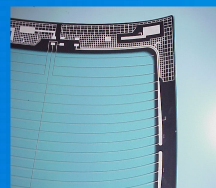
     

Functional Glass Coatings

by:
George E. Sakoske

IMI International Workshop on Scientific Challenges
of New Functionalities in Glass
Washington, DC
April 16, 2007

Functional Coatings on Glass

- Introduction
- Glass Ceramic Enamels
- Glass Fabricating Process Performance
- Strength and Coatings
- Solar Control Coatings
- New Innovative Coatings

Introduction

- Most glass products would not have the properties that make them so useful without coatings.
  - 550 MM ft^2 of flat glass coated annually in NA by either the manufacturer or an end user.
  - 95% of all glass containers manufactured in US (36 BB/yr) and 75% Worldwide (180 BB) are produced with one or more coatings
- Application of coatings are an essential part of glass manufacturing.
- Opportunities exist for improved Functionality and improved Processes.

Opportunities for the glass industry

- Energy savings
- Improved Processes
- Environmental Initiatives
- New Chemistries
- Glass Strengthening
- Self Cleaning
- Other Functionality

Markets

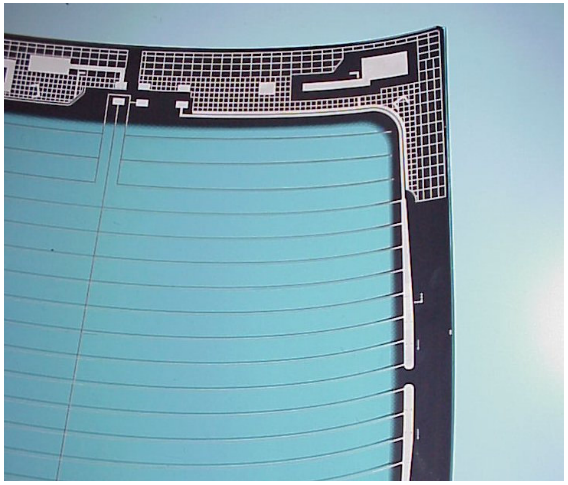
Automotive glass (windshields, sidelights, conductive)

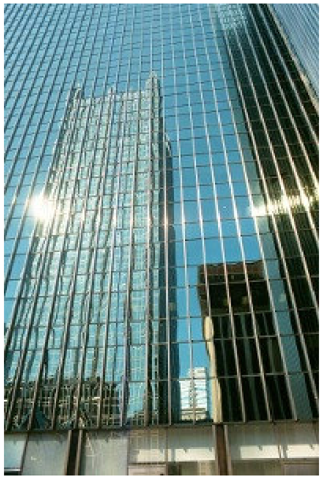
Architectural (exterior spandrel, specialty glass)

Appliance (oven, microwave, etc)

Container (glass beverage and cosmetic decorative inks and coatings)

Decoration (gold and precious metals for glass and ceramics)





Driving Forces for Regional and Global Specifications

Three criteria drive the specifications of glass coatings

- Product Performance Requirements
  - Physical, chemical, aesthetic properties
- Government Regulation
  - Local, country, and international laws
- Glass Fabricating Process Requirements
  - Ease of Application and performance during forming

Automotive Glass Design Trends

More Glass Surface Area
Improved Visibility

More Complex Shapes
Better Aerodynamics
Styling

Faster Production Rates

Lighter Vehicle Weight
Thinner Glass
Stronger Glass

Increasing Functionality
Heat reflecting
Privacy
Conductive Circuits

Environmentally Friendly
Lead and Cadmium Free
Ability to Recycle

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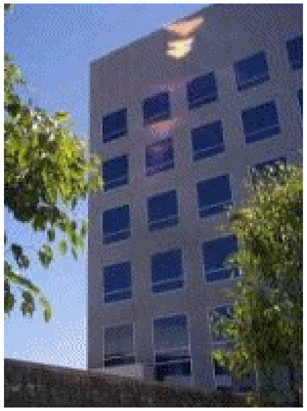
Glass-Ceramic Enamel Coatings



Protective Function

From UV degradation of adhesive bonding glass to frame

Bonded glass contributes to structural integrity

Decorative Function

Hides adhesive layer unevenness and conductive circuits

Enhances appearance of glass

Functional Material of Choice

Long Term Durability

Ease of Integration into Glass Forming Processes

- Screen print enamel
- Dry
- Screen print silver heater bands or antennas
- Fuse during forming of glass substrate

Composition

Glass frit fluxes (50–85 wt%)

$PbO\text{-}B_2O_3\text{-}SiO_2$

$ZnO\text{-}B_2O_3\text{-}SiO_2$

$Bi_2O_3\text{-}B_2O_3\text{-}SiO_2$

Other oxides: TiO_2, ZrO_2, Al_2O_3, Na_2O, K_2O, Li_2O, CaO, F^-

Inorganic pigments (10-40 wt%)

$CuCr_2O_4$

$(Ni,Fe)(Cr,Fe)_2O_4$

$(Co,Fe)(Fe,Cr)_2O_4$

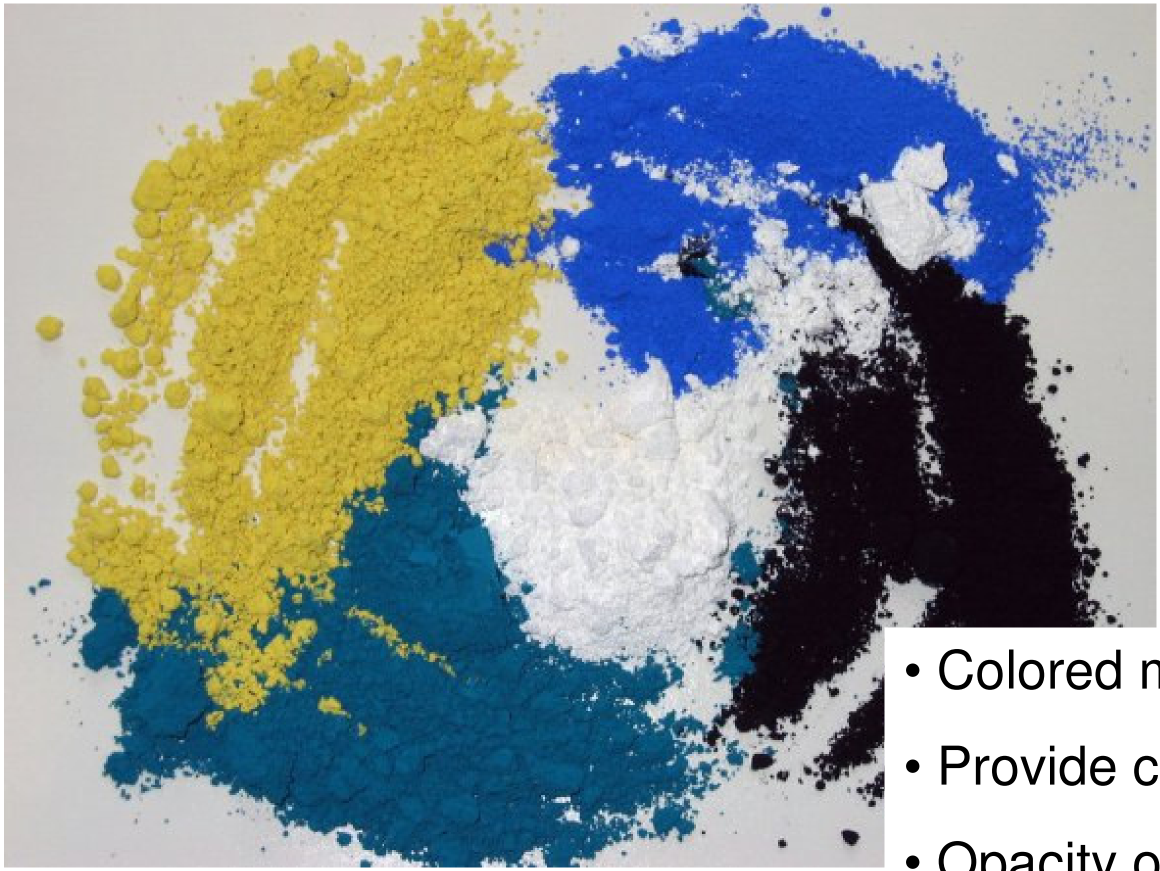
Modifiers: CuO, MnO or others

Additive oxides, sulfides, or metals (0-20 wt%)

Function of the glass flux

- Firing range of the enamel
- Chemical Durability
- Surface Gloss
- Fusion of the Color to glass surface

Function of the pigments and additives



- Colored metal-oxides
- Provide color to the enamel
- Opacity or transparency
- Reduce silver migration
- Improve Anti-stick

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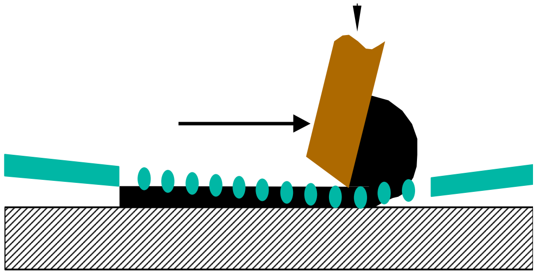
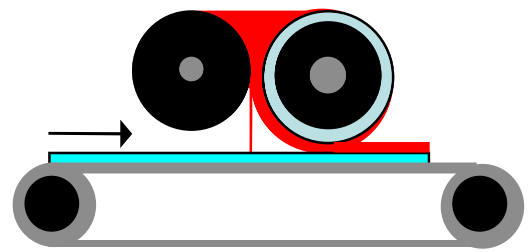
Application methods

Screen-print
•Option for Design prints
• Wet film 5 - 60 µm

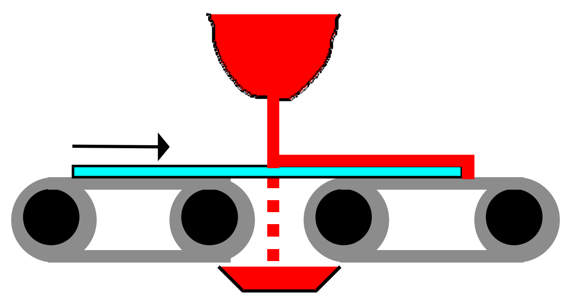


Roller Coating
•Wet film 20-150 µm
•Clean borders



Spraying
• Wet film 10-250µm
• Electrostatic

Curtain-Coating
• Wet film 150-350µm
• fast decoration process



Carrying Vehicle or Medium

Infrared (IR) heat curing vehicles:

pine oils, vegetable oils, mineral oils, low molecular weight petroleum fractions, tridecyl alcohol, and other modifiers.

Ultraviolet (UV) radiation cure vehicles:

polymerizable monomers and oligomers with functional groups as acrylates or methacrylates, photoinitiators, and polymerization inhibitors.

Thermoplastic vehicles:

waxes

Special oxidative cure (IS) resin systems:

reactive alkyd and other organic resins, oils, and oxidizers

Medium Must Provide:

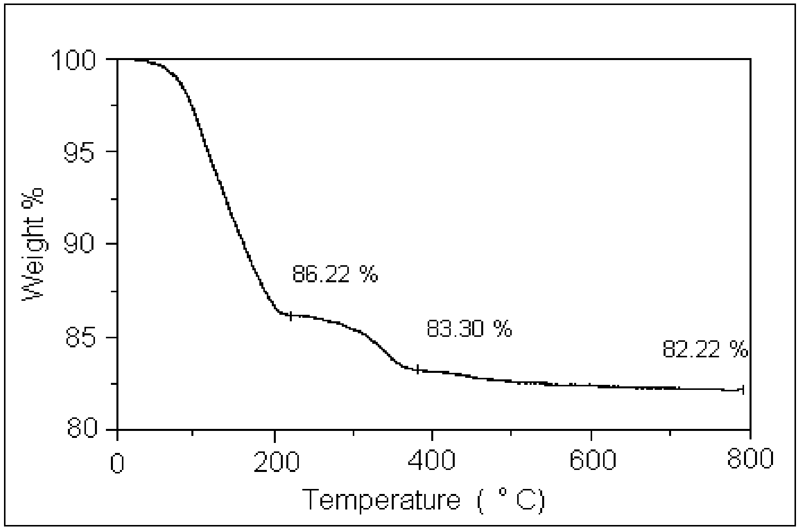
Good particle suspension

Good rheological properties for print registration

Storage stability

Adhesion/green strength after printing and drying

Burn off completely upon firing of enamel



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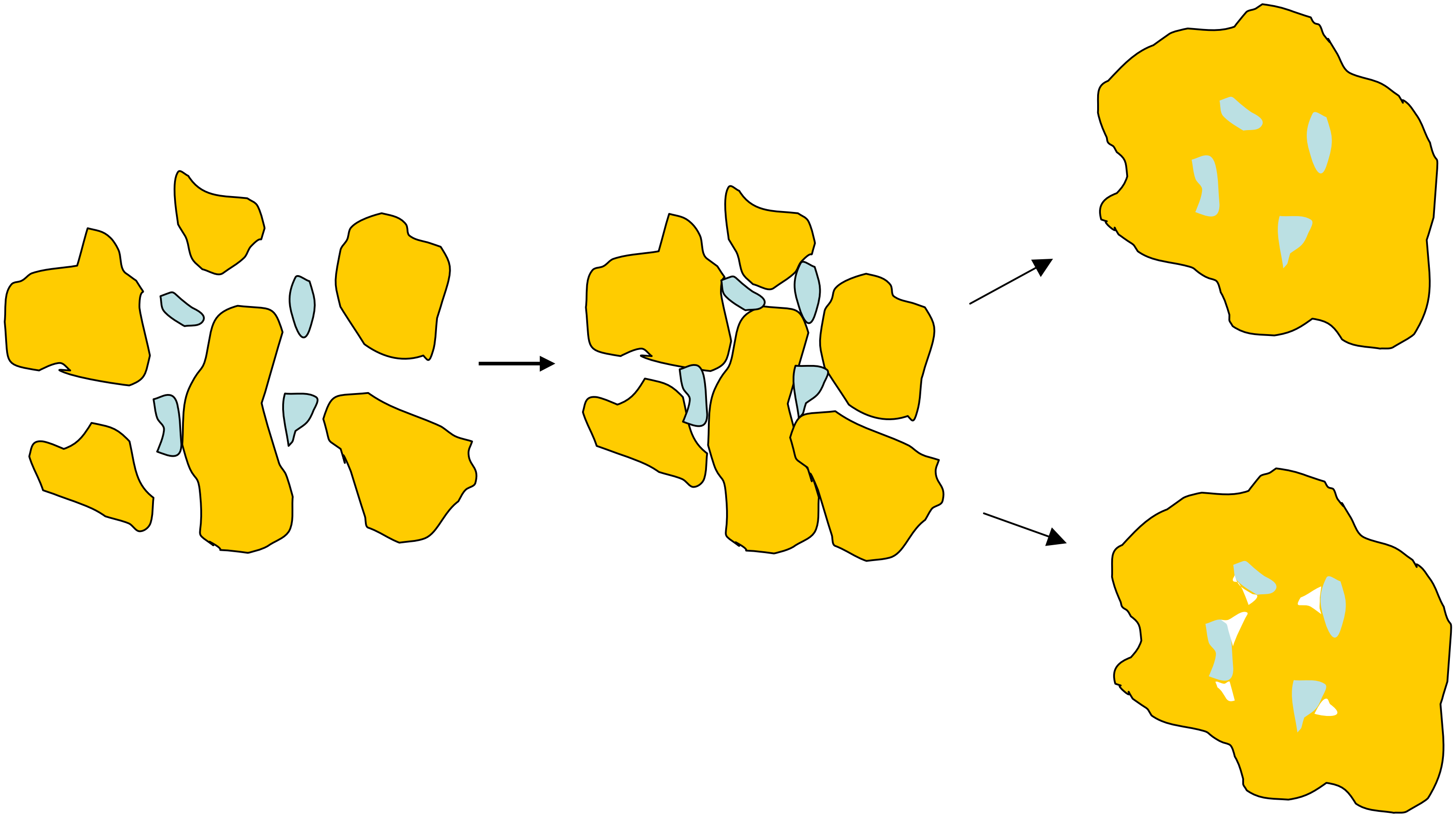
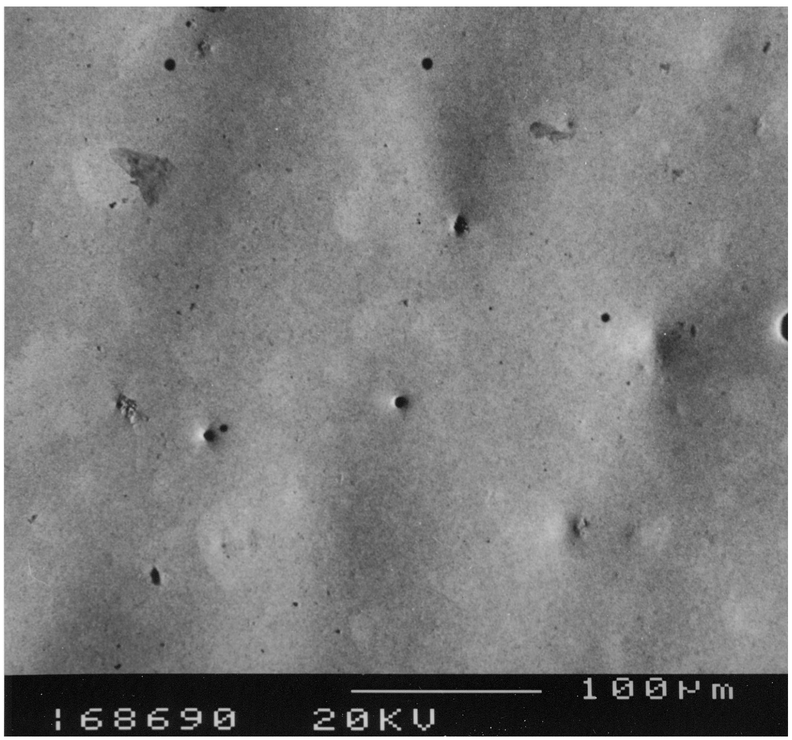
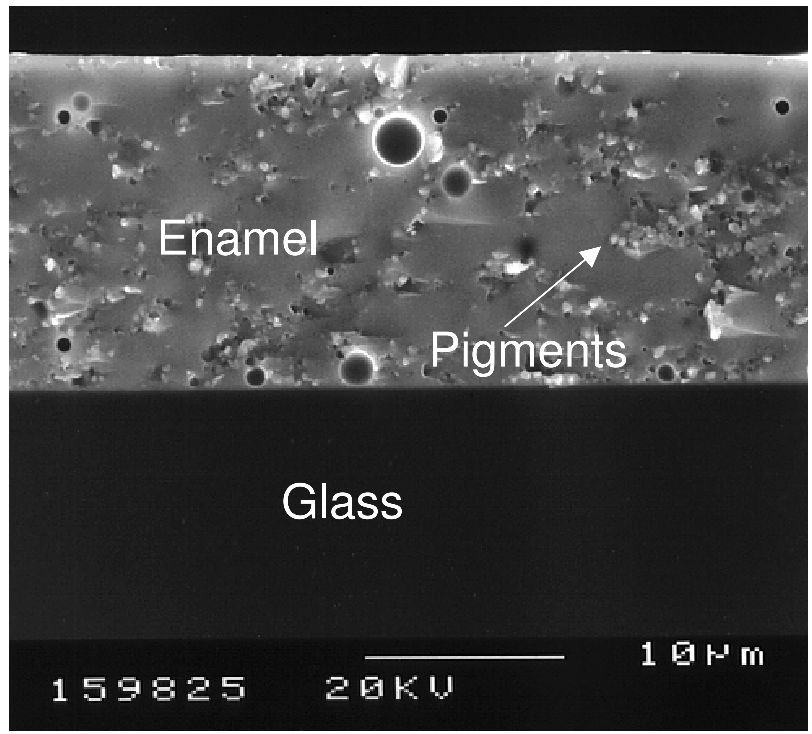
Incomplete medium burnout, residual oils, dust, can cause porosity



Pigments, Fillers, Crystallization: can inhibit sintering

Enamel layer is fused on glass surface
Pigments and additives dispersed in the molten glassflux





Fired Film Properties

Chemical durability

Opacity

High Scratch, Abrasion Resistance

Color

Gloss - Surface Roughness

Adhesive Bond Strength

Glass substrate strength

Silver bleed through resistance

High silver solder adhesion

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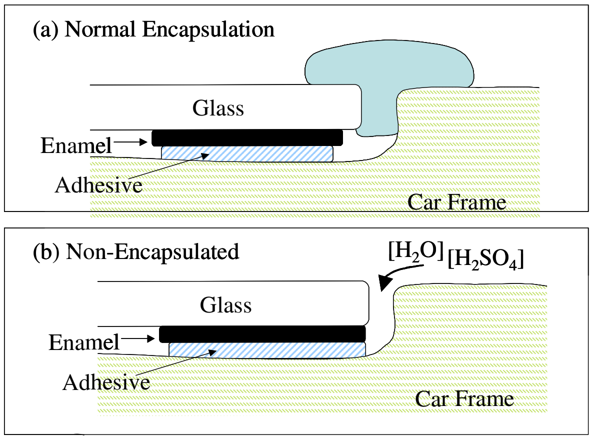
Evolution of Specifications

The globalization of a specification is an evolutionary process.

- Example, in western Japan in the mid 1990's
  - Consumer complaint regarding enamel exposed to elements
  - Industrial pollution causing acid rain leaving stains and sometimes erosion
  - A major auto manufacturer specified artificial acid rain resistance test
  - Other manufacturers also established severe acid resistance specifications
  - Could be considered a Local requirement, however, glazings supplied from several nearby countries making this a regional requirement
  - Japanese transplants to NA evolves acid resistance to a global requirement

- Automobile designs improve and reduce costs so additional enamel performance requirements will evolve
  - Edge to edge printing
  - Durability requirements



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Governmental Regulations

Safety issues such as vehicle crash strength and optical distortion

- Almost all countries have some kind of requirement concerning the strength with which glass is adhered to the frame of the vehicle
- Testing is required in a weathering chamber with exposure to intense light from an arc lamp and extreme changes in temperature and humidity.

Governmental Regulations

Environmental legislation also shapes the industry

- Waste stream disposal
  - US manufacturers were first to specify lead free compositions
  - Initiated by local costs of disposing glass fabricating plant waste streams
  - Toxicity Characteristic Leaching Procedure currently < 5ppm Pb, Cd, Cr^{+6}
- SARA Title III reporting of hazardous chemicals.
- Proposition 65 in California
- End of Life Vehicles (ELV), EU Directive 2000/53/EC
  - 1990 Germany ELV's 2 million, at 75% reuse, still resulted in 400,000 metric tons or plastic, rubber , glass in waste stream
  - Goal is 85% reuse by 2006, and 95% by 2015
  - In US ELV's 11 million/year with average of 86 Lbs of glass
  - Collection, transportation,and separation are key barriers
  - Directive also requires <1000 ppm of Pb, Cd, Cr^{+6}
- VOC Requirements
  - Non-photochemically reactive material legislation
  - Jan. 2007, CA needs to be at 120g/L VOCs

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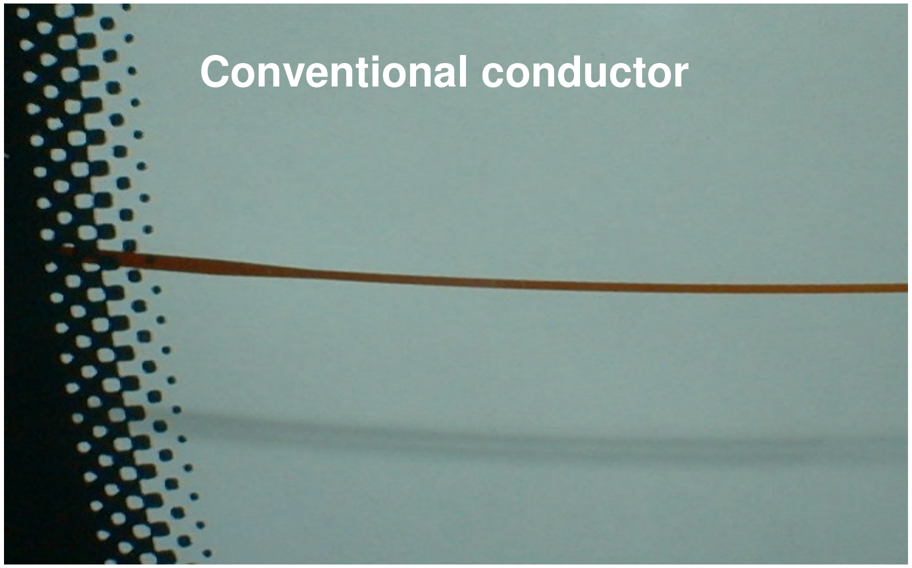
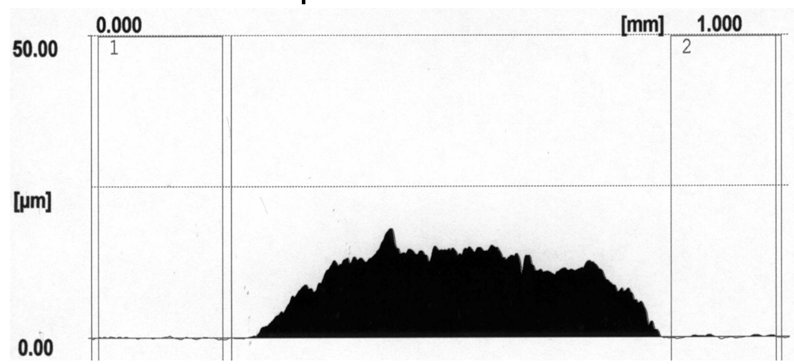
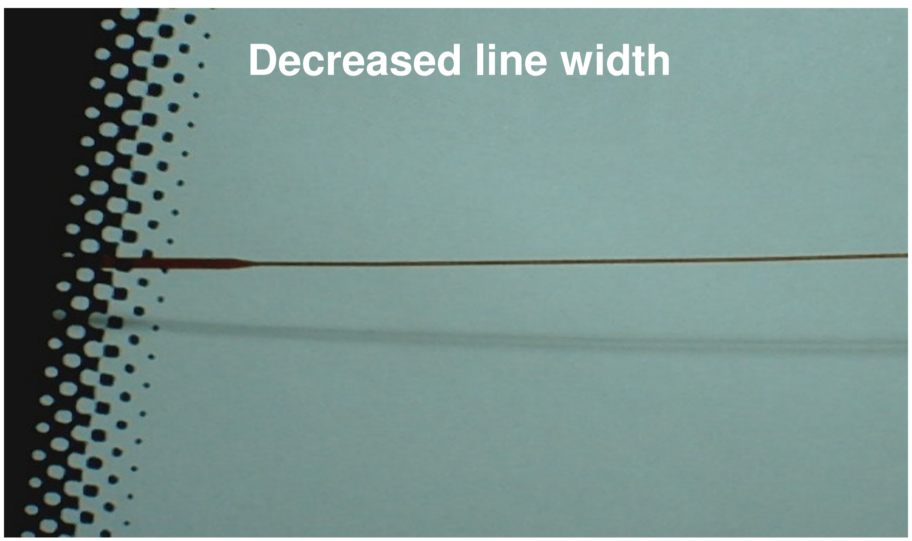
Conductive Coatings: Fine Line Silver Printing



600 to 800 µm width

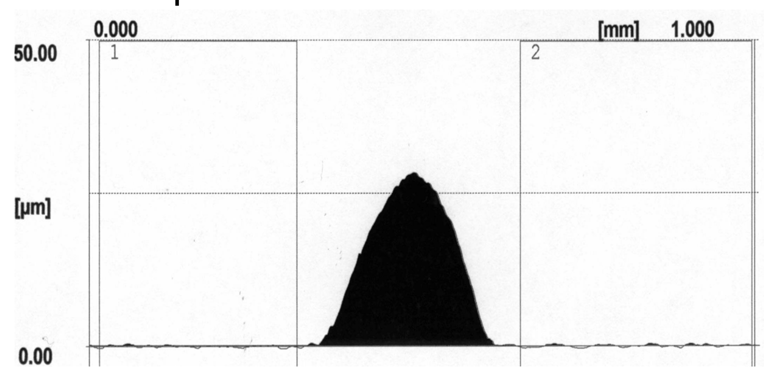
5 to 16 µm thickness





100 to 300 µm width

25 µm thickness



Specific Resistance 1 – 50 [µΩ·cm]

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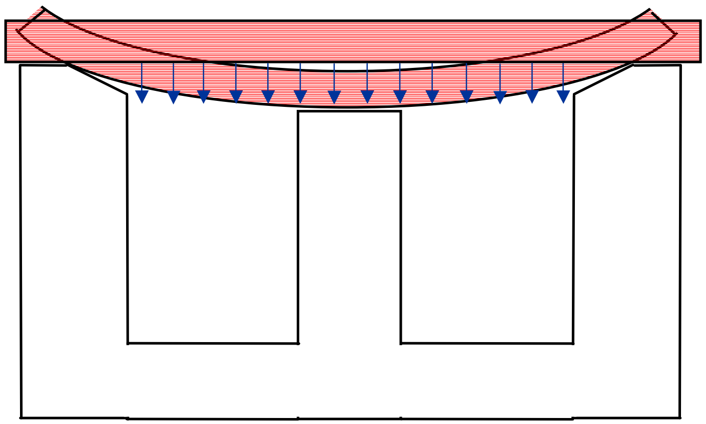
Functional Performance in the Glass Forming Process

