ENJEUX ET OPPORTUNITÉS DES MODIFICATIONS SURFACIQUES DU VERRE LORS DE L'ÉMAILLAGE

DAMIEN MEY
SAINT-GOBAIN RESEARCH COMPIÈGNE

Ecole Thématique 2023: Surfaces et interfaces du verre

SAINT-GOBAIN RESEARCH COMPIEGNE

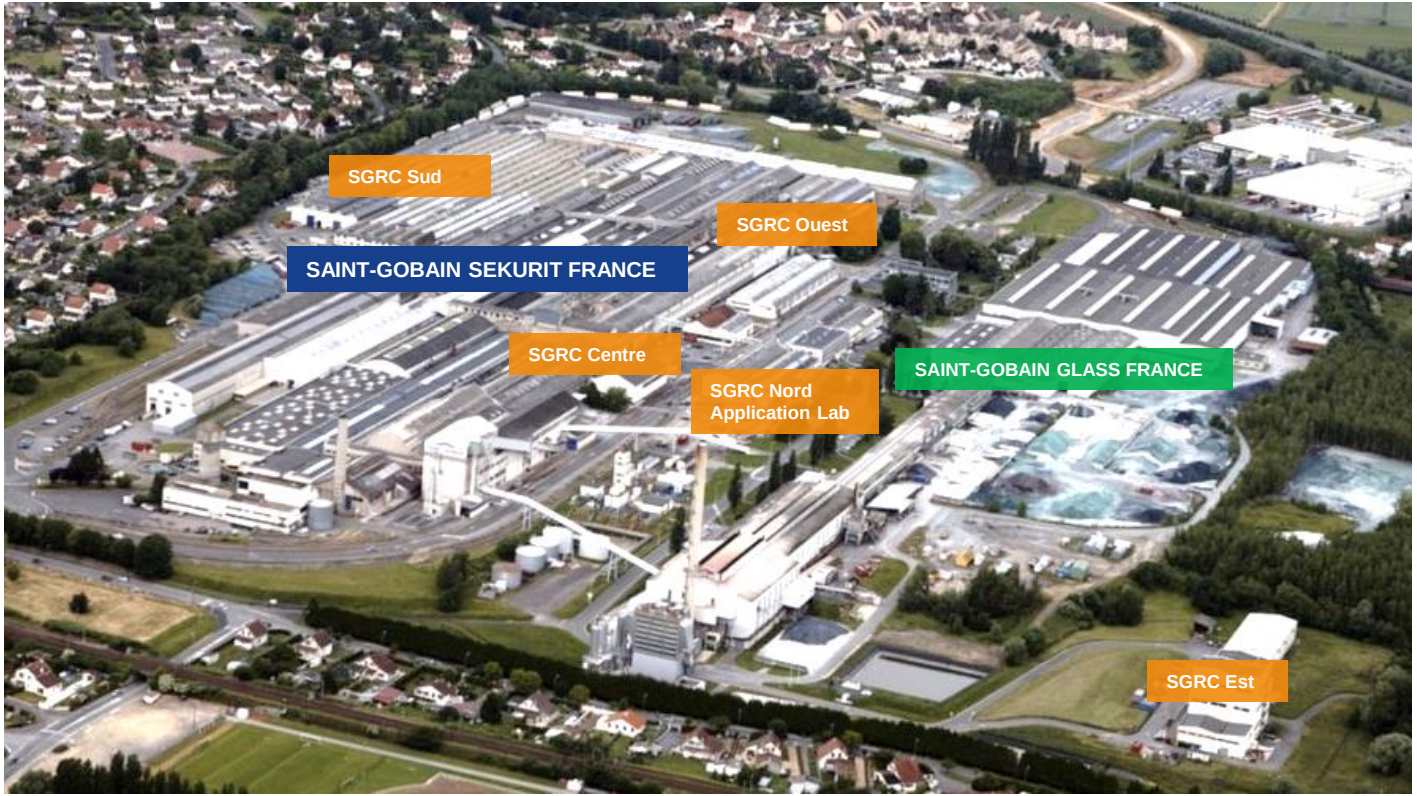
ONE OF THE 8 TRANSVERSAL R&D CENTRES MULTI-BUSINESS

Saint-Gobain Research Compiègne

- Created in 1982
- ~ 200 collaborators
- 30% of women
- ~ 12 nationalities
- 20 000 m²
- ~ 120 invention disclosure per year

SAINT-GOBAIN RESEARCH COMPIEGNE

AT THE HEART OF A GLASS INDUSTRIAL SITE



100 years
65 ha
3 entities

Glass
800t glass per day

Sekurit
1,5M car set per year

SGR Compiègne
>80 patents per year

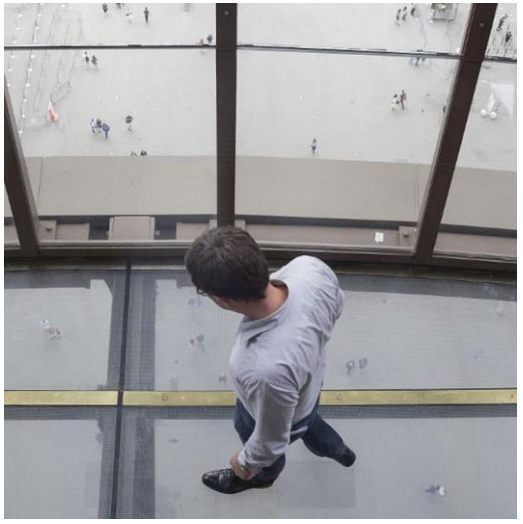
COMMON FEATURES

Enamel on diff nt surfaces

- Ceramic
- Metal
- **Glass**

?

EXAMPLES OF ENAMELED GLASS



Eiffel Tower
LiteFloor XtraGrip

Facade Spandrel

House of music Budapest

AGENDA

Introduction

- Enamel formulation / Processing / Selection
- Properties of enameled glass: Color / Adhesion / Mechanics

Examples of enamel surface & interface

- Glass surface modification by enameling
- Generation of antistick

INTRODUCTION

WHAT IS AN ENAMEL MADE OF ?

