360 YEARS YOUNG

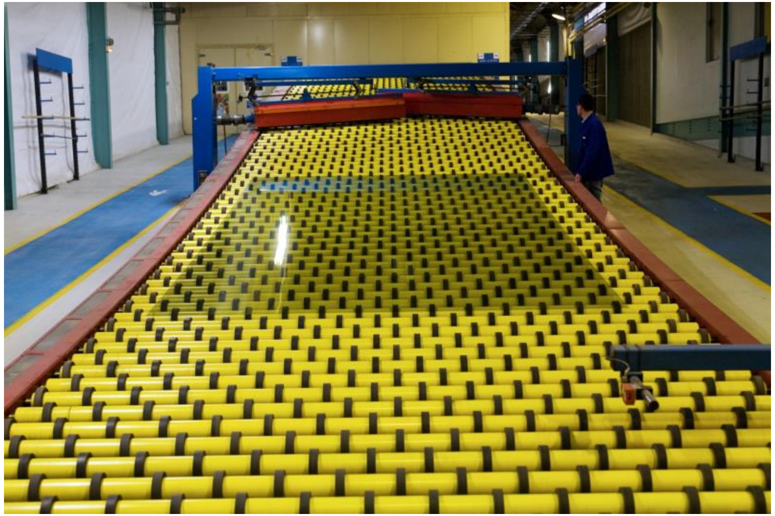
MAKING THE WORLD A BETTER HOME

SAINT-GOBAIN

PROPRIÉTES OPTIQUES DU VERRE DÉCORÉ

D. Mey Saint-Gobain

CONTENTS



Float Glass 3,2x6m and **coated products**

Transformed Products for user’sfinal dimensions

https://www.saint-gobain.com/fr/news/ampliskyc-la-conquete-de-nouveaux-horizons

CONTENTS

SAINT-GOBAIN

DECORATED GLASS

Automotive and building applications

01

DECORATED GLASS

A LONG STORY

Stained glass-St Jean-Baptiste
Sainte-Chapelle XIIIth Century
Cf Verrerie de Saint-Just

Bulk colored Glass
Colored by selected TMOs

Planilaque™ by Saint-Gobain

Organic Painted Glass

Vitrail des cent visages (2015), Strasbourg Cathedral

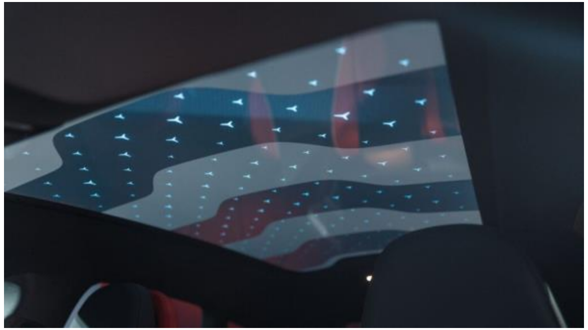
Emalit™
Seralit™

Industrial Enameled Glass

AUTOMOTIVE APPLICATION

DECORATIVE AND FUNCTIONAL REQUIREMENTS :

- Protect Gluing system from UV ageing
- Aesthetic for end user (color, opacity, gloss)
- Matching designer requirements: color, color matching
- Matching with process parametes: shaping process
- Matching system requirements (active systems, magnetron coatings…)



Complex system : New GLC sunroof

Individual Marking

Complex shape

Panoramic sunroof with solar Active and passive solar control, inner thermal confort (Solarbay)