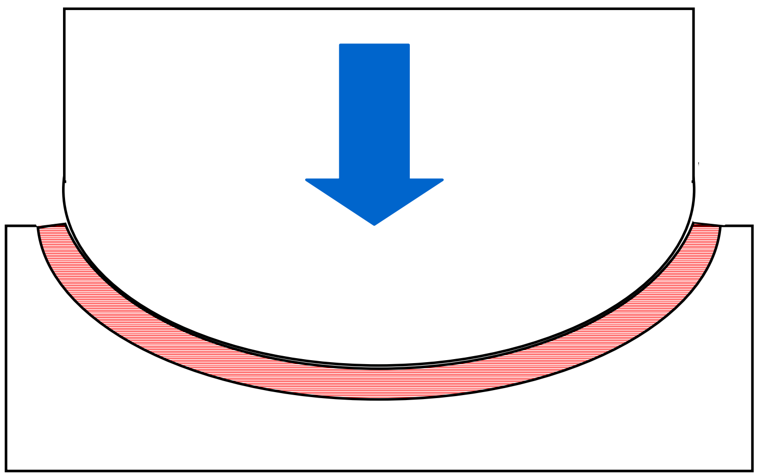
is CRITICAL

Automotive Glass Manufacturing has Evolved



Sag Bend Forming

- Slow
- Capital Intensive
- Labor Intensive
- Minor Bend Capability



Press Bend Forming

- Fast
- Reduced Labor
- Complex Bend Capability
- “Antistick” Enamel Required

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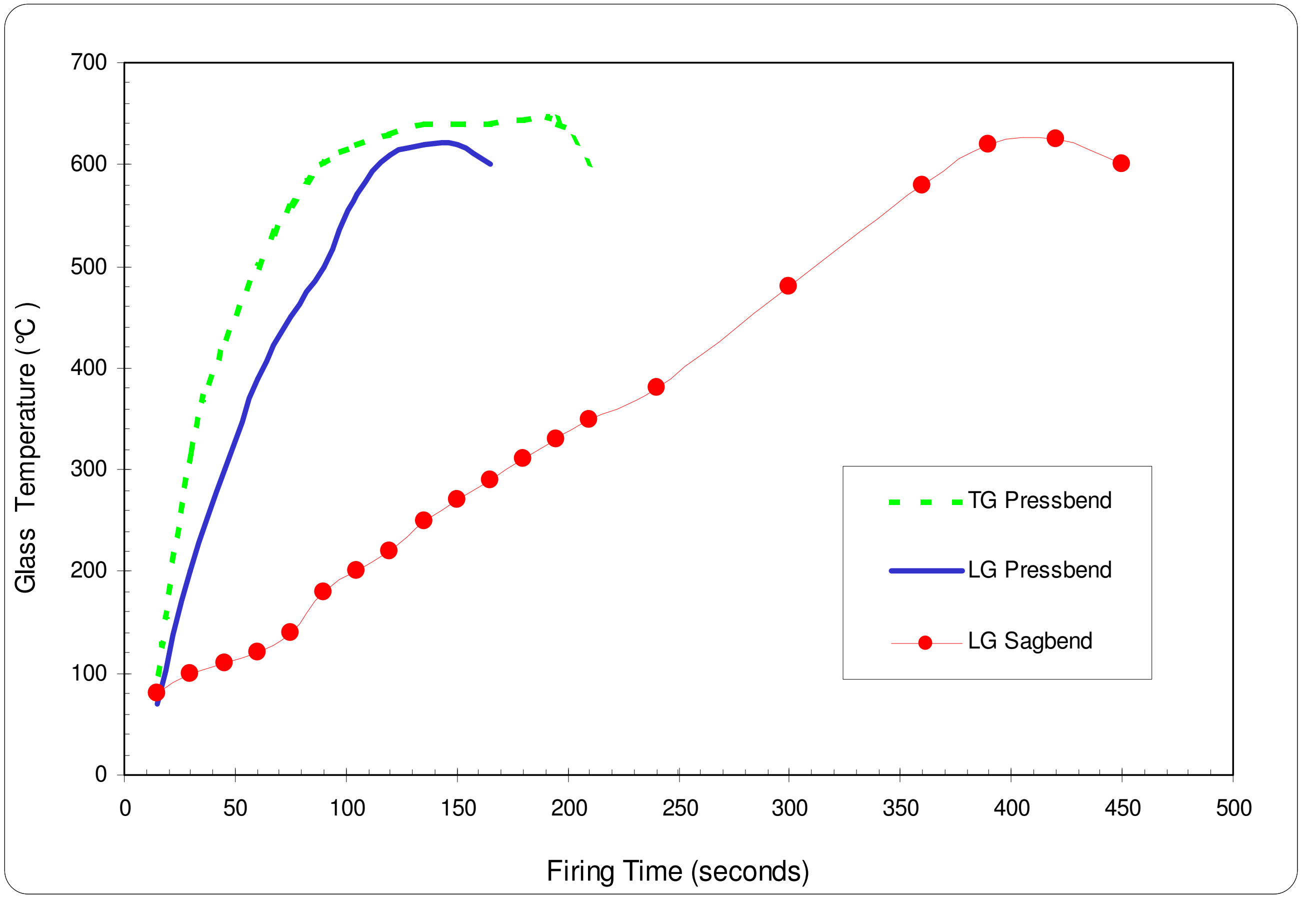
Heating curves for Automotive Glass Forming



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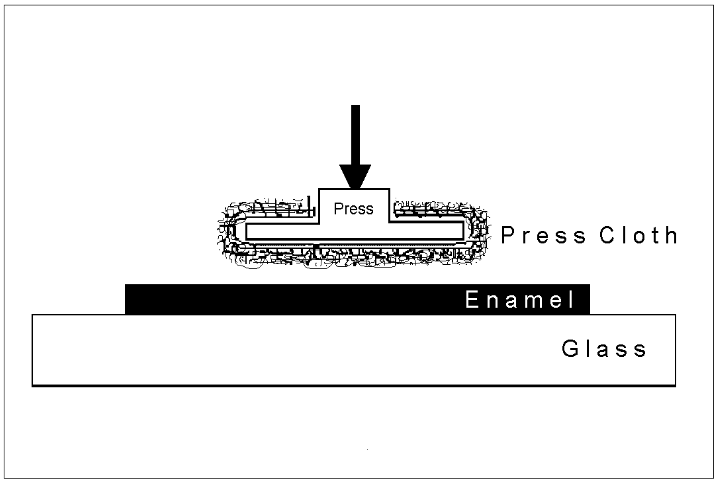
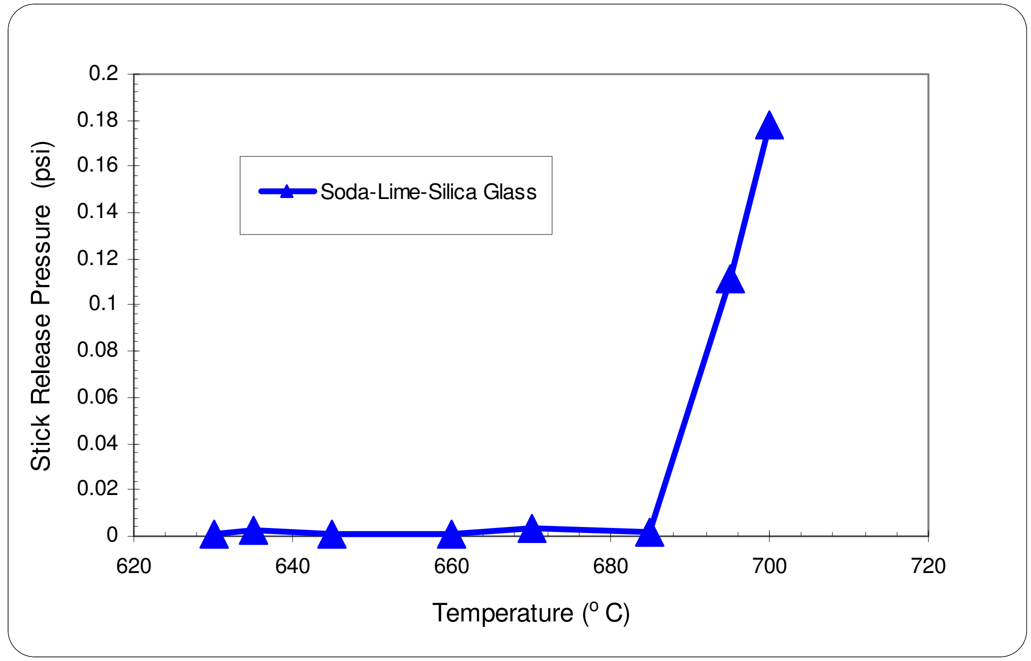
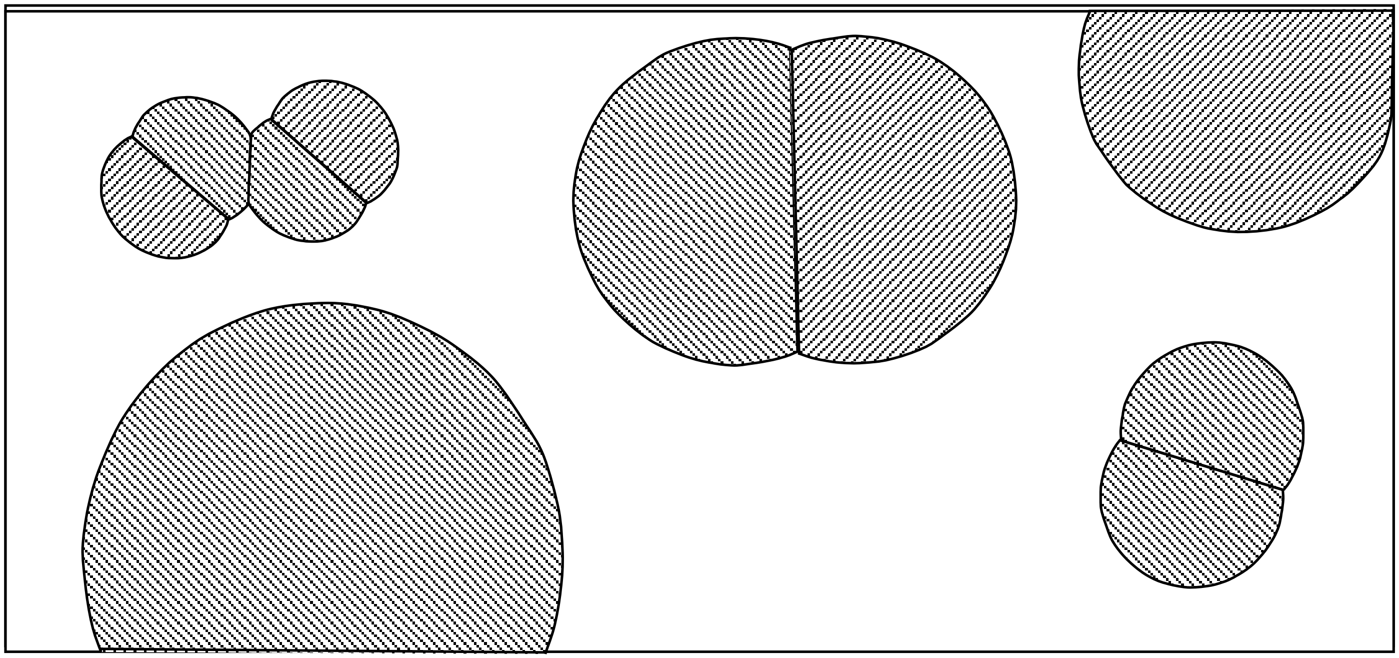
Soda-Lime Glass Substrate Stick Response Curve at 2.2 psi Pressing Pressure



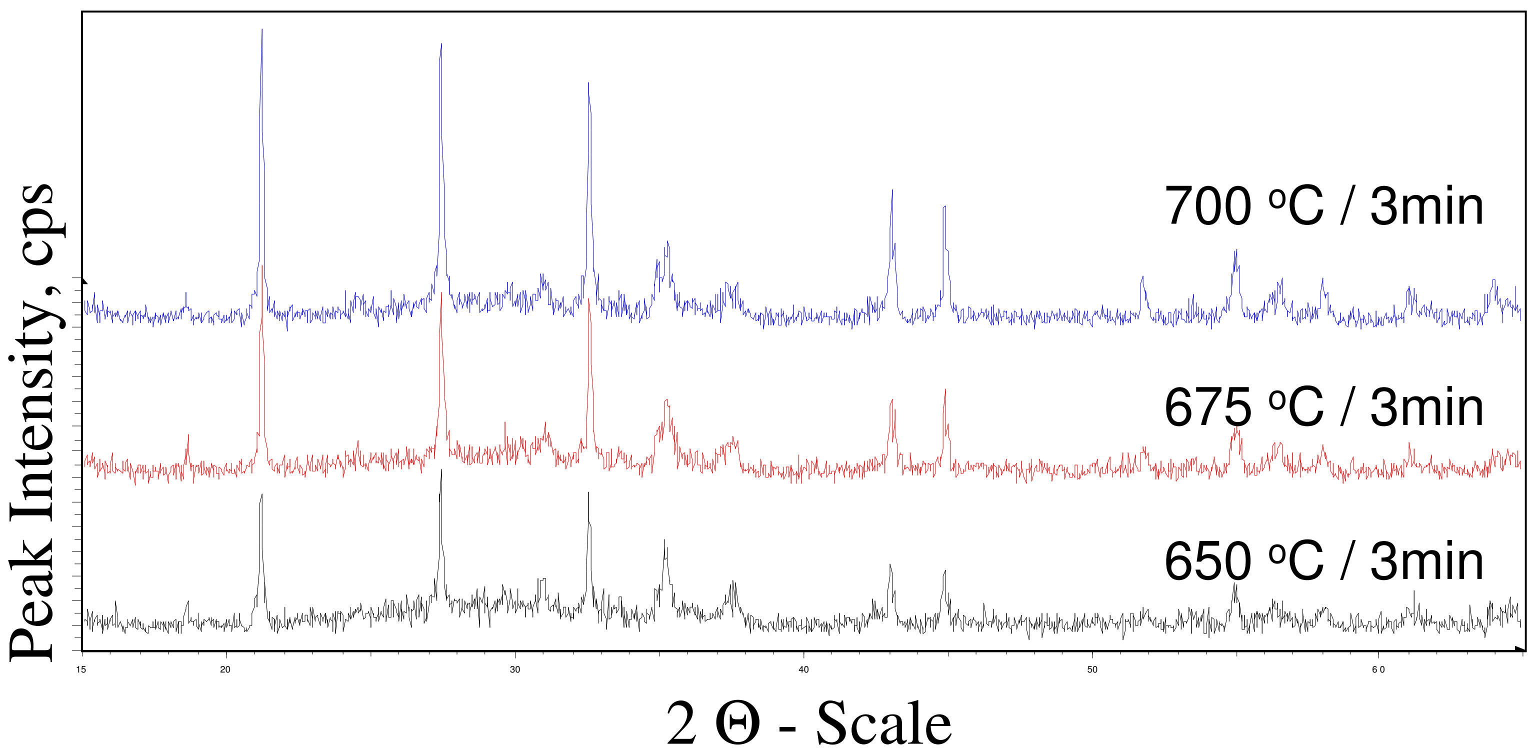


High Performance Crystallizing Enamels



Bi_2SiO_5
$Bi_4Si_3O_{12}$
$Bi_{12}SiO_{20}$

ZnB_2O_4
$Zn_3B_2O_6$
Zn_2SiO_4



700 °C / 3min
675 °C / 3min
650 °C / 3min
Peak Intensity, cps
2 Θ - Scale
15
20
30
40
50
60