Glass frit
40-70% (1)

+

Pigments
10-20% (1)

+

Medium
15-30% (1)

Bismuth/Zinc silicate glass
Ø 1-10 µm grain size

Cu, Cr, Fe, Mn spinel : black
TiO_2 : white
Ø ≈1µm

Solvent + Resins + Additives
viscosity 20 Pa.s

- Adhesion on glass
- Firing range
- Chemical resistance
- Glass weakening / mechanical resistance
- Specific properties (anti-stick)

- Color
- Opacity
- IR absorption (in furnace)

- Rheological properties, according to process (screen printing, spray, drying process, glass handling…)
- Greenstrength
- Water based, water friendly, IR,UV
- Burns out during firing

(1) Ref : Understanding Glazes, R. A. Eppler et Al. Wiley ,The american chemical Society 2005

INTRODUCTION

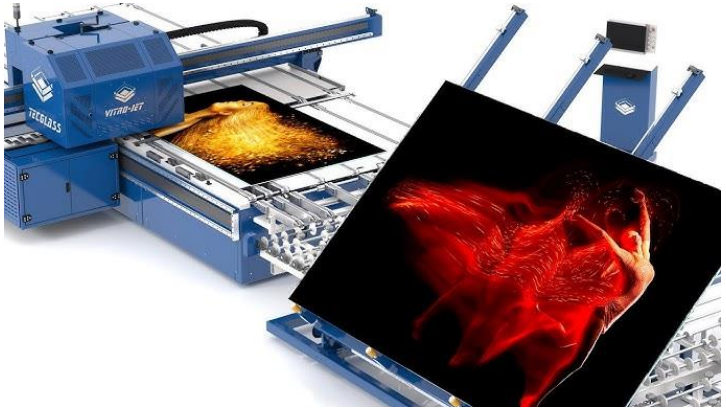
HOW IS AN ENAMEL PRINTED ON GLASS 10 -20 µm