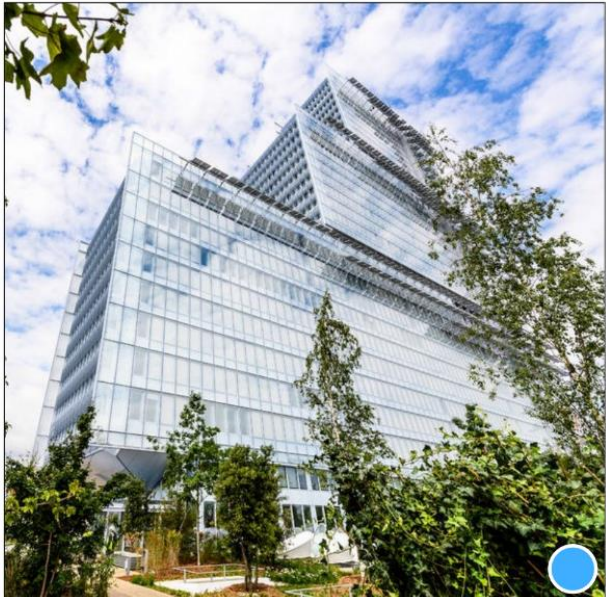
Patterned design

BUILDING APPLICATIONS

DECORATIVE AND FUNCTIONAL GLASS

- Interior decoration

- Façade Aesthetics



Picture It ™ – Printed glass

Cool-Lite™ - Silver solar control coating + Enameled Spandrels

Individual Marking

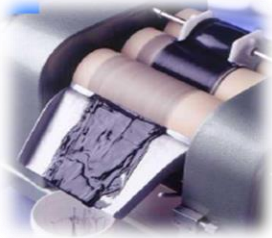
GLASS DECORATION TECHNIQUES

Process for glass printing

02

PRINTED GLASS

PRINTING RAW MATERIALS



Enamel Paste

Particle size
- **Average = 5µm**
- Max >10µm

Viscosity/Rheology
- **10 to 15 Pa.s**
- **Shear thinning**

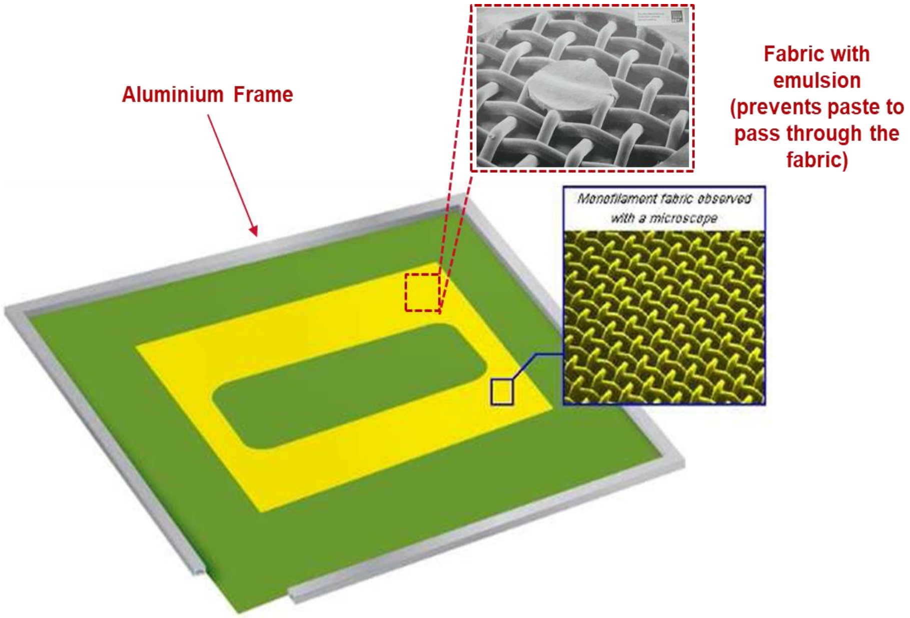
Digital Ink

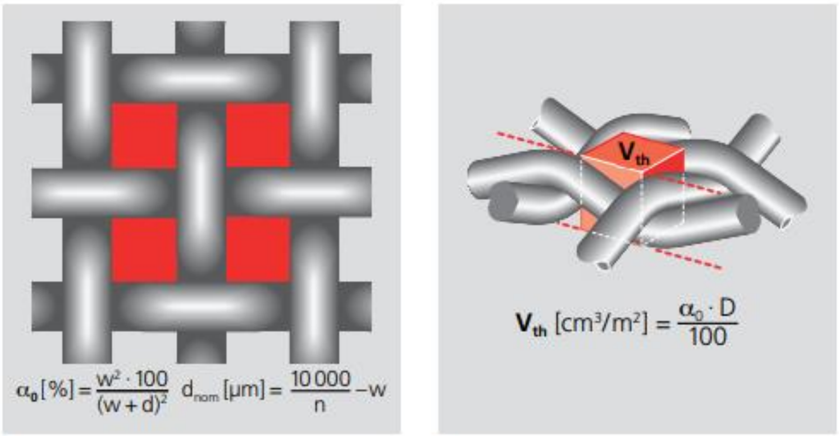
Particle size
- **Average ~ 500nm**
- Max < 1 µm