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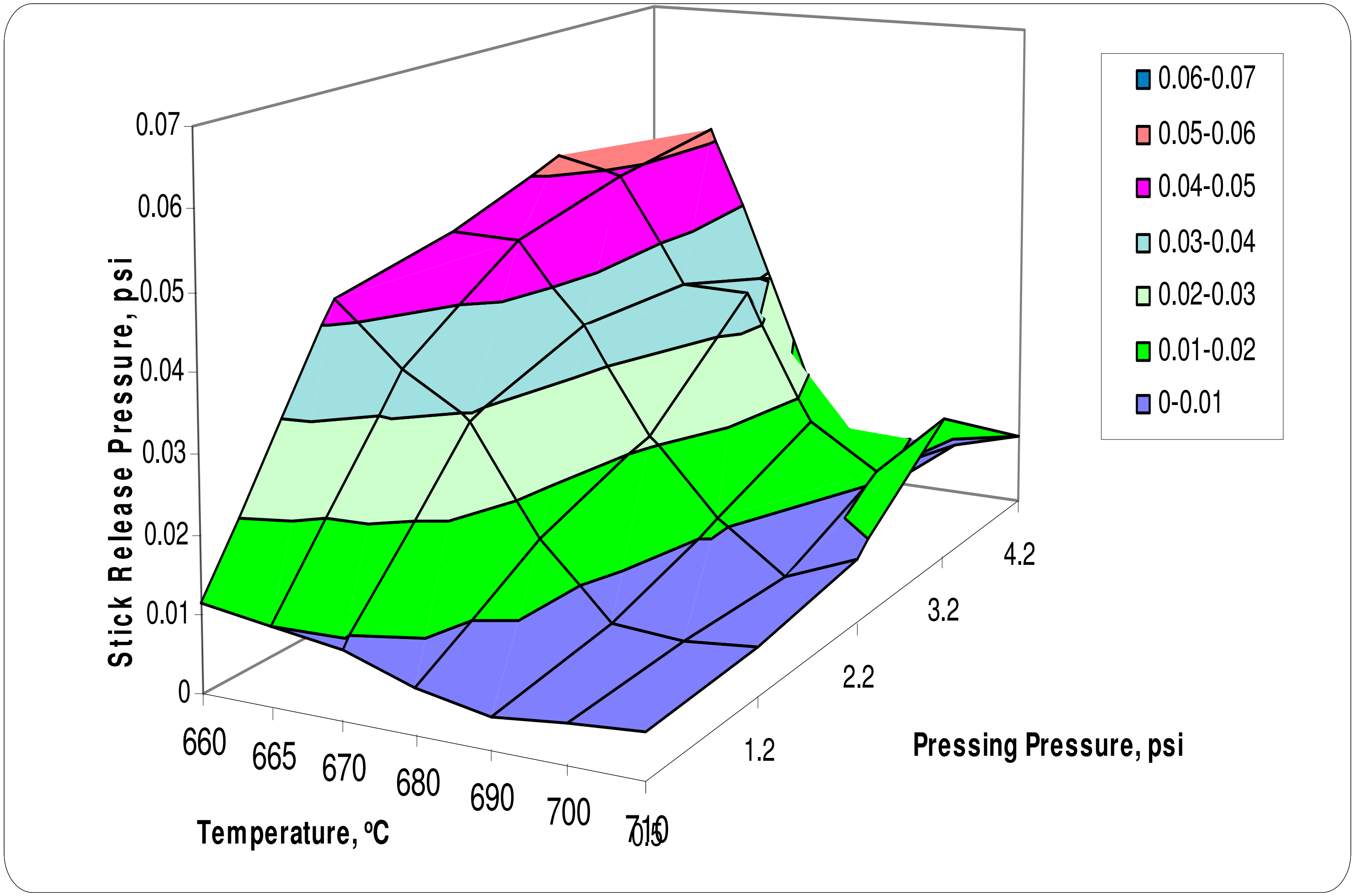
High Performance Crystallizing Enamels

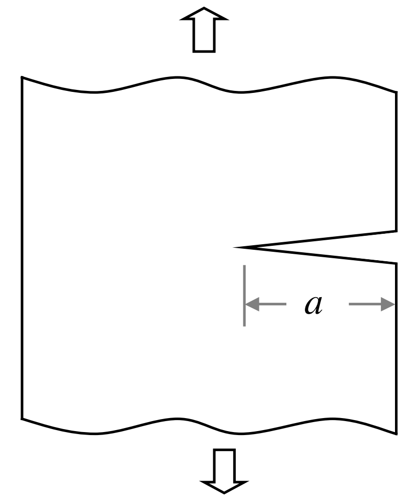


Glass Strengthening Coatings

Theoretical Strength	4×10^6 psi
Fibers in vacuum	2×10^6 psi
Acid etched & coated rod	2.5×10^5 psi
As received glass rod	6.5×10^3 psi
Severely sandblasted rod	2×10^3 psi
Design limit	1×10^3 psi

Four Conditions affect the Strength of Glass

$$K_{IC} = 1.18\,\sigma_{appl}\sqrt{\pi a}$$



- Surface Condition
- Rate of Application of Load
- Ambient Conditions
- Thermal History

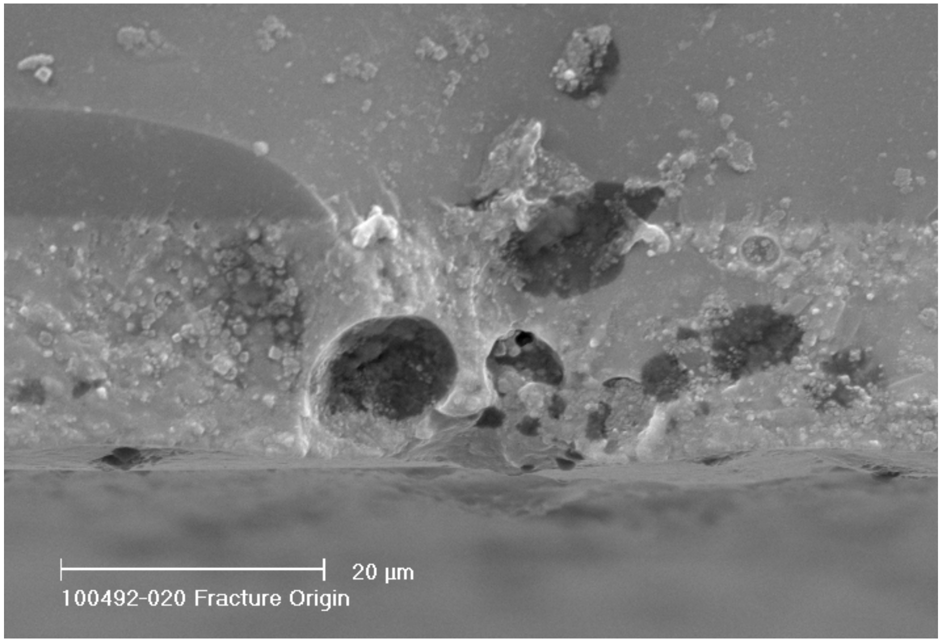
$$-[-\mathrm{Si}-\mathrm{O}-\{\mathrm{Na}\}] + H_2O \longrightarrow -\mathrm{SiOH} + Na^{+} + OH^{-}$$

$$-[-\mathrm{Si}-\mathrm{O}-\mathrm{Si}-] + OH^{-} \longrightarrow -\mathrm{SiOH} + -\mathrm{SiO}^{d-}$$

$$-[-\mathrm{SiO}^{d-}] + H_2O \longrightarrow -\mathrm{SiOH} + OH^{-}$$

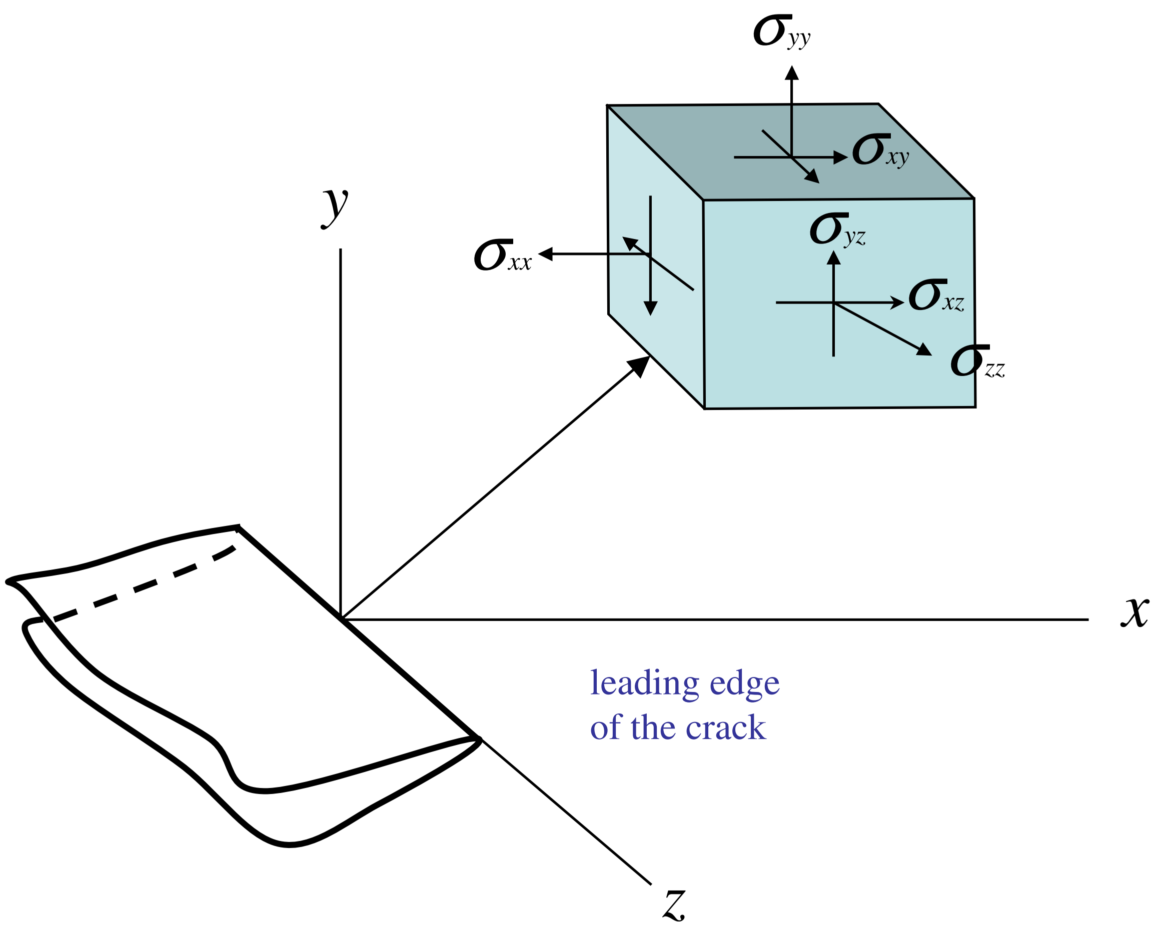
Flaw initiation and growth in the enamel dominate the failure process

- Elastic discontinuities
  - Pores
  - Pigment agglomerates
  - Pinholes
- Surface flaws
- Thickness variations



Handling of pristine glass surfaces reduces strength of un-enameled glass below enameled glass

Opportunity exists to design the stress state and microstructure to control flaw propagation in an enamel



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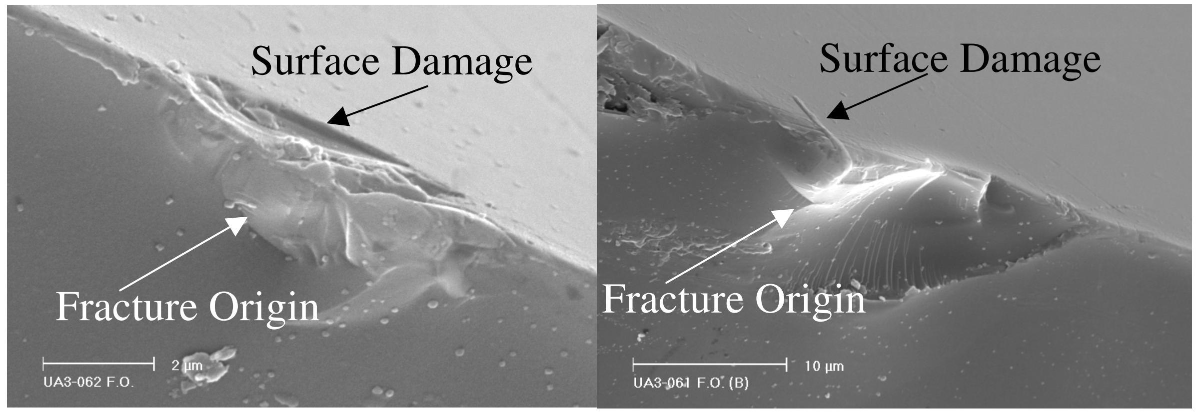
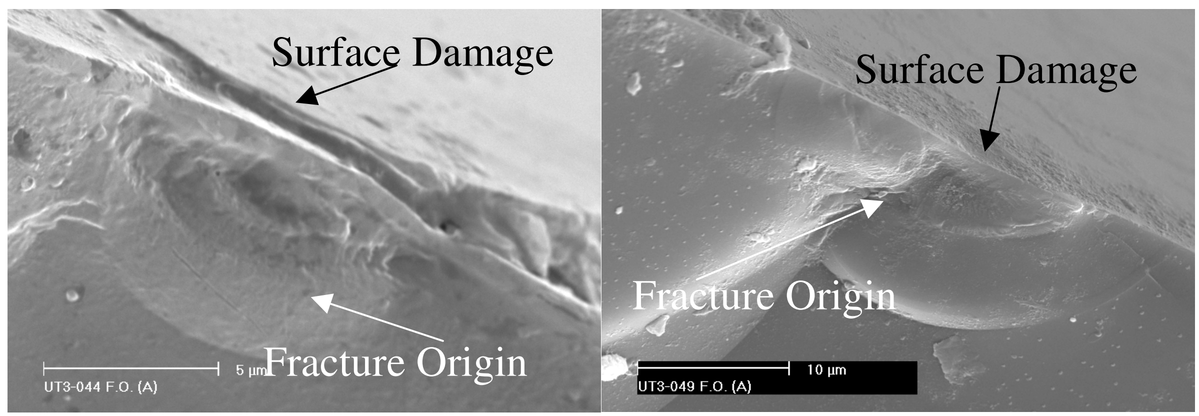
Lower strength of Tin side due to:

- More severe Flaws

- Effect of diffused tin on mechanical properties



Example of fracture origins on the tin-poor surface



Example of a fracture origin on the tin-rich surface

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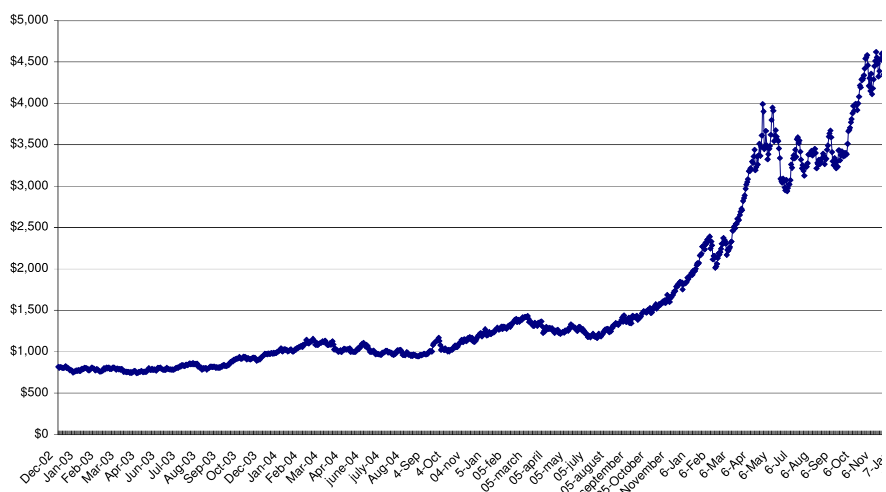
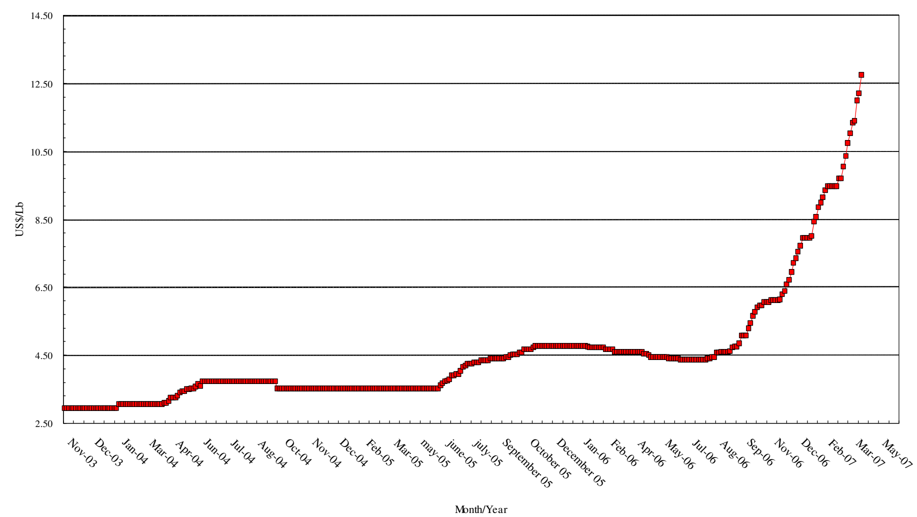
New novel low cost chemistry opportunities

LME Zinc Cash Daily Official US$ per tonne

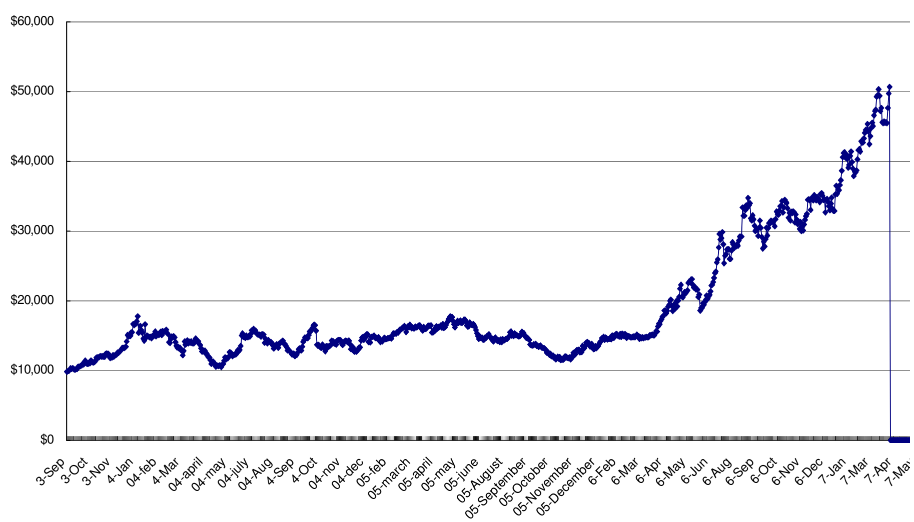


Bismuth MB free market tonne lots in WH $ per lb

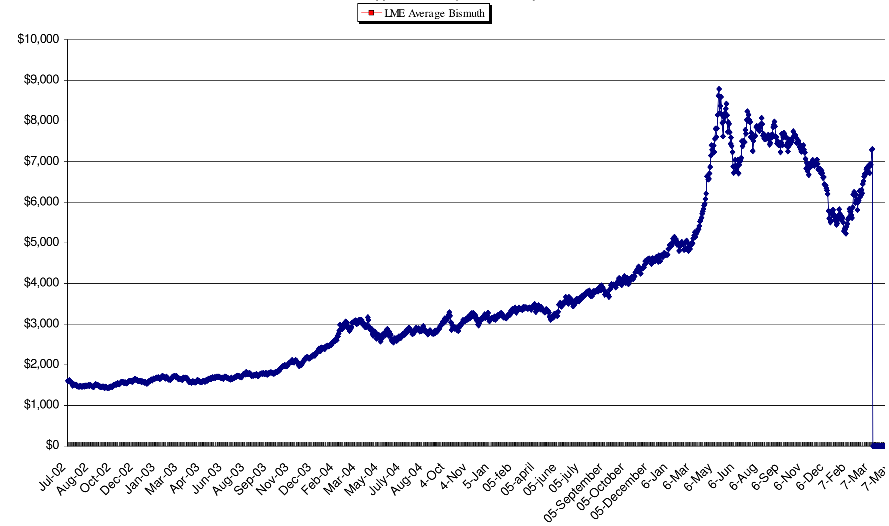
November 2003 to present



LME Nickel Cash Daily Official US$ per tonne



LME Copper Cash Daily Official US$ per tonne



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Solar Control Coatings

- According to U.S. DOE 1/3 of building's cooling load is due to solar heat gain through the building windows
  - Over 50% of the windows in non-residential buildings are energy-inefficient, doing little to reduce solar heat gain into the building

- According to EU Directorate General for Energy and Transport (01/2001)
  - Cooling consumes 4% of total energy in the tertiary sector
  - Energy use for air-conditioning will double by 2020.
  - Active and passive solar design and systems, improved daylighting and natural cooling can reduce energy demand by up to 60%

- Solar Control Glazing Definition:
  - Glazing which selectively absorbs, reflects, and/or transmits solar energy, especially in the infrared, to aid in controlling interior environments and minimizing HVAC requirements.

What is available for Solar Control today?

Heat Absorbing Tinted glass

PVB – pigmented, IR absorbing / reflecting

Reflective coatings and Reflective films

Double (triple) glazing unit + Gas fills

Multi functional thermal & solar coatings

Double skin façade + Blinder/Stores systems + Sunscreens + Natural or forced ventilation

Reflective Glass

- Ordinary float glass with a metallic coating
  - "low-E" to reduce solar heat for improved energy efficiency of buildings and automobiles.

    The energy lost through building windows in US exceeds that which travels through the Alaskan pipeline

  - Special metallic coating also produces a decorative mirror effect, preventing the subject from seeing through the glass.
  - It is mainly used in façades.
  - Other electro-optical, catalytic, or conducting properties of glass can also be achieved.

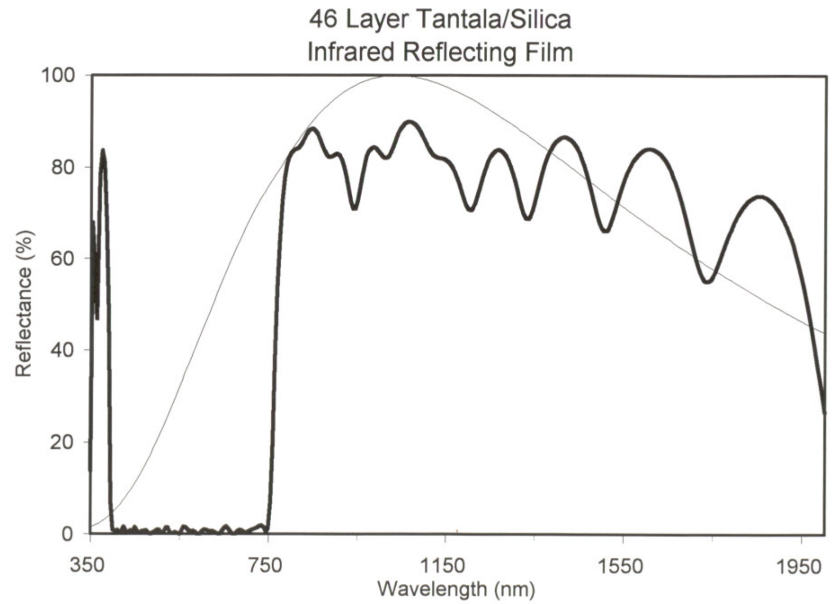
Reflective Glass Production

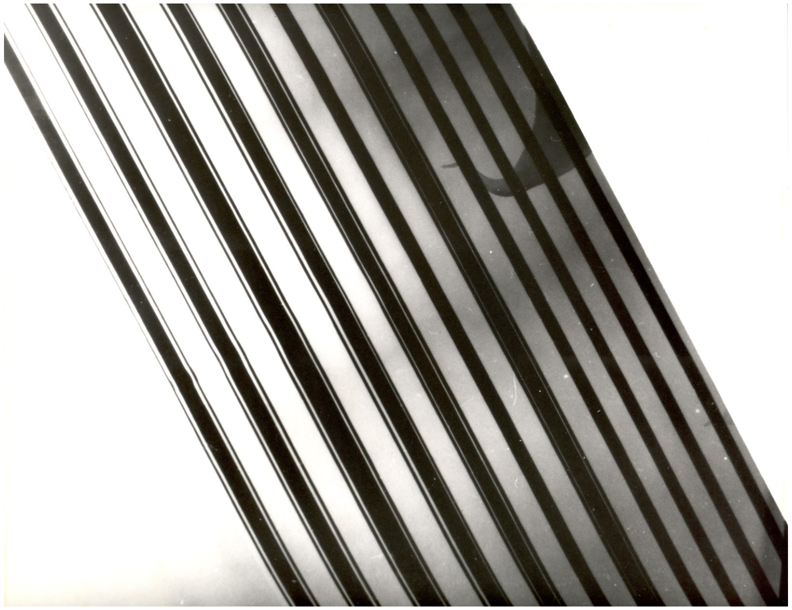
On-Line CVD or Pyrolitic processes,

- Metal oxides directly applied during the float glass production while the glass is still hot in the annealing lehr (600 – 700 ^{o}C).
- Advantages: Low cost, high productivity (300+ tons/day), hard, high density coatings with good adhesion, most elements can be deposited-unique materials with wide range of microstructures.
- Disadvantages: Complex poorly understood chemistry, on-line requires very fast deposition (60 – 100 nm/s), best case yield ~70%, solid sources difficult to vaporize, some substrates attacked by chemicals and temperatures involved, optical properties not as good as sputter-deposited coatings, not easily patternable.

Off Line Multi-Layer CVD Films

- Advantages: Very energy efficient
- Disadvantages: Expensive, high intrinsic film stresses, interference colors





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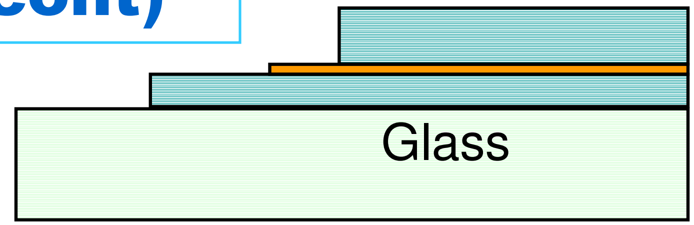
Reflective Glass Production (cont)



- Off-line PVD or Vacuum (magnetron) processes
  - One or more coats of metal oxide are applied under a vacuum to finished glass.
  - Advantages: Ability to deposit pure metals and metal compounds (oxides, nitrides, etc.), readily available precursers, better reflectors of UV and IR
  - Disadvantages: Relatively soft, cannot be used in any exposed exterior application, cannot be bent, costly-batch process, not easily patternable
- Other techniques for Off-line coating:
  - Immersion Processing
  - Foil
  - Screened glazing

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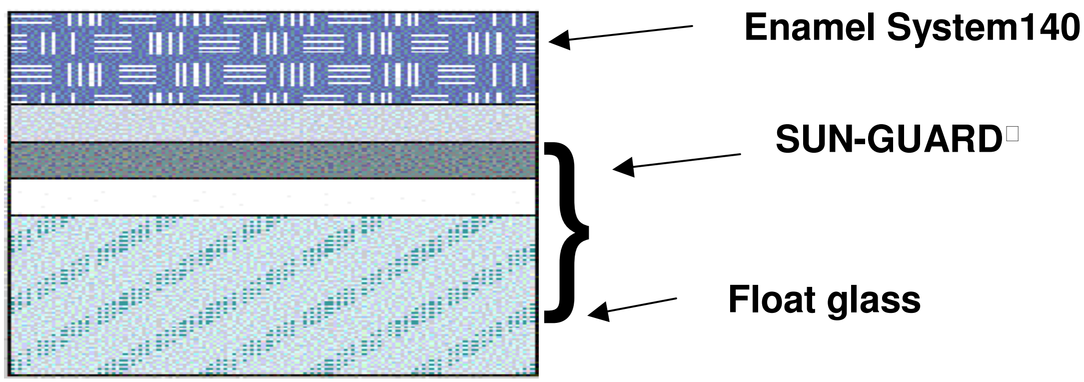

