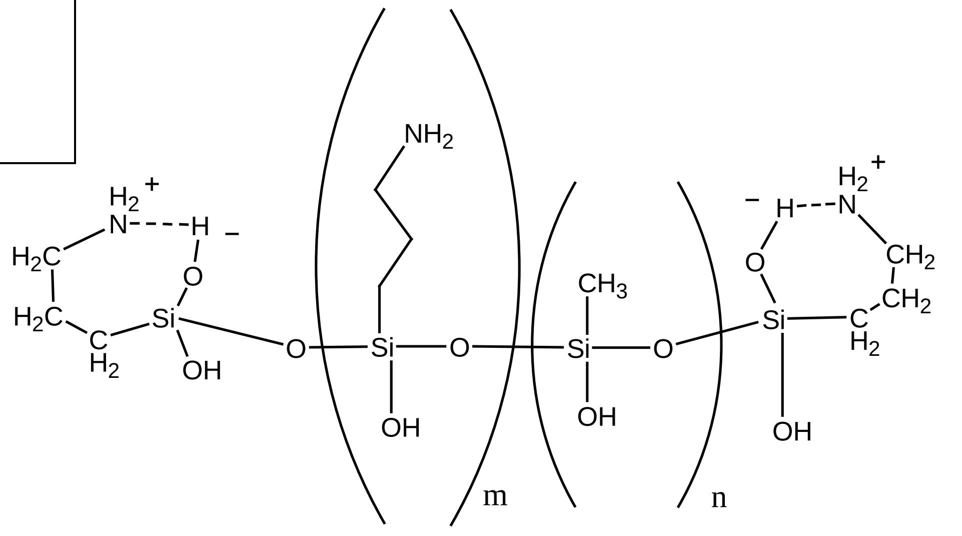
- **γ-aminopropyltriethoxysilane**



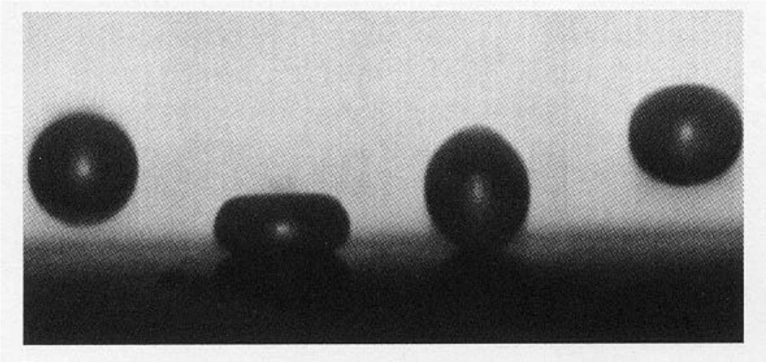
- **3-aminopropyldimethylethoxysilane**



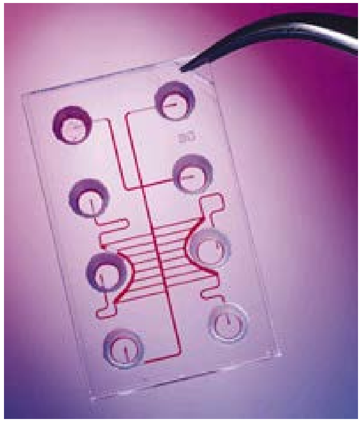
- **Aminoalkylsilsesquioxane**

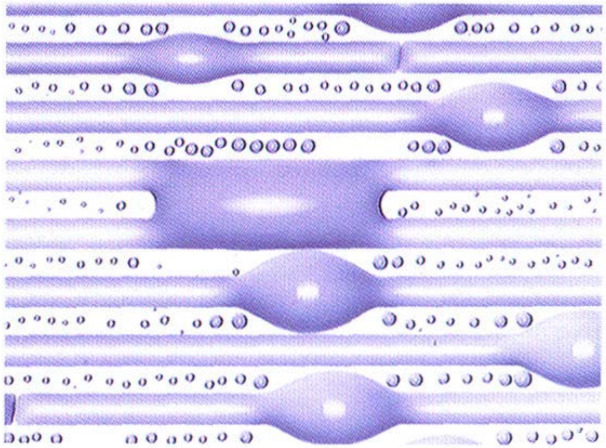


organic polymer coatings



- hydrophobic/hydrophilic
- patternable for microfluidics
- anti-bacterial/anti-fouling
- substrates for biotechnology (ELISA, super-aldehyde, GAPS, etc.)
- molecular electronics (OLEDs, conductors, transistors)
- fiberglass sizing/ coupling layers
- ‘precursors for inorganic coating





Journal of Non-Crystalline Solids 19 (1975) 251–262

EFFECT OF SURFACE TREATMENTS ON THE CHEMICAL DURABILITY AND SURFACE COMPOSITION OF SODA-LIME GLASS BOTTLES

P.R. ANDERSON, F.R. BACON and B.W. BYRUM
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Fluorine Treatments of Soda-Lime Silicate Glass Surfaces

RICHARD K. BROW* AND WILLIAM C. LACOURSE*
New York State College of Ceramics, Alfred University, Alfred, New York 14802

JAmCerSoc, C124, 1983

Thin Solid Films, 77 (1981) 23-39
METALLURGICAL AND PROTECTIVE COATINGS

"EXPERIENCE IN THE CONTROL AND EVALUATION OF COATINGS ON GLASS CONTAINERS"

J. Am. Ceram. Soc., **91** [3] 736–744 (2008)
DOI: 10.1111/j.1551-2916.2007.02079.x

Leached Layer Formation on Float Glass Surfaces in the Presence of Acid Interleave Coatings

Nicholas J. Smith[†] and Carlo G. Pantano

Optical Materials 33 (2011) 1927–1930
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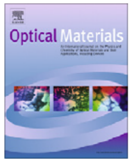

Precise XPS depth profile of soda–lime–silica float glass using C_{60} ion beam

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