Viscosity/Rheology
- **~ 10mPa.s at jetting Temp**
- **Newtonian behaviour**
- (η_{water} = 1 mPa.s)

PRINTED GLASS

FROM SCREEN PRINTING ….



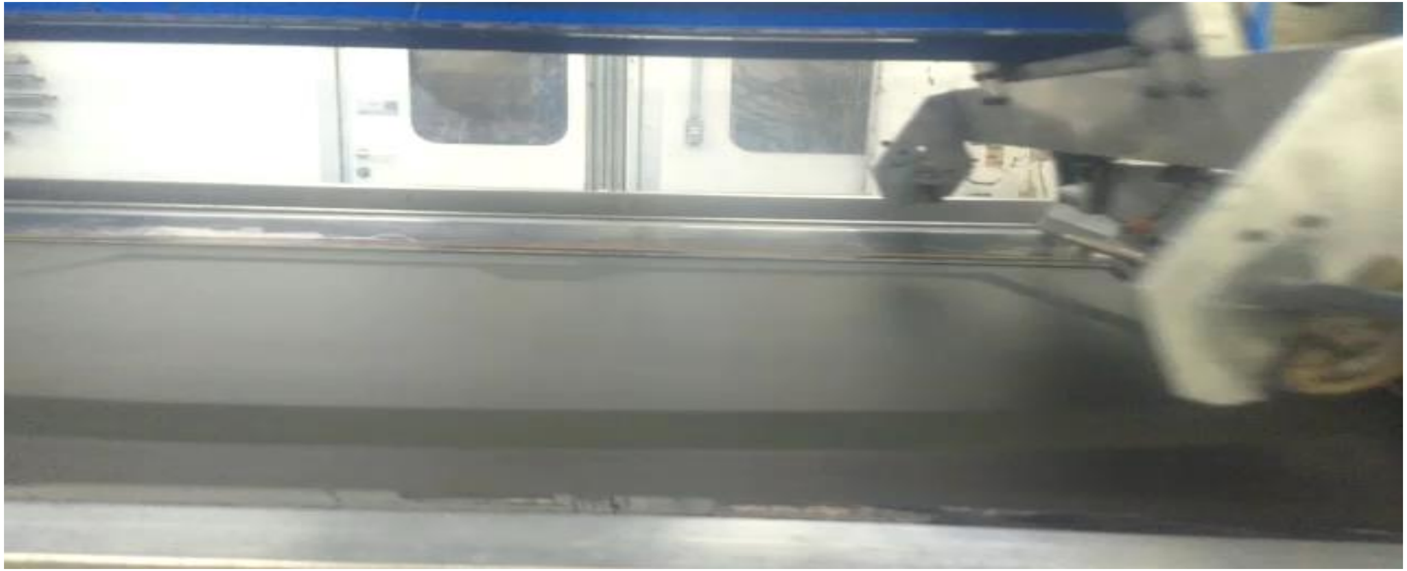


Percentage of open area α_0 [%] **Theoretical ink volume**

Opening defines the printed design

Screen mesh tunes the fransferred thickness for shear thinning fluids

PRINTED GLASS
FROM SCREEN PRINTING ….