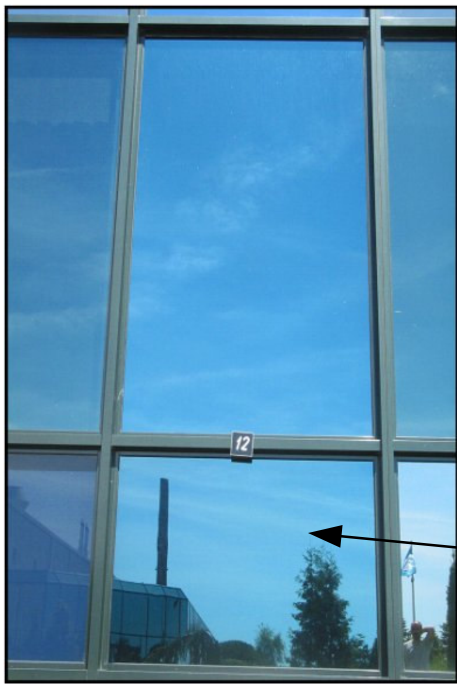

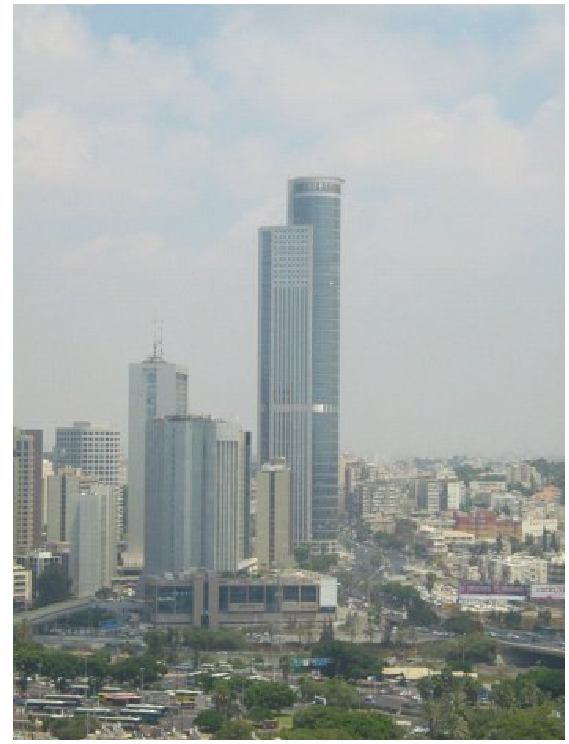

Ramat Gan Gate Tower, Tel Aviv
SUN-GUARD® Solar ***Silver Grey 32***
Spandrel: Coating + System140 ***15 4001***

Spandrel Solution:

Reflective Solar coating + Enamel

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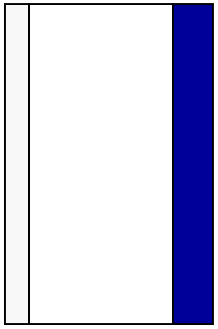
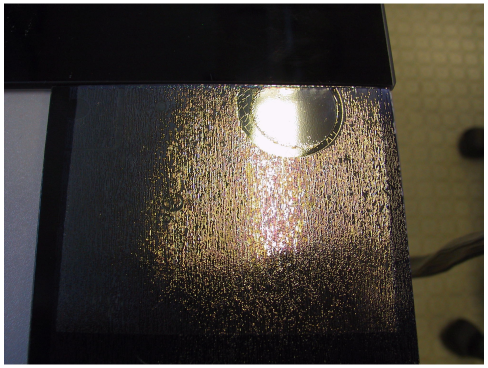
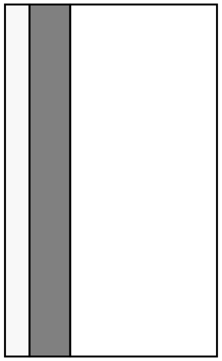
Screen Printable Reflective glass coatings

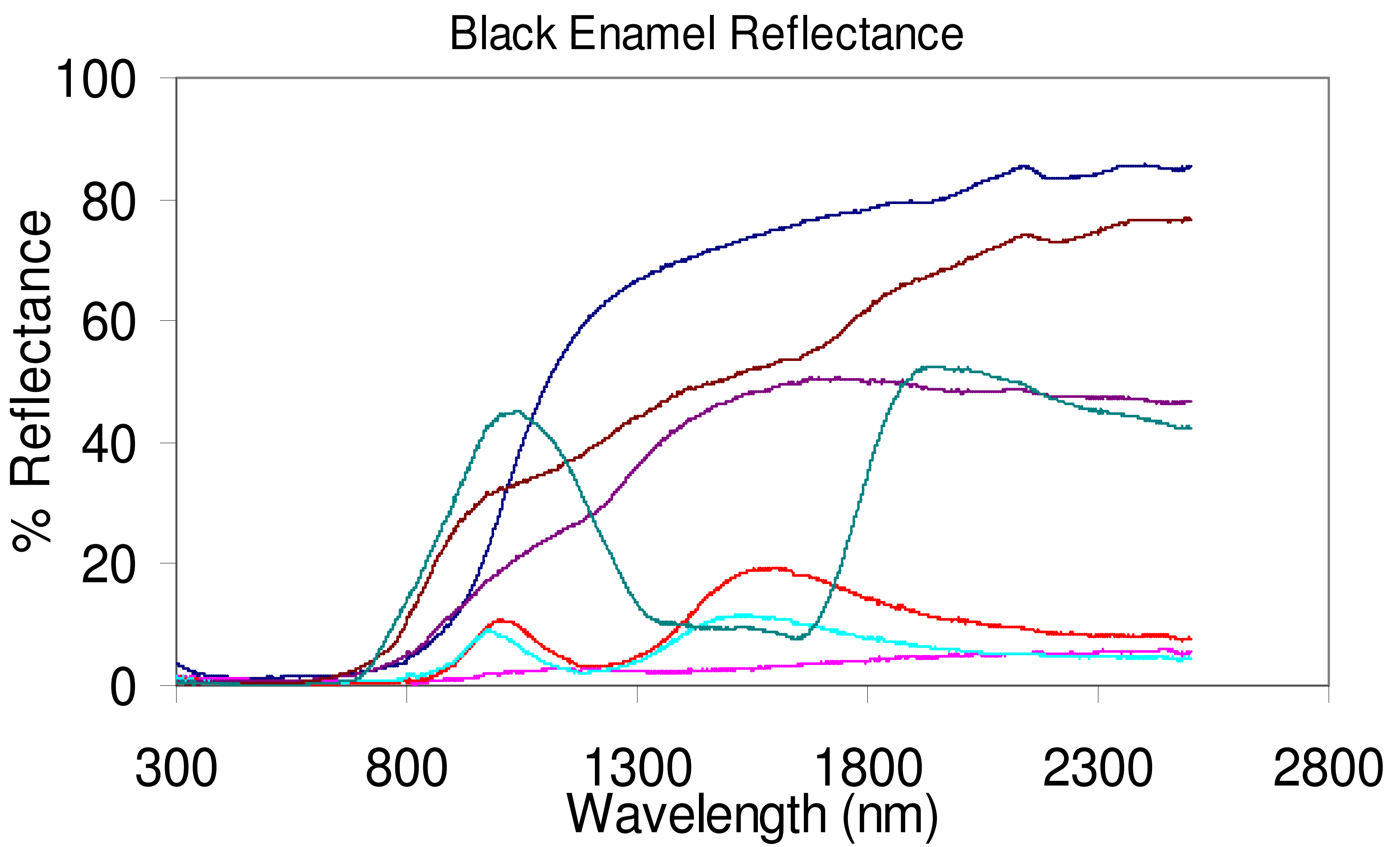


- Easy to Use
- Low Investment Necessary
- Fast
- Design Flexibility
  - Patternable
  - Large Surface Areas Possible
  - Multiple surfaces
  - Combinations with enamels
- Durable
  - Handled
  - Cut
  - Bent
  - Heat-strengthened and Tempered





Unique functional combinations with IR Reflecting Black Enamels



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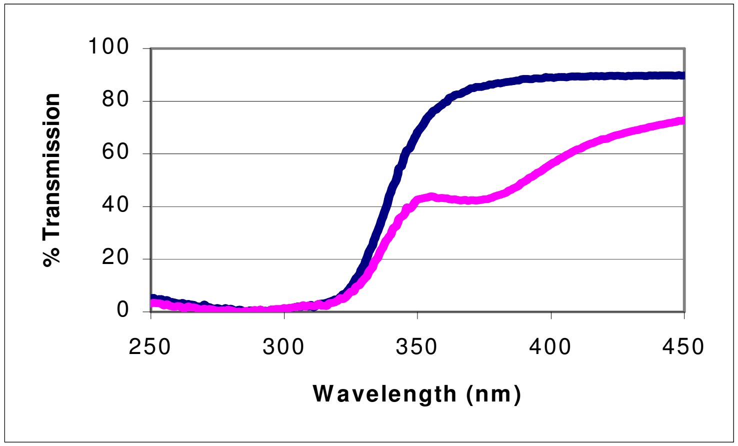
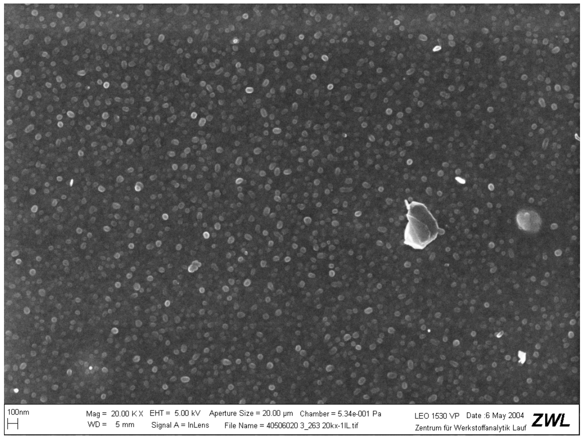
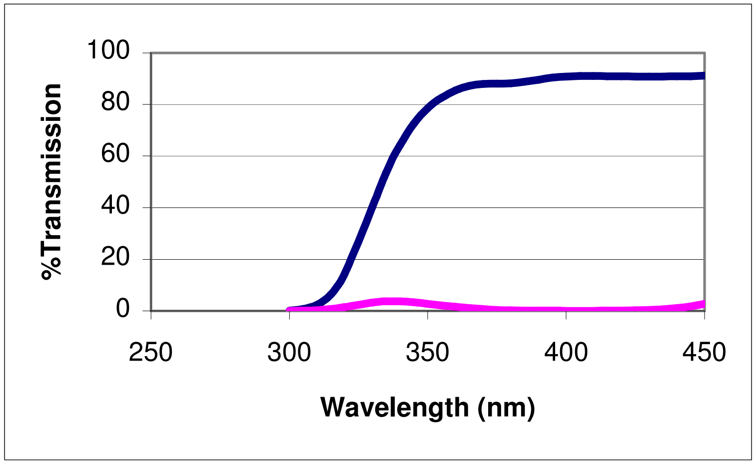
UV Functional Screenprintable nano-coatings



348-101

Blocks 50% of UV in transmission
Reflects UV
Appearance is a greenish silver





348-149A

Blocks 70-90% of UV in transmission
Absorbs UV
Appearance is a transparent amber yellow

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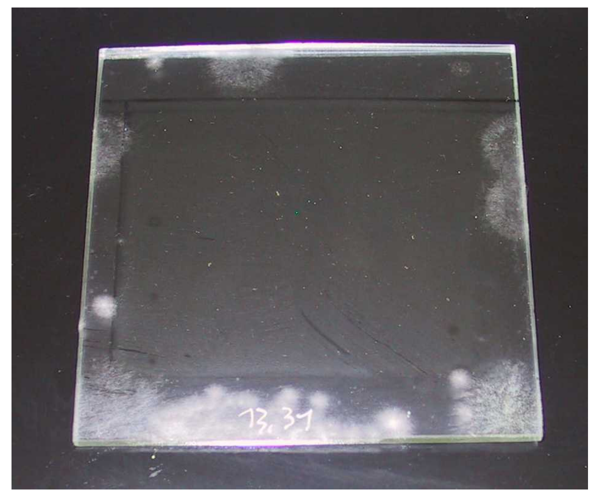
Other Reflective / Functional Nano-coating Possibilities

Optical appearance	Functionality	Status
Silver shade transparent	partially reflective photocatalytic	LustReflex TLU0050a Product
Orange shade transparent	partially reflective	Lab Formula
Gold shade transparent	partially reflective	Lab formula
Brownish transparent	partially reflective	Lab formula
Greenish transparent	antibiotic	Lab formula
Clear	antireflective	New Product
Clear	barrier	New Product
Clear	Low Condutivity 100KOhm/sq	Model



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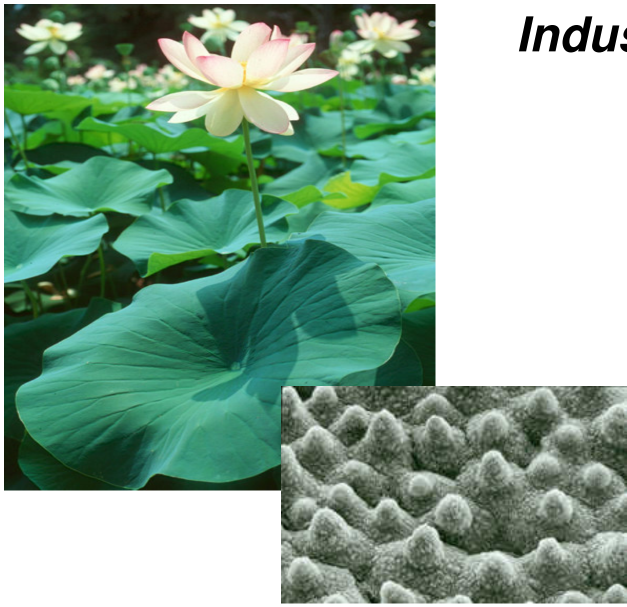
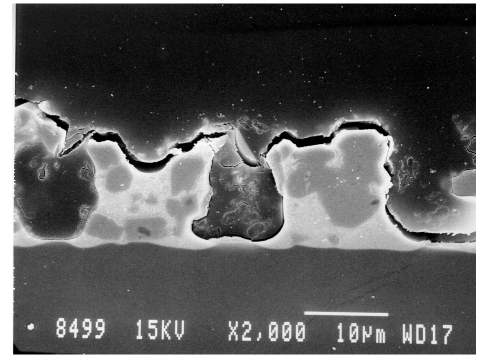
Lotus-*Effect*® a biological model