Screen printing

+ Robustness
  Raw materials

- Flexibility
  Screen management

Digital printing



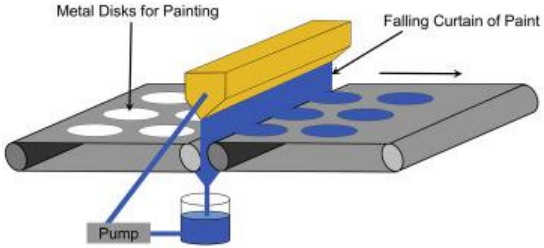
+ Flexibilty
  Multi material

- Cost
  cycle time

Roller

Spray

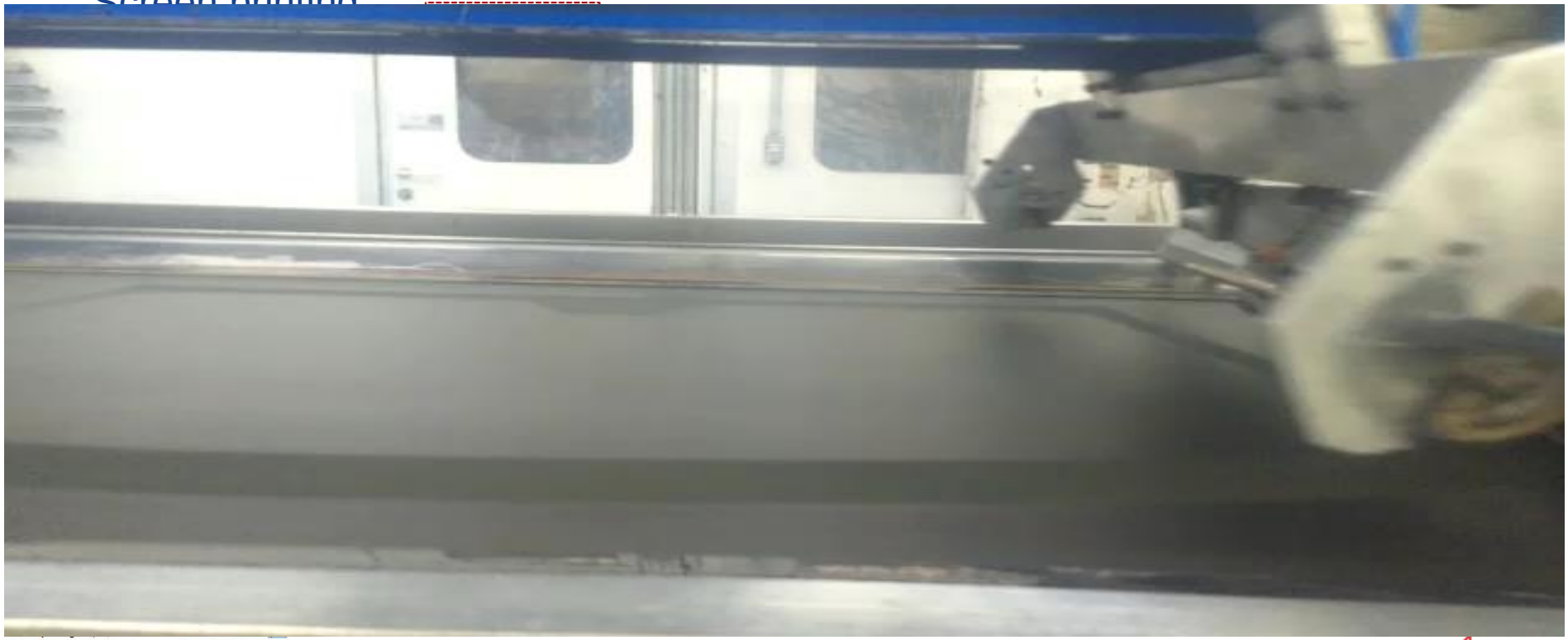
Curtain



INTRODUCTION

HOW IS THE ENAMEL PRINTED ON GLASS

Screen printing



INTRODUCTION

PASTE RHEOLOGY FOR RIGHT PROCESSING

TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

Shear thinning behaviour required for deposition

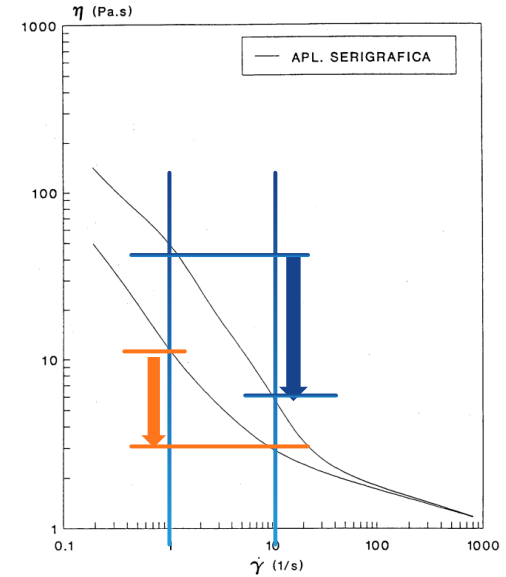
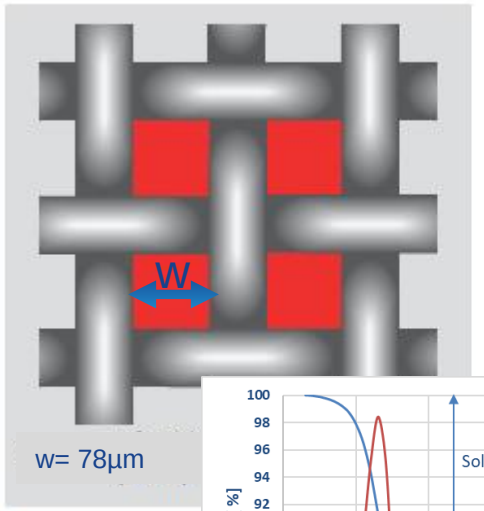
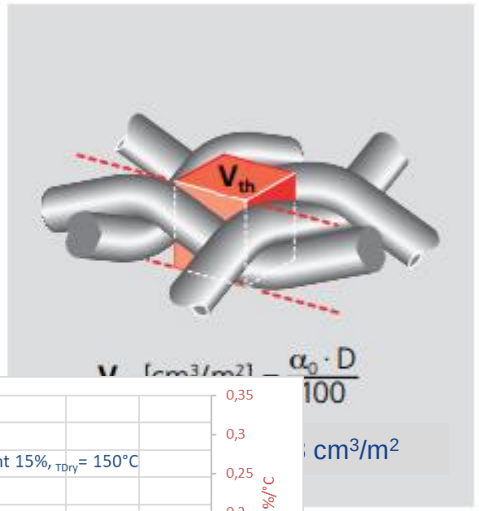
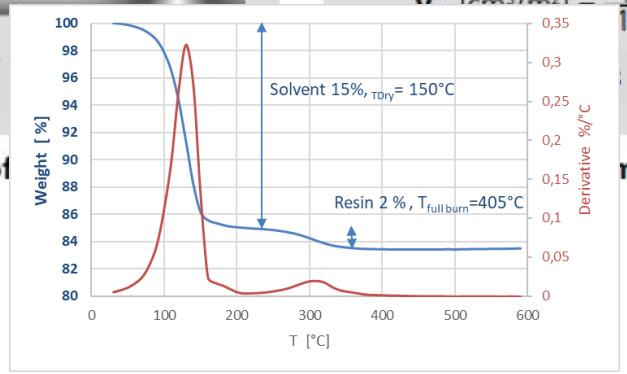


Figure 8: The viscosity curve of a serigraphic application compared to the deformation gradient. (2)





Percentage of ne



(1): US 10 , 047 , 004 B2

(2) https://doi.org/10.1002/9780470294642.ch4

INTRODUCTION

ENAMEL PROCESSING FOR AUTOMOTIVE GLAZING

Enamel firing must be compliant with glass shaping process

INTRODUCTION

ENAMEL PROCESSING

Firing : microstructure evolution during process steps Drying / prefiring and tempering of the enameled glass

Dried state

Pre-fired 570°C

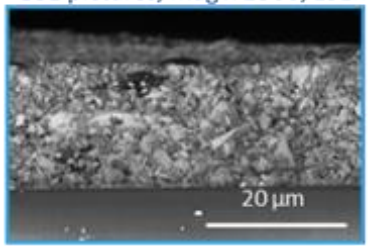
Pre-fired 590°C

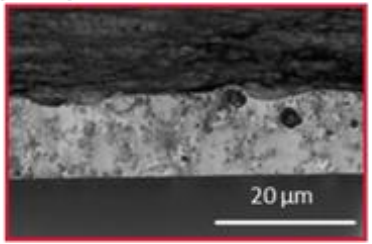
Pre-fired 610°C

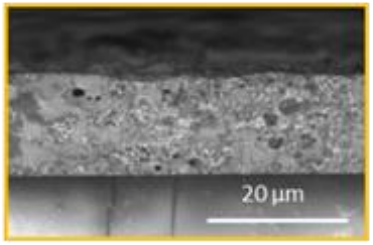
Fired 620°C

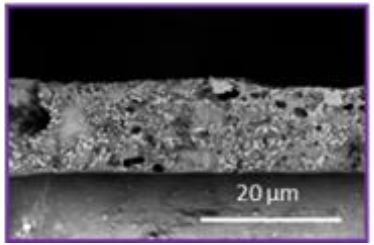
Evolution of microstructure of enamel toward temperature

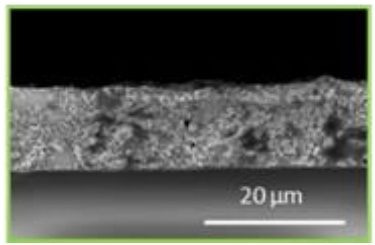
BSE pictures, mag x 2500, ESEM (80 Pa), HV = 10 kV