Example of black enamel contour printing on windshield

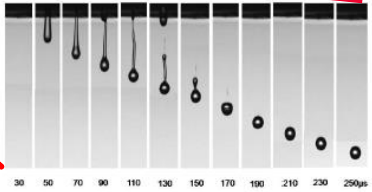
PRINTED GLASS

….TO DIGITAL PRINTING

Individual Marking

Digital printing machine - Multi or Single Pass

Printhead Xaar 1003



Ink droplets

Flexible achievable design

PRINTED GLASS

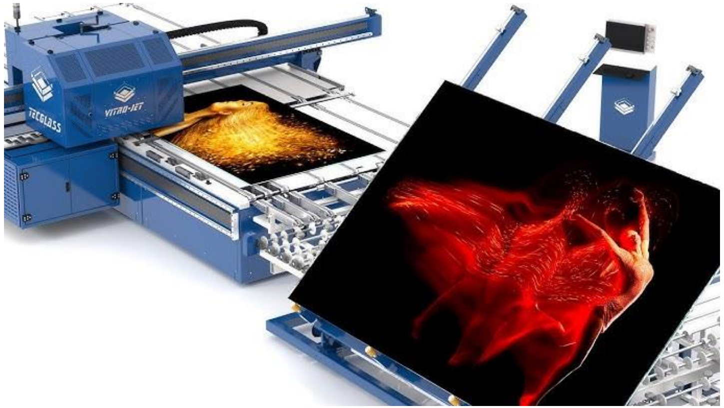
BENCH MARK OF INDUSTRIAL PRINTING TECHNIQUES

Screen printing

+ Robustness
  Raw materials

- Flexibility
  Screen management

Digital printing



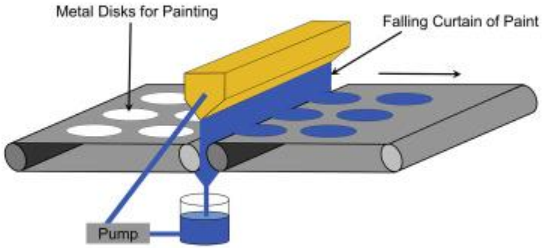
+ Flexibilty
  Multi material

- Cost
  cycle time

Roller

Spray

Curtain



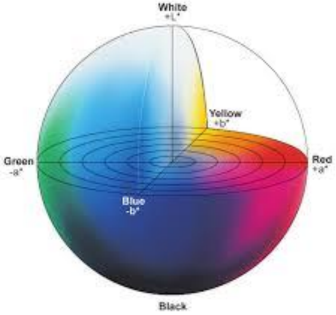
CHARACTERIZATION OF DECORATED GLASS

Laboratory vs onsite measurement

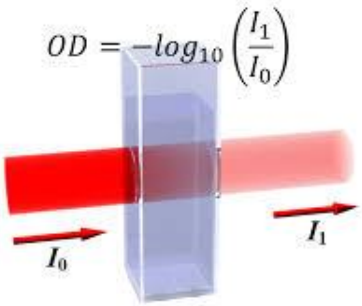
03

COLOR MEASUREMENT

MOBILE COLOR MEASUREMENT VS SPECTROCOLORIMETER



Integrated **L*,a*,b* color** measurement



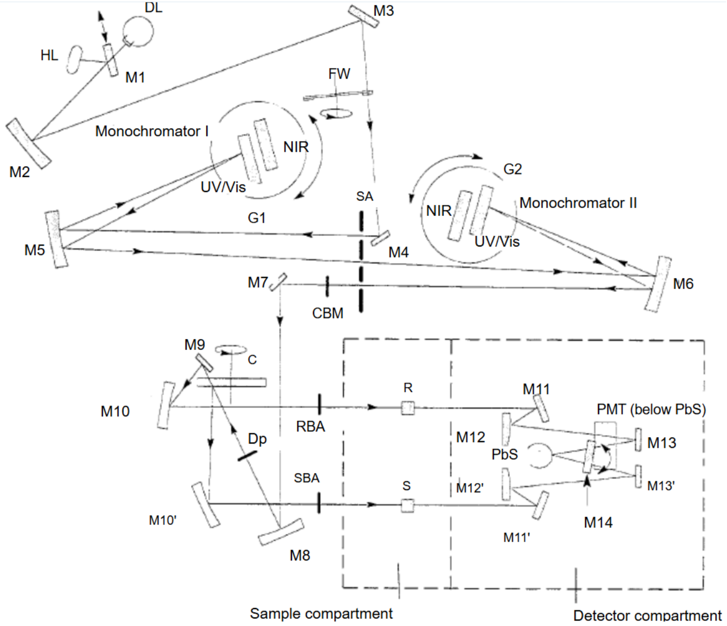
Opacity - Optical density

Gloss

COLOR MEASUREMENT

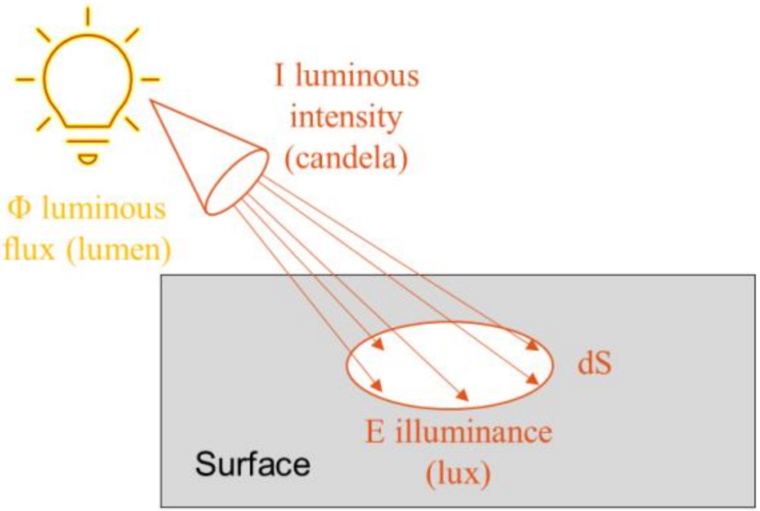
MOBILE COLOR MEASUREMENT VS SPECTROCOLORIMETER

Full spectrum in transmission or reflexion
(Perkin Elmer Lambda 1050, Agilent Cary 60)