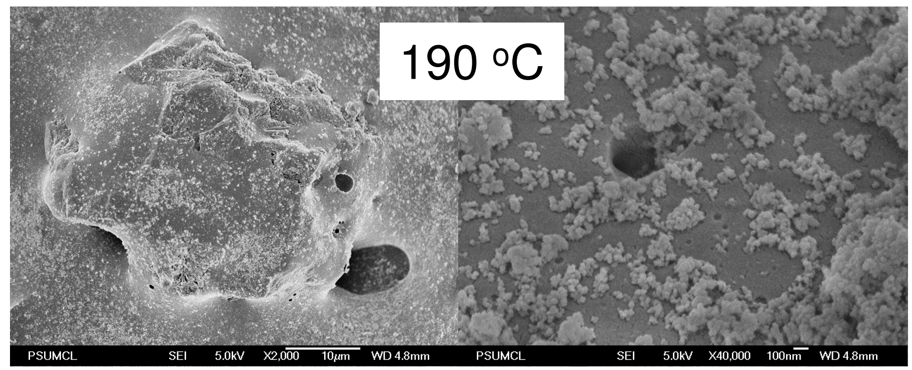


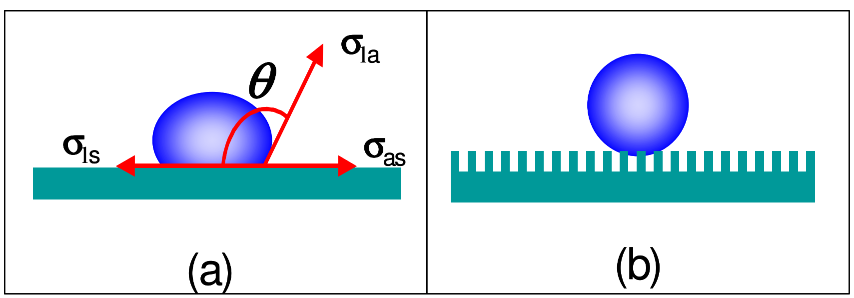
Industrial Glass Processing

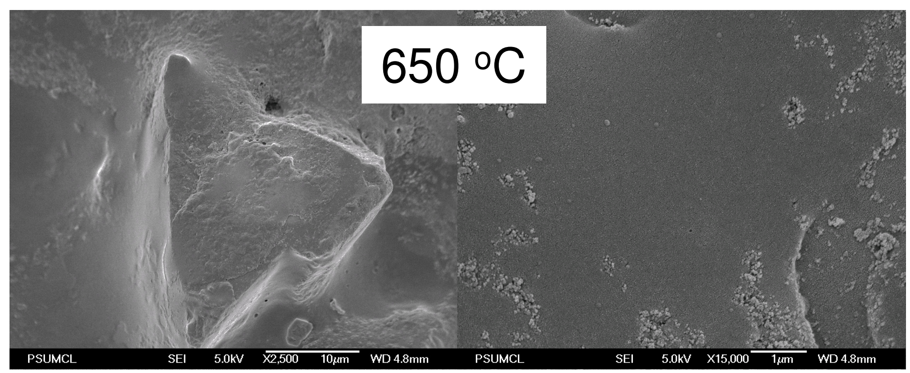
1) Base Structure coating

2) Top Hydrophobic coating









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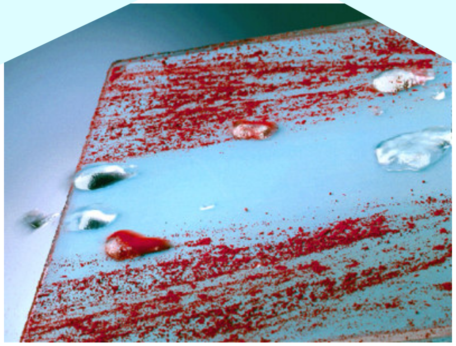
Self-Cleaning Technical Approach

Barriers	Pathways	Critical Metrics
Durability	Glass Fluxes	Mechanical abrasion resistance
	Nano-particle adhesion	Optical properties (UV, Vis, IR)
Oleo-Hydrophobicity	Sol-gel	Off-rolling angle (contact angle)
	Metal Acrylate	Chemical resistance
	New silane chemistries	Outdoor weatherability
	Hot end "float" process	Targeted product performance
	Thermal plasma spray	
	Bio-engineered self assembly (diatom)	
	Etching	



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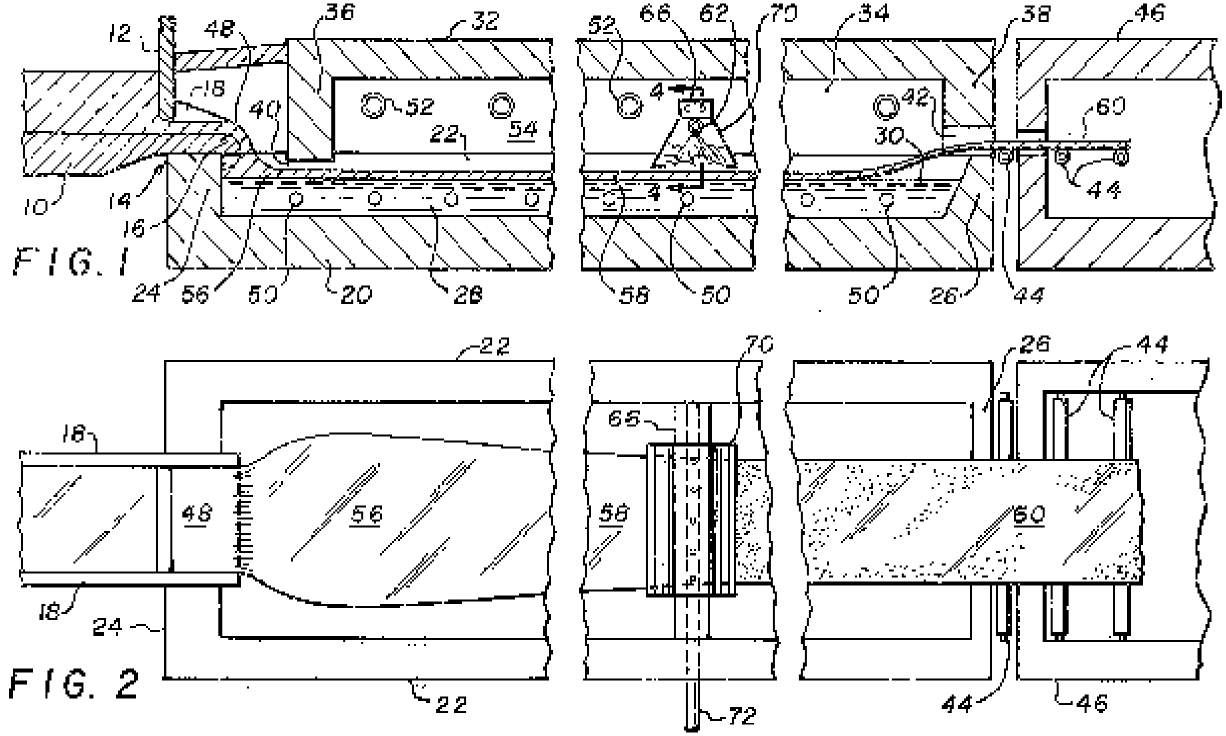
How to form a durable low cost nano-structure



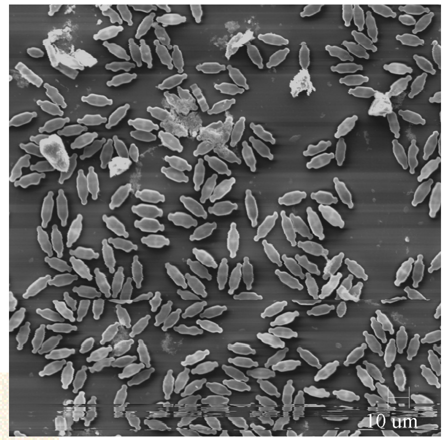
Structure during hot end forming

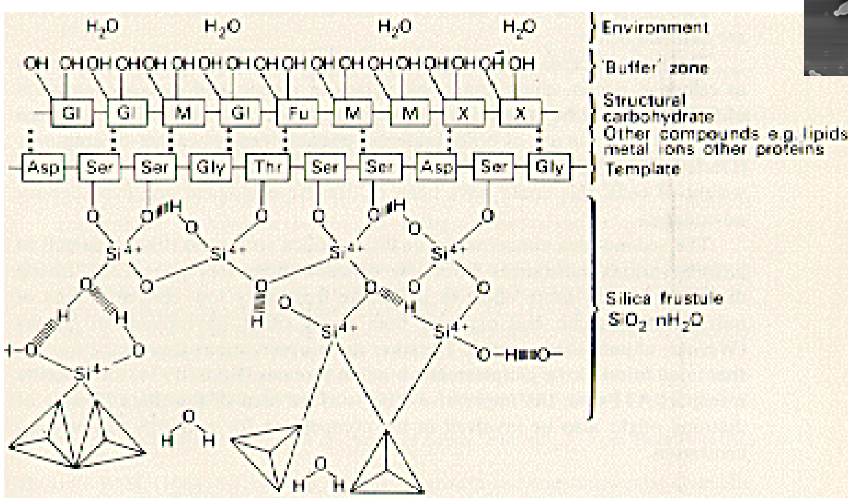
Diatom Bio-engineered Self-assembly of Smart Surfaces

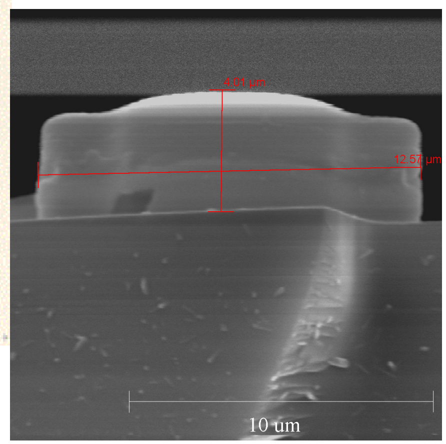
- Biology excels at bottom up fabrication
  "Master" of ambient condition materials science

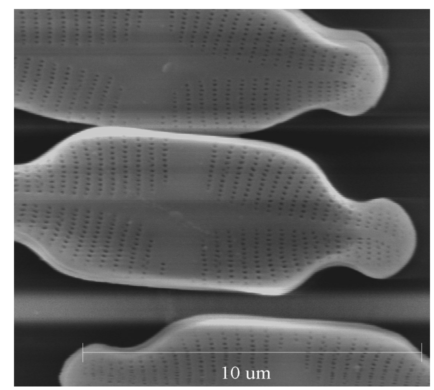
- Bio-structuring of glass surface (diatoms)
  - Set up of trials and concept ongoing
  - 2nd and 3rd species being grown

- Diatoms grown on glass.
- Panes fired at 660 C
- Spray primer and nano
- Panes fired at 350 C
- Spray primer and topcoat
- Cure at 190 deg. C









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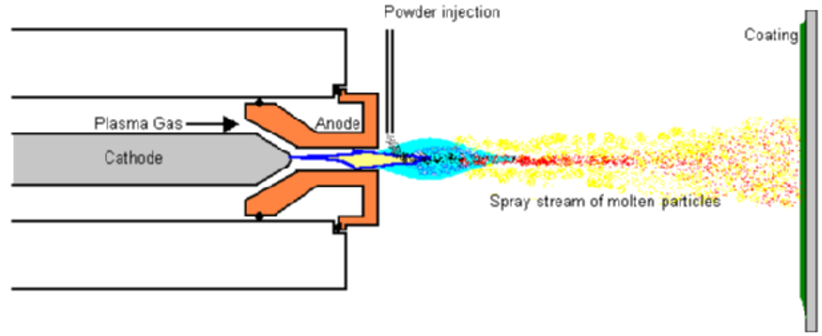
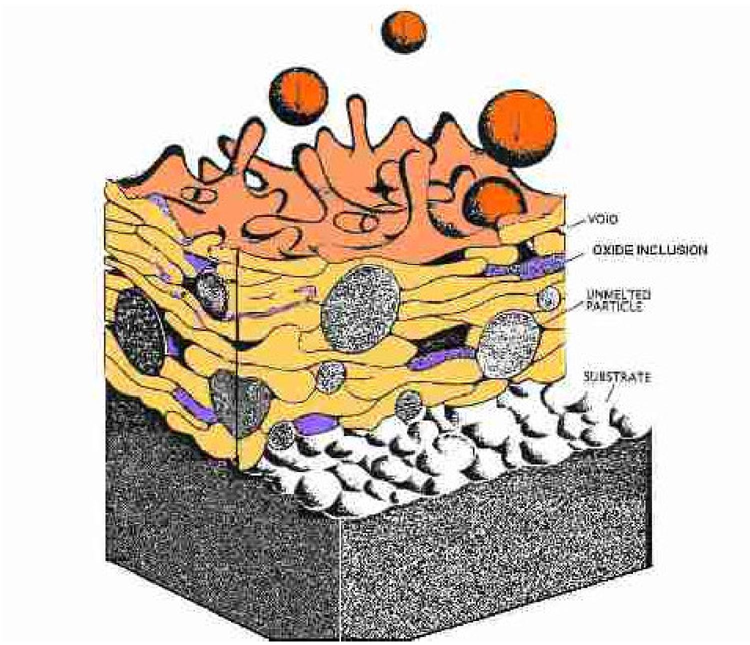
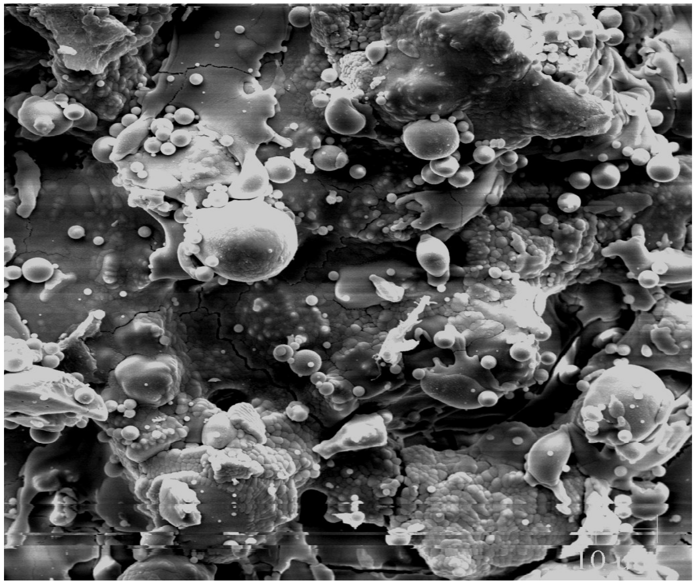
Structuring by Plasma-Spray

- Coatings made with ZrO2, Al2O3, SiO2







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Solar is a significant opportunity

• A Lotus coating potentially raises the efficiency of solar modules **by 10 %**

- self cleaning
- antireflection
- cooling
- avoiding hot spots)

• Solar Cells have been built

• A G-Plus Project has been written and submitted to DOE.