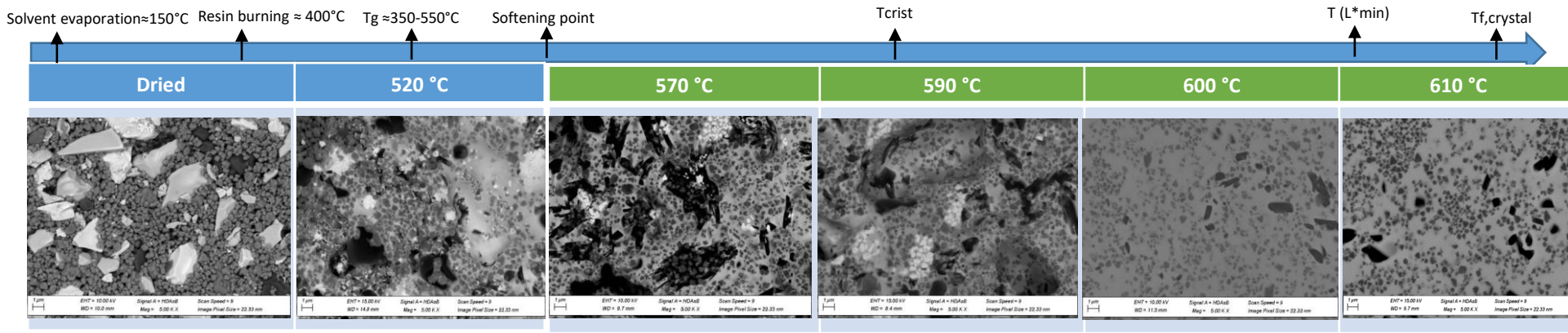


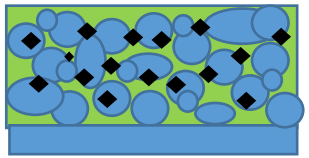




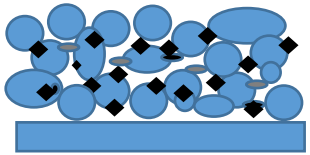
GLASS SURFACE MODIFICATION BY ENAMELING

MICROSTRUCTURAL EVOLUTION OF ENAMELED GLASS

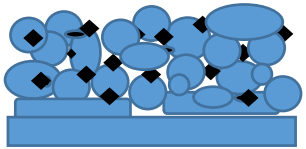




Solvent evaporation and resin Burning:



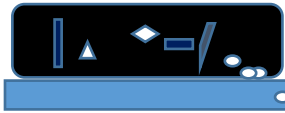
Carbonaceous residue trapping



Porosity – 4 types:
P1 trapped air
P2 carbonaceous residue
P3 fritt gaseous release
P4 surface reaction with glass

Continuous liquid phase :
Reduction of inter-granular porosity
evolution =f(high temperature viscosity)

Crystalization
(intrinsic or from seeds)
L* increase



(Cristal fusion)
L* increase
Gloss increase

Separate final resin removal temperature from softening point

INTRODUCTION

ENAMEL SELECTION = IT'S A MATCH !

Constraint functions for enamel selection:

- Optics: Aesthetic rendering, hiding function
- Process compliance : Firing range, coating interaction, antistick
- Mechanical, chemical properties

…Tuned by :

- Chemical composition and overall formulation
- Processing conditions

Resulting from Surface and interface reactions

INTRODUCTION

ENAMEL SELECTION: ENTANGLED PARAMETERS

Example of CTE tuning and consequences

Substrate		Enamel
Material	CTE 10^6K^{-1}	CTE 10^6K^{-1}
Steel	11-16	15
SLS - Glass	7-10	7-10
Ceramic Cordierite Mullite	 2,3 4,3	5-6
Boro-Silicate	3,3	4-5

Defects occurring from CTE mismatch (1)

“Crazing” - Tressaillage:

CTE (Enamel) > CTE (Substrate)15% difference

Flaking - Peeling: *CTE (Enamel) < CTE (Substrate)*

CTE = f (Composition):

1) In frit composition

$$\alpha = \alpha_1 p_1 + \alpha_2 p_2 + \cdots + \alpha_n p_n = \sum \alpha_i p_i.$$

Tabulated coefficients Ref :

Scholze, *Glass Nature, structure and Properties*, Springer 1991

Appen, A.A., *Chemie des Glases. 2. Aufl.* Leningrad: Verlag Chemie 1974

2) As additives

Synergy with other parameters : E, Chemical composition, thickness, processing

(1) https://www.emaux-soyer.com/media/wysiwyg/Collection-Emaux-Soyer-Ceramique-faience_1.pdf

(2) Understanding Glazes, R. A. Eppler et Al. Wiley ,The american chemical Society 2005

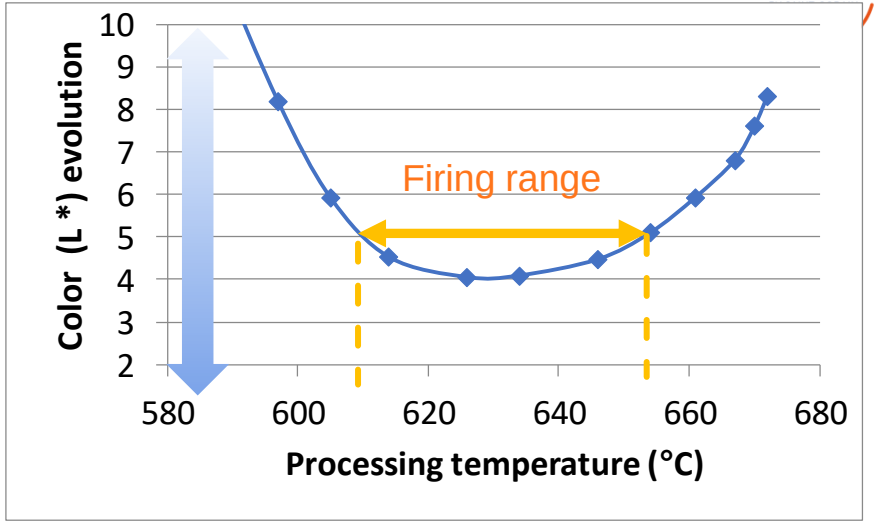
PROPERTIES OF ENAMELED GLASS

COLOR RENDERING

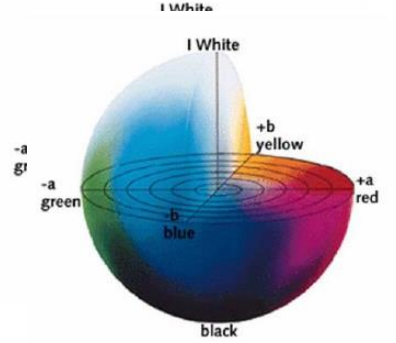
TRANSVERSAL R&D CENTERS

Gradient Firing of Black enamel sample:

T°C - +



Lab color measurement: CM600d MINOLTA (SCE, D65, 10°)



L – Lightness
White (L = 100) to black (L = 0)

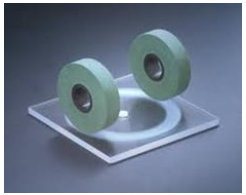
a/b – Color

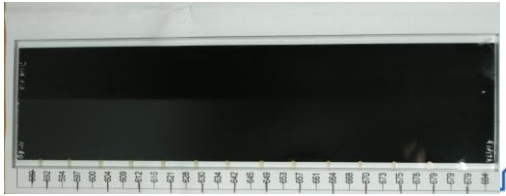
ΔE – Color Difference
Distance between 2 data in the sphere

Firing range determination from L^*_{min}

Color measurement also base for chemical ageing and abrasion resistance

Normalized abrasion Taber test



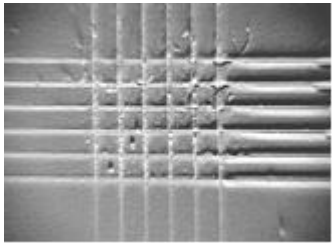


Acid immersion test

PROPERTIES OF ENAMELED GLASS

ADEHSION AND MECHANICS

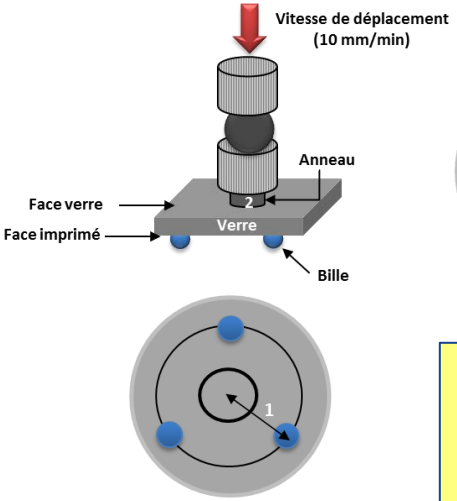
Adhesion



Peel test

Erichsen scratch test
Elcometer 3092 16N testing
(WO2021023965)

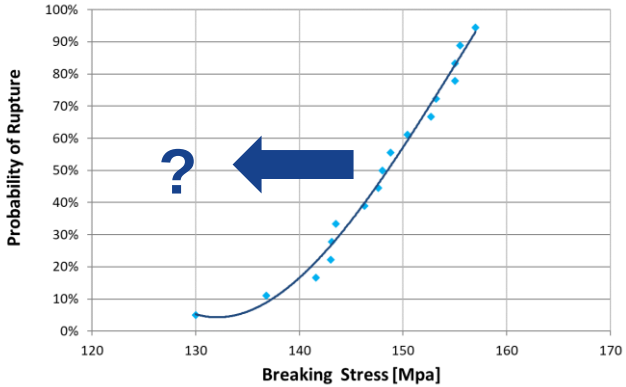
Setup for tripode testing



1: Rayon formé par les trois billes = 20 mm

2: Diamètre de l'anneau = 10 mm

Glass Mechanics

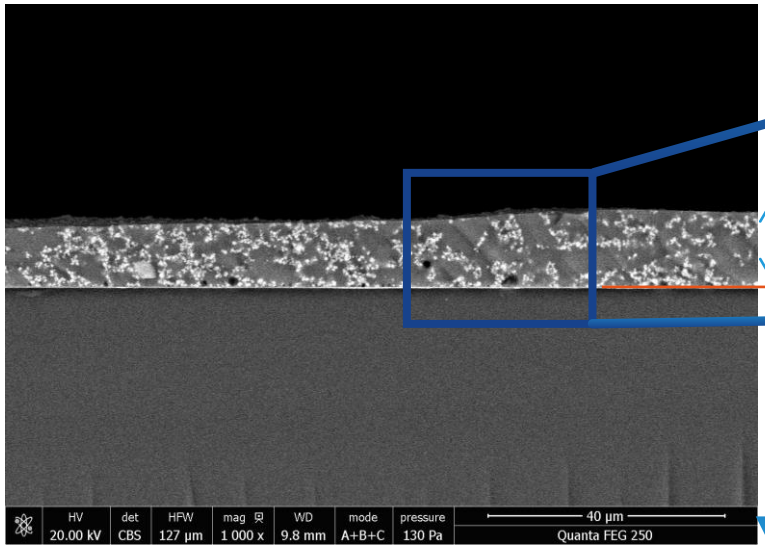


Statistical distribution of MoR:
=> Weakening of the system through enamel coating

GLASS SURFACE MODIFICATION BY ENAMELING

SYSTEM ORDER OF MAGNITUDE

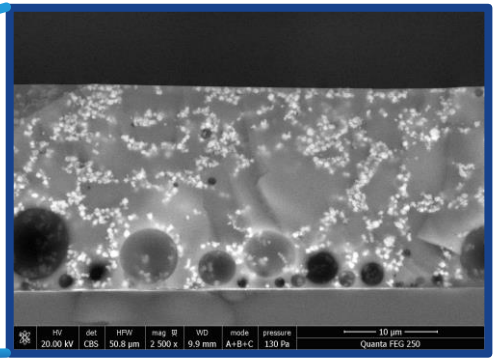
Glass weakening from **surface** modification