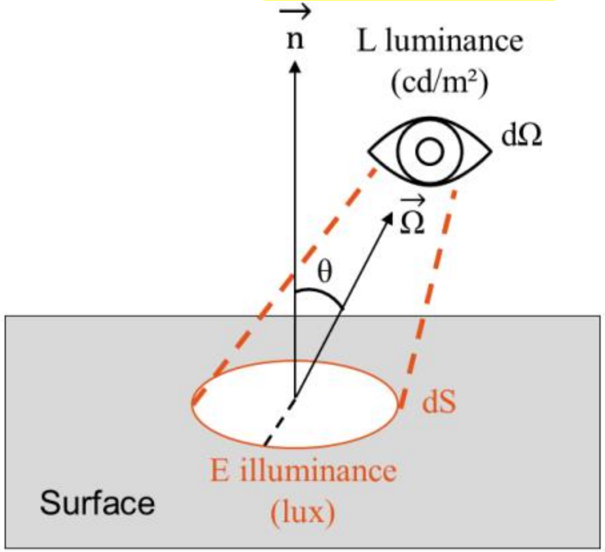


Optical path: **through** Sample or In reflection **onto** sample , vs Reference

Illuminant D65



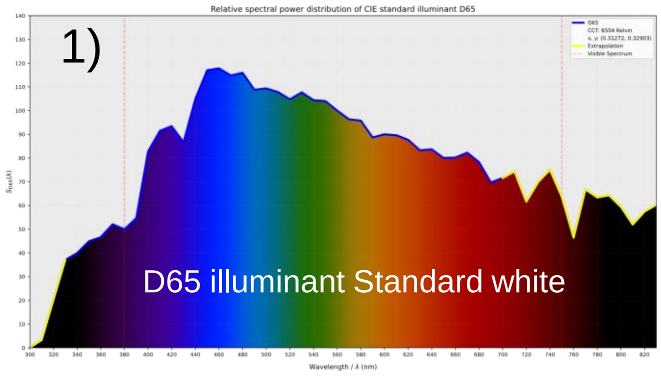
XYZ and LAB



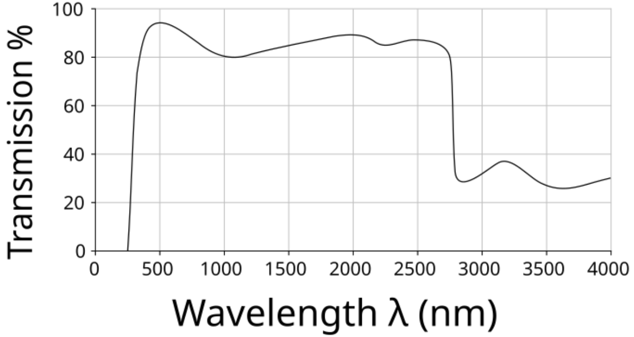
COLOR MEASUREMENT

L*,a*,b* color scale

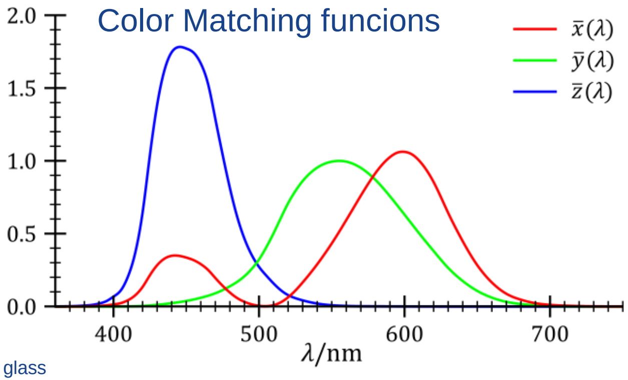
1)



2)



3)



4)

Répartition spectrale énergétique de l'illuminant D65

$$X = \sum_{\lambda = 380\,nm}^{780} \frac{d\phi}{d\lambda} x_{barre}(\lambda)\tau(\lambda)\Delta\lambda$$

Composante chromatique de l'observation de référence

$$Y = \sum_{\lambda = 380\,nm}^{780} \frac{d\phi}{d\lambda} y_{barre}(\lambda)\tau(\lambda)\Delta\lambda$$