Organic Coatings

New Technology

Low Temperature

Heavy Metal Free

Thermoplastic

UV

Waterborne

Pencil hardness: 3H to 5H

Solvent resistance: 100+ acetone rubs w/o effect

Tape adhesion: no loss after 30 minutes boiling water

Dishwasher: 300+ cycles with no effect

Future Challenges

- Faster Cure Inks
- Lower Cost
- Flat Glass:

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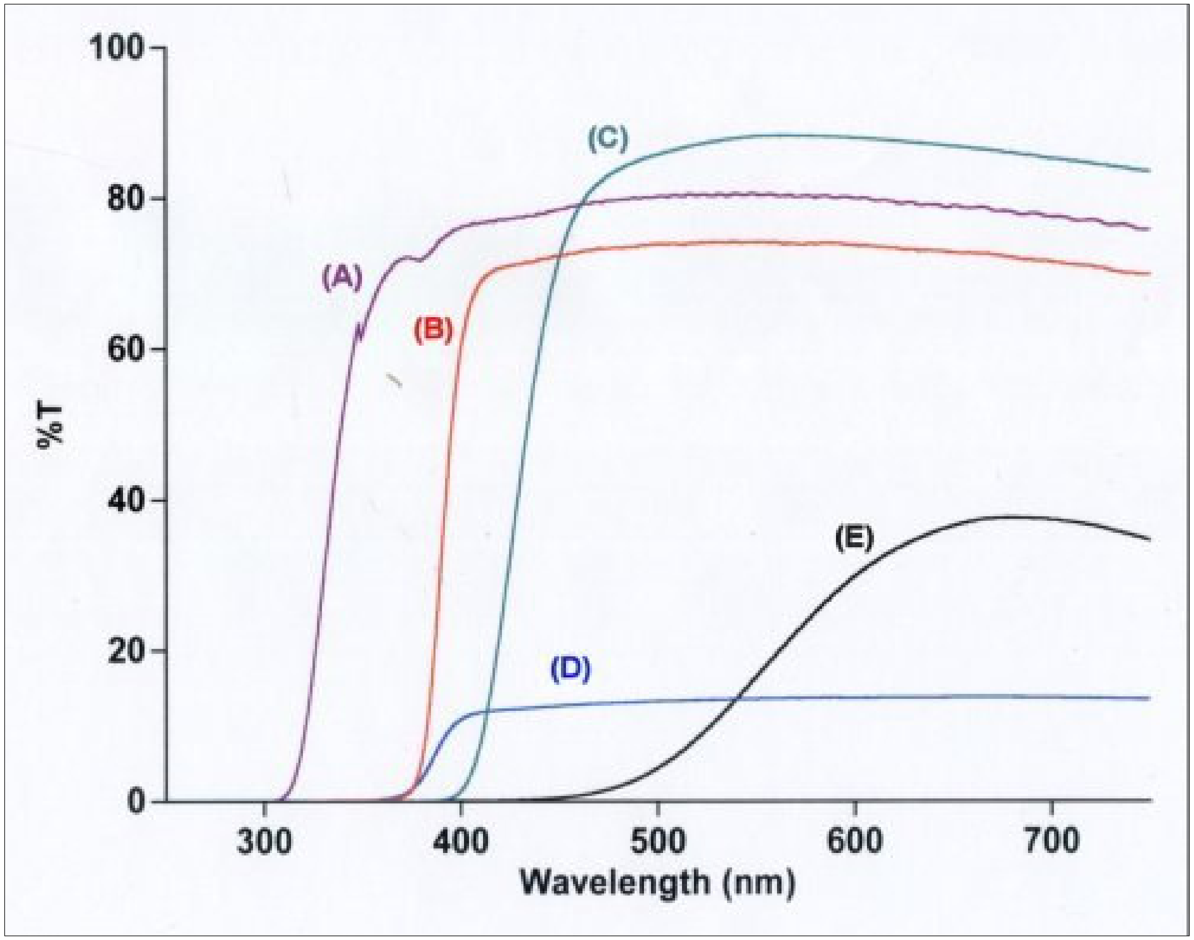
New technologies:

Protective coatings: selective protection from ultraviolet and/or select wavelengths of visible light.



(A) Flint glass

(B) UV blocking clear – no absorbance in visible

(C) UV blocking to 400 nm pale yellow in color

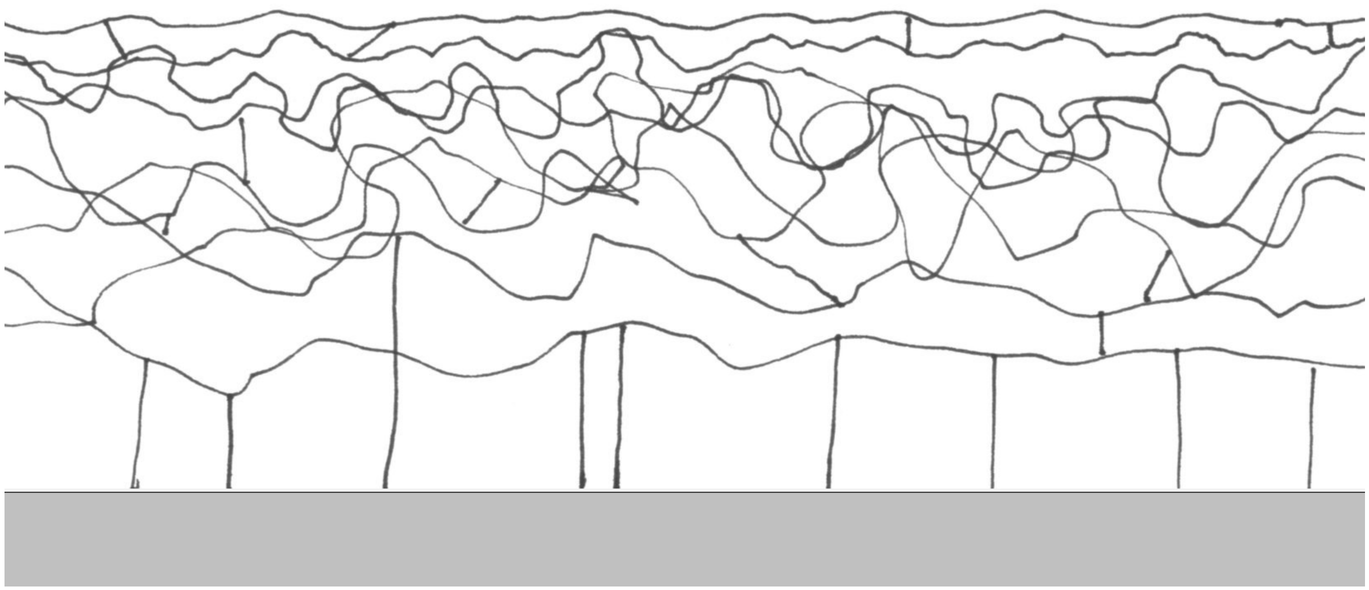
(D) UV blocking frost – only 20% transmittance in the visible region

(E) Amber glass

Krongauz, V., Schmid, S., Vandeburg, J., *Progress in Organic Coatings* 26 (1995)

Kapp, D., SGCD, San Diego Ca, 9 (2000)

Polymer to glass bonding only takes place at discrete locations, where the silane binds to the glass surface.



Water can penetrate the polymer film and ‘pool’ underneath, then dissolve the silane-glass bond.

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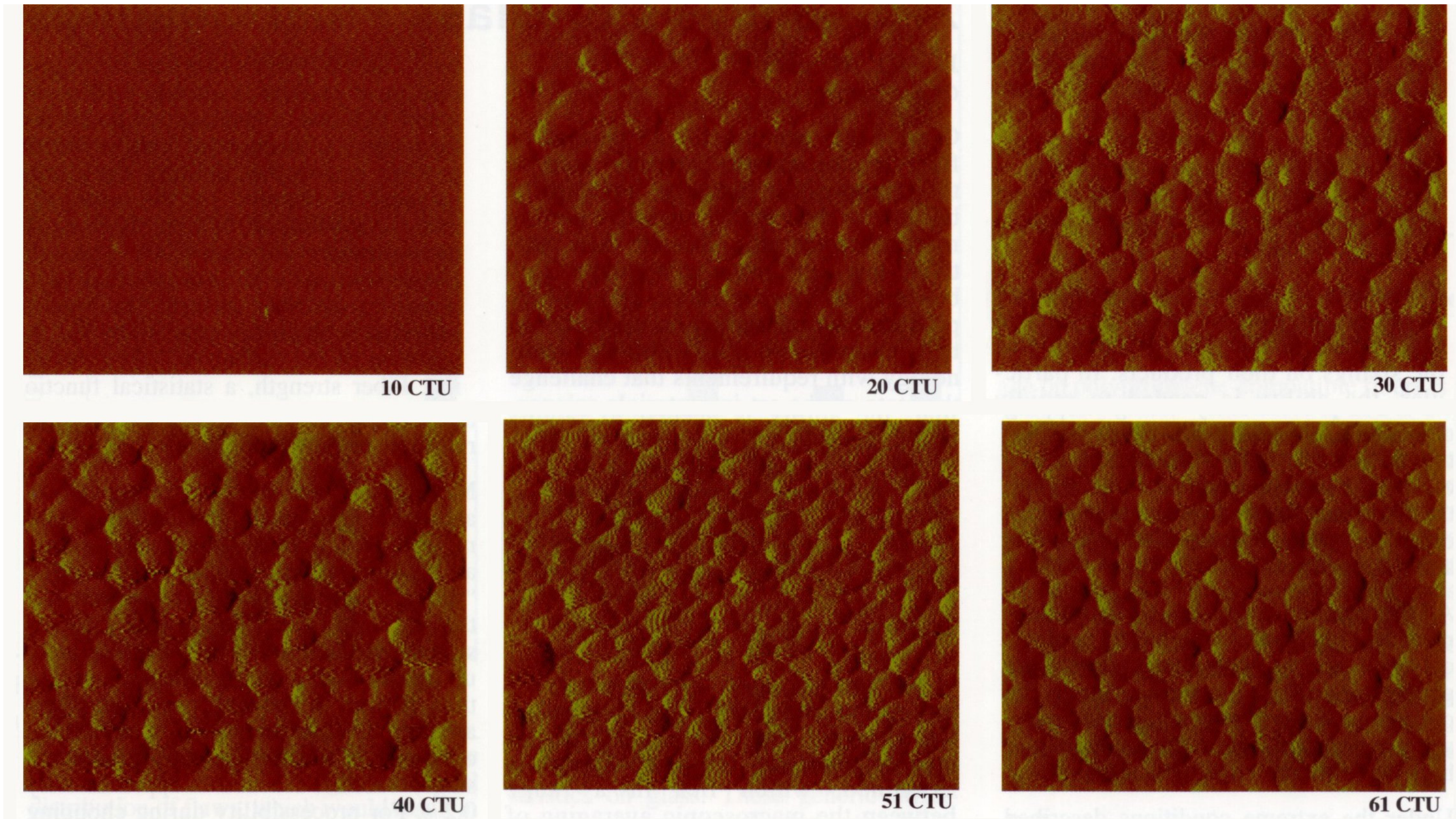
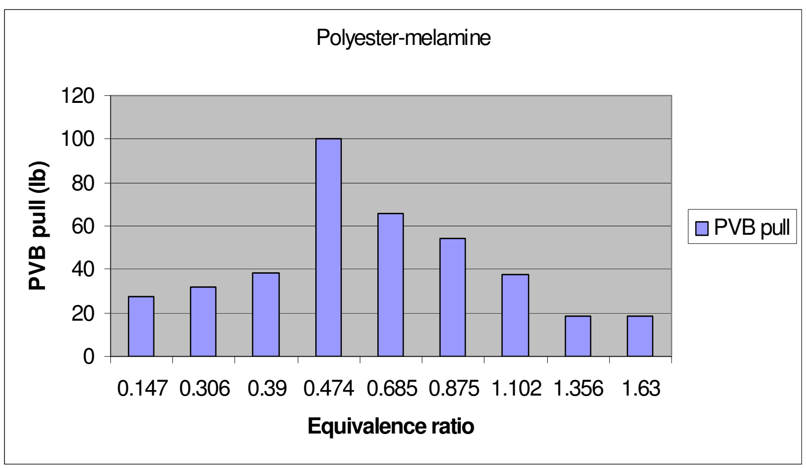
Pantano, C., Bojan, V., Smay, G., *The Glass Researcher* Vol. 9 No. 1 (2000) 12-13

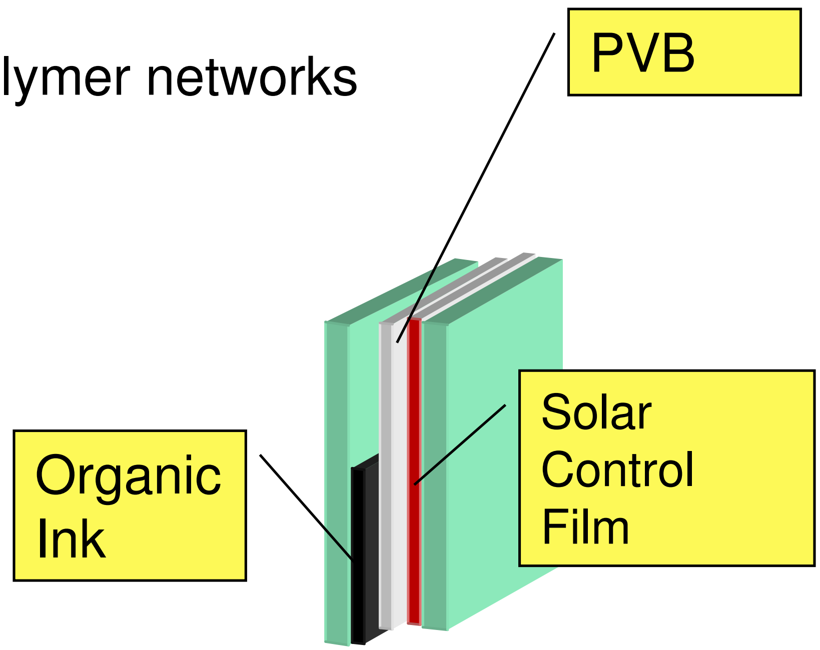


Tin increases the three dimensional nature of the surface and replaces the glass surface with a tin oxide surface.

Organic Coatings for Flat Glass

- New flat glass decoration technology
- Well suited for flat laminated safety glass
- Heavy metal free
- Low energy, fast process
- $$ cost effective
- Easy to handle, acceptable shelf life
- Key to adhesion between acetal film and organic coatings is controlling the degree of interpenetration between the two polymer networks





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Conclusions

- Glass forming processes becoming more severe
- Protective and aesthetic functions must be maintained
- High Performance functionality is critical to success
- Nano-structured glass surfaces can enable
  - Energy savings
  - Homeland security-increased blast and hurricane resistance, improved sensors
- Globalization and Environmental legislation will continue to shape the glass industry

Challenges Summary

- New low melting (Tg<400 ^{o}C), low cost, environmentally friendly chemistries
- Low VOC, low Td application mediums
- New high volume defect free surface processing
- Surface protective or healing coatings
- Understanding nature of glass surface – organic bonding
- Characterization of nano-structures
- Processes to form durable nano-structures
- Understanding how strong is a nano-structure

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- *Thank you*