10-20µm **Enamel** layer

100-200 nm Magnetron coating

2 – 4, 6,10 mm **Glass substrate**

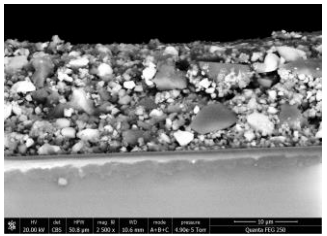


Heterogeneous surface layer :

- Glass matrix, pigments , crystalline species
- Local defects : Bubbles, cavities

GLASS SURFACE MODIFICATION BY ENAMELING

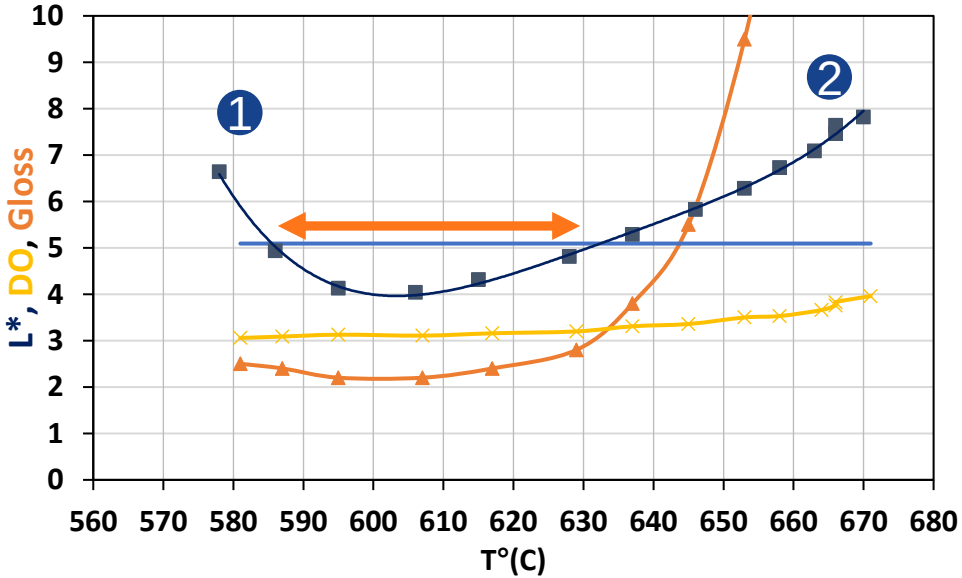
COLOR EVOLUTION FROM SURFACE MODIFICATION



1 Dried State – Underfired enamel

Porous heterogeneous

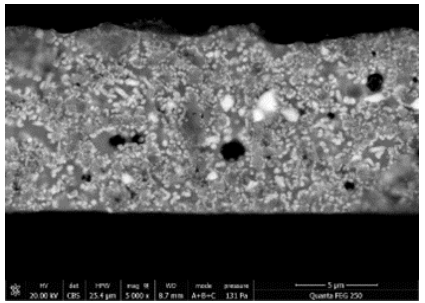
Low optical density



2 Fired enamel

Dense opaque layer (limited porosity =few %)

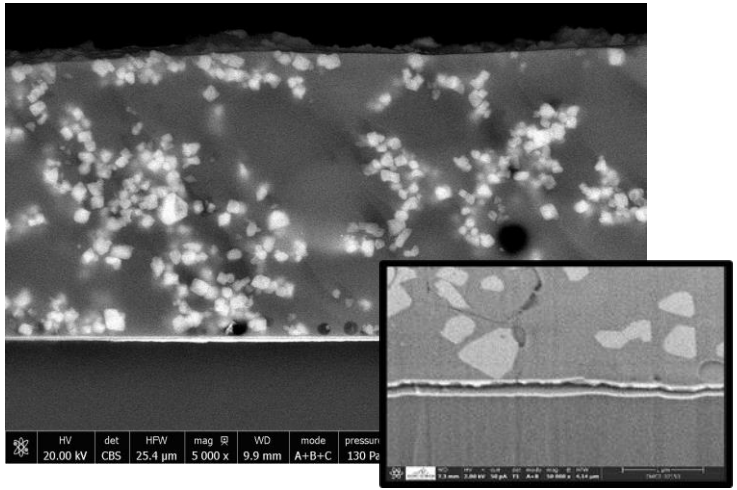
Pigment encapsulation



GLASS SURFACE MODIFICATION BY ENAMELING

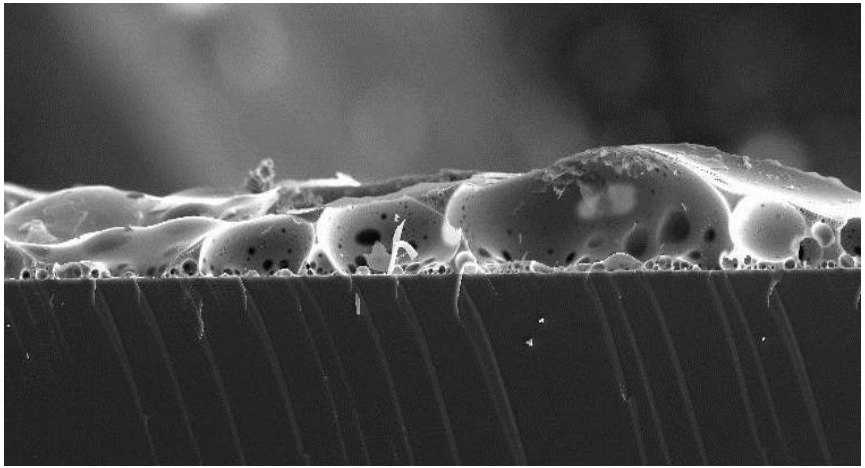
CASE OF COATED GLASS – 2 EXTREME BEHAVIOUR

Compatible enamel



After enamel firing: integrity of the magnetron coating is kept (bright contrast area at the interface for Ag-coatings)

Coating removal enamel



Coating digestion by the fused frit material :

Highly fusible frits, oxidizing frit [1, 2]