Facteur de transmission ou réflexion

$$Z = \sum_{\lambda = 380\,nm}^{780} \frac{d\phi}{d\lambda} z_{barre}(\lambda)\tau(\lambda)\Delta\lambda$$

Pas (5 nm)

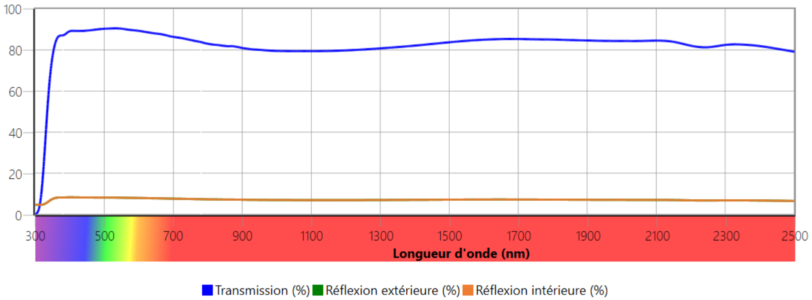
COLOR MEASUREMENT

L*,a*,b* color scale

5)
$$
\begin{aligned}
L^* &= 116 f(Y/Y_n) - 16 \\
a^* &= 500\left[f(X/X_n) - f(Y/Y_n)\right] \\
b^* &= 200\left[f(Y/Y_n) - f(Z/Z_n)\right]
\end{aligned}
$$

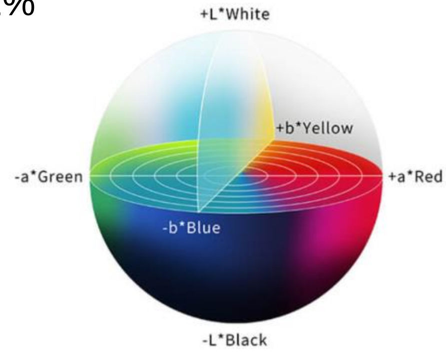
With
$$
f(t) = \begin{cases} t^{1/3} & \text{if } t > \left(\frac{6}{29}\right)^3 \\ \frac{1}{3}\left(\frac{29}{6}\right)^2 t + \frac{4}{29} & \text{Else} \end{cases}
$$