(1) : WO 2021/023965 A1

(2) : WO 2014 133929 A2

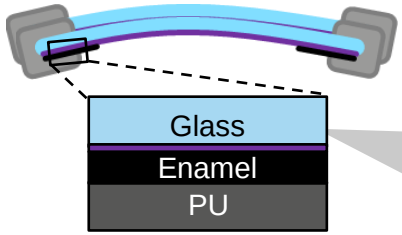
GLASS SURFACE MODIFICATION BY ENAMELING

CASE OF COATED GLASS – 2 EXTREME BEHAVIORS

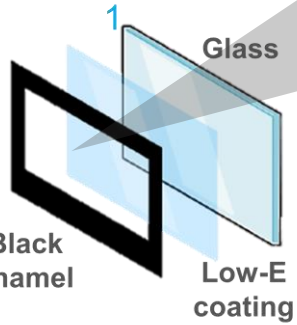
TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

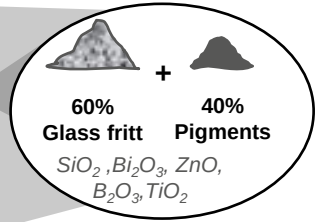
Interest of complete coating removal or coating compatible solutions

LowE sunroofs



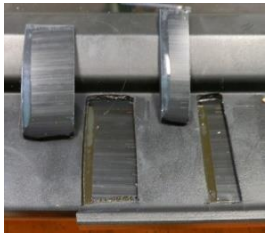
LowE oven doors





Possible Defects observed after tempering

Grey and rough aspect



Lack of adhesion of encapsulation

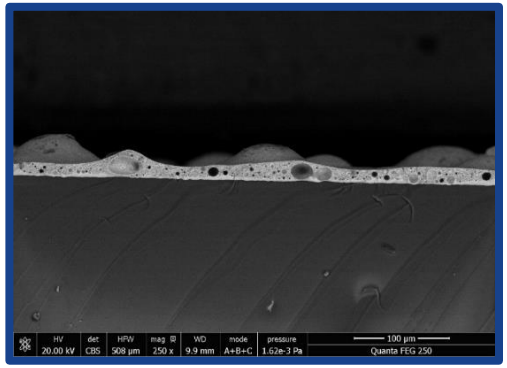
Inhomogeneous and color shift

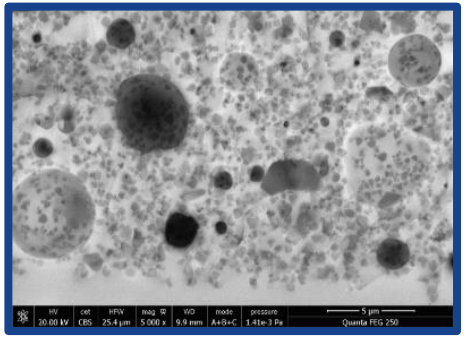
Lack of scratch resistance

GLASS SURFACE MODIFICATION BY ENAMELING

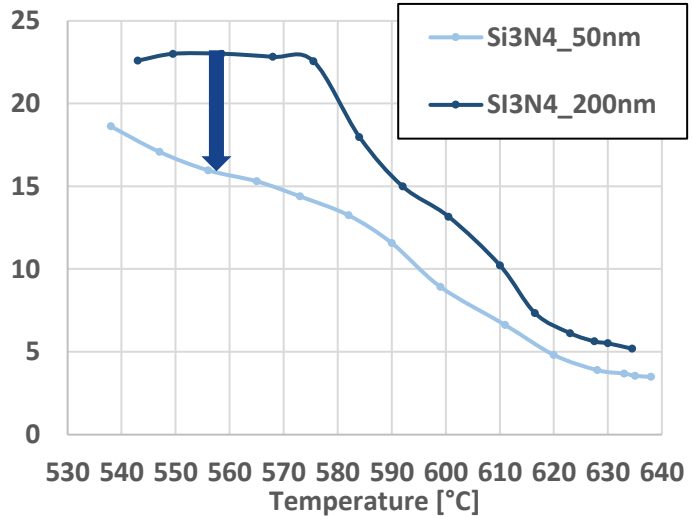
CASE OF COATED GLASS – COLOR EVOLUTION DURING COATING DIGESTION

Chemical reaction dependant on frit & coating stack design (monolayer digested by CR enamel)





N_2 release from nitride oxydation
Final rough surface
Big bubbles with Si_3N_4



Final color tuned by :
-coating material thickness to be digested
-final coating material residue

GLASS SURFACE MODIFICATION BY ENAMELING

CASE OF COATED GLASS – COATING DIGESTION

Interest of coating removal: Control of final rendering without interaction with the coating ;

No need for coating peripheral demarging (corrosion protection)

2 competing reactions

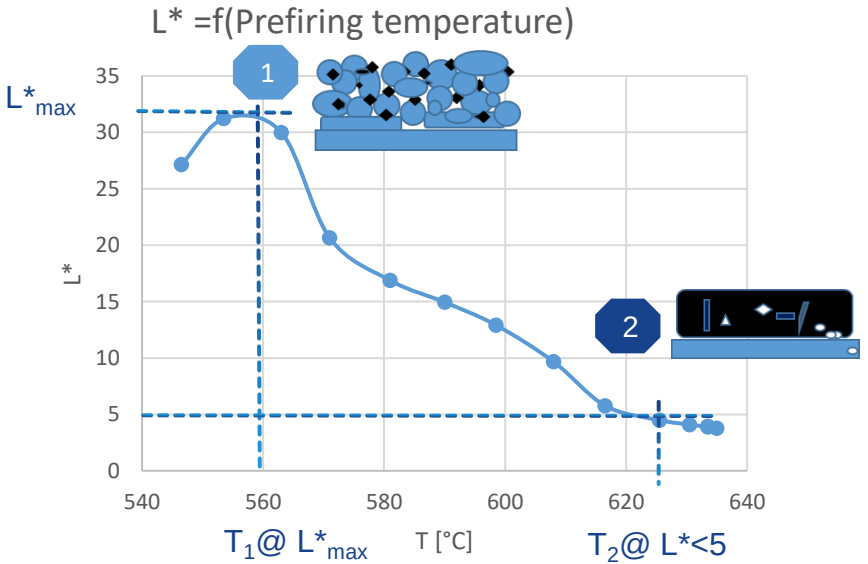
- Chemical digestion of the coating

❶ Intermediate porous structure from nitride oxidation [(1)]

$$2\,Bi_2O_3 + Si_3N_4 \rightarrow 4\,Bi + 3\,SiO_2 + 2\,N_2$$

- Enamel firing:

❷ Intrinsic and Reaction generated porosity removal



[(1)] J. Am. Ceram. Soc., 96 [3] 774–780 (2013)

ENAMEL SURFACE PROPERTIES MANAGEMENT FOR ANTISTICK

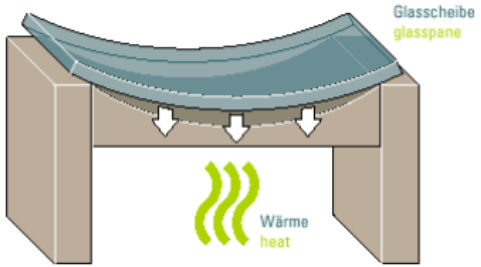
WHAT IS ANTISTICK?

Manufacturing process of laminated glazing

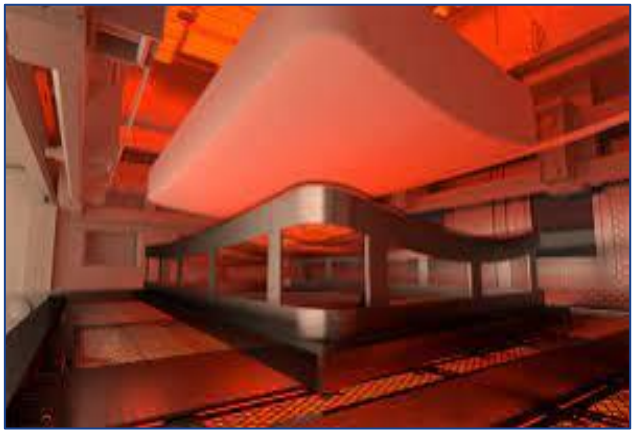
Printing → Pre-firing → Bending → Lamination

Bending processes and challenges:

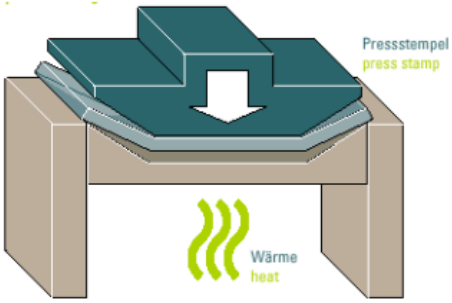
Sag Pair Bending



=> Antistick behaviour between required between both glasses



Single press Bending

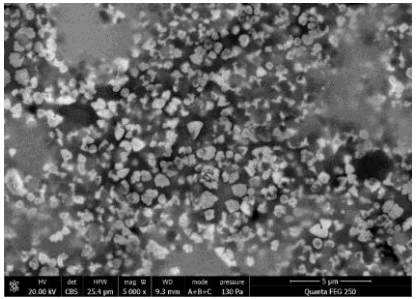


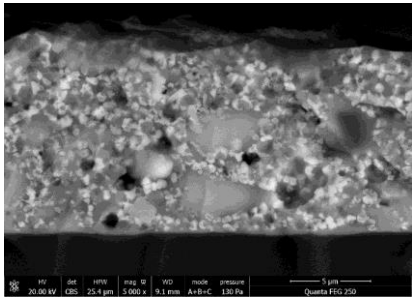
=> Antistick behaviour between glass and pressing tool

ENAMEL SURFACE PROPERTIES MANAGEMENT FOR ANTISTICK

ANTISTICK GENERATION

1) Crystallization route (1): roughness generation, surface wettability, viscosity

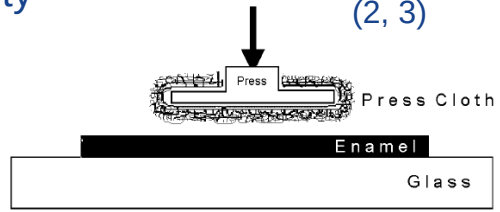




- Cristalline species in top surface and over entire thickness
- Rough surface
- Low Gloss evolution

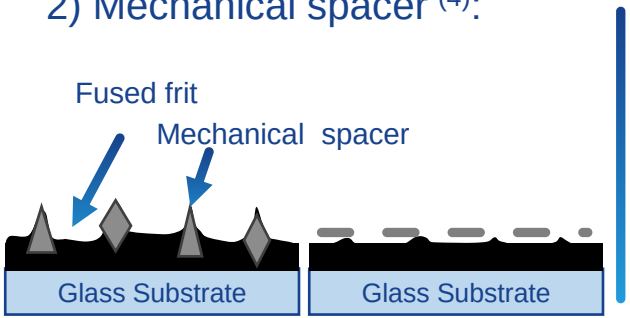
Intrinsic crystallization of Bi-frit or supported by seeds $Bi_4 (SiO_4)_3$ (1)

(2, 3)



Anti-stick value (N) at 620°C/600 sec (specification value <5N)	1.3
Anti-stick value (N) at 640°C/600 sec (specification value <5N)	1.3

2) Mechanical spacer (4):



3) Chemical composition on the frit for surface roughness and wettability

- Tuning of high temperature viscosity
- Surface chemistry

(1) : US 6207285 B1
(2) : https://www.researchgate.net/publication/279529391
(3) :WO 2023146392
(4) : US 4,828,596

CONCLUSIONS

Complex surface modification during enamel firing, to address process compatibility and desired final properties

Opportunities for common collaboration to leverage current and future challenges:

- Surface chemistry

- Surface texture

- Optical rendering

THANKS

Thank you for your attention

Contribution: Enamel Group from Saint-Gobain Research Compiègne

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