And Xn, Yn, Zn : coordinates of neutral white



TL = 90,5% R=8,2%

L*	=96	34,3
a*=	-1	-0,4
b*=	0,2	-0,5



Example : Transparent frit onto 6mm clear glass ;
Reflection and transmission spectrum

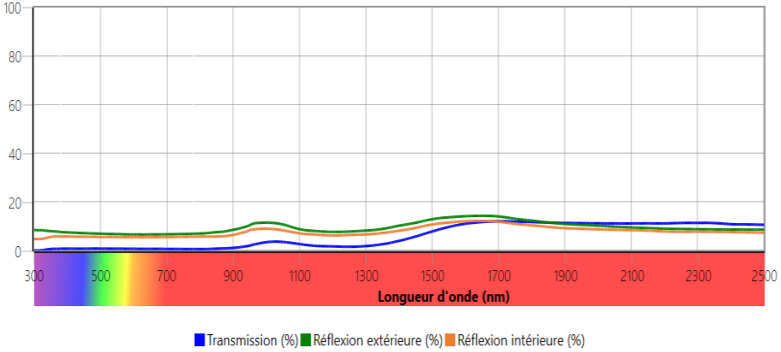
COLOR MEASUREMENT

L*,a*,b* color scale

5)
$$L^* = 116 f(Y/Y_n) - 16$$
$$a^* = 500\,[f(X/X_n) - f(Y/Y_n)]$$
$$b^* = 200\,[f(Y/Y_n) - f(Z/Z_n)]$$

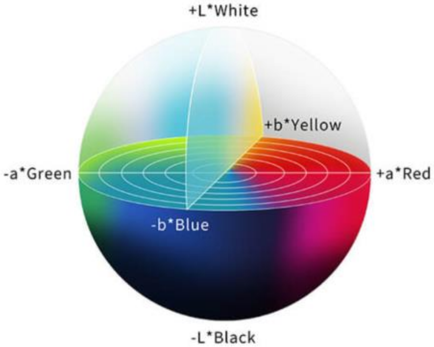
With
$$f(t) = \begin{cases} t^{1/3} & \text{if } t > \left(\frac{6}{29}\right)^3 \\ \frac{1}{3}\left(\frac{29}{6}\right)^2 t + \frac{4}{29} & \text{Else} \end{cases}$$

And Xn, Yn, Zn : coordinates of neutral white



TL = 0,7% R=6,7%

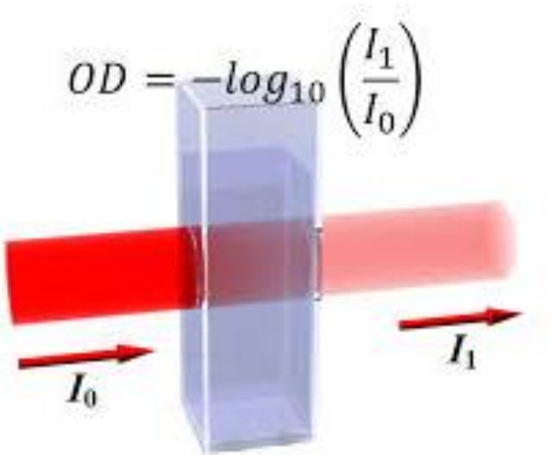
L* = 6,7 31,2%
a*= -0,8 0,1
b*= -0,5 -1,5

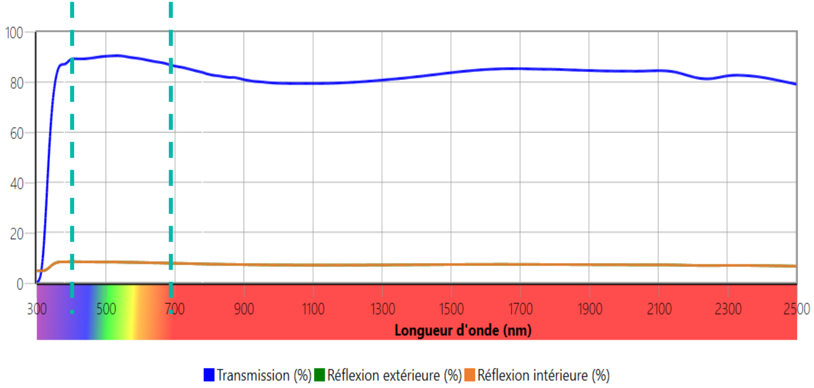


Example : 20µm Black enamel onto 6mm clear glass ;
Reflection and transmission spectrum

COLOR MEASUREMENT

OPACITY





Transmission	OD
1	0
0.5	0.3
0.2	0.7
0.1	1.0
0.05	1.3
0.02	1.7
0.01	2.0
0.005	2.3
0.002	2.7
0.001	3.0

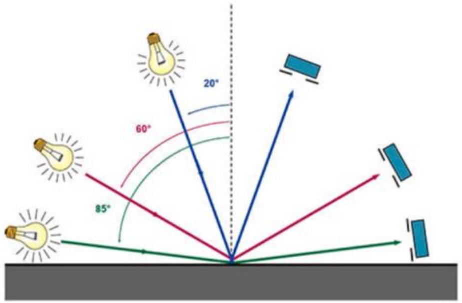
Optical Density = $-\log_{10}(\frac{I_1}{I_0})$ $\Rightarrow$ $OD = -log_{10}(T) = \frac{-1}{(700-400)} \oint_{400}^{700} log_{10} T(\lambda) d\lambda$

TL = 0,7% => OD= 2,1

SAINT-GOBAIN

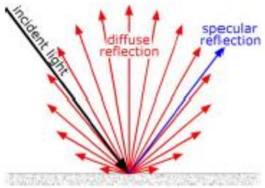
COLOR MEASUREMENT

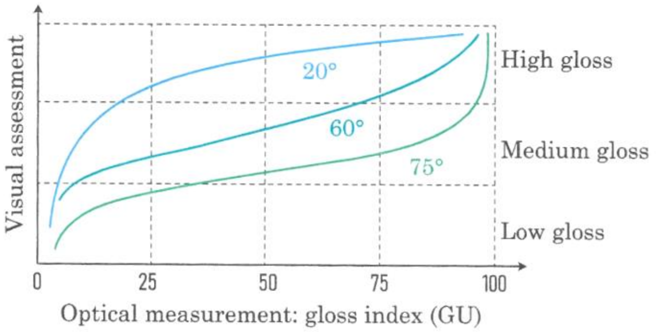
GLOSS

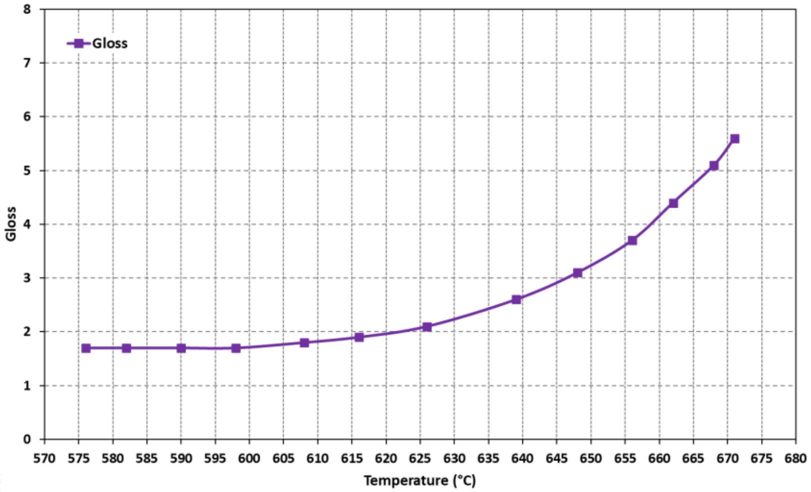


$$\text{Gloss} = 100 * \frac{F}{F_{Ref}}$$

F : Flux measured on the sample
F_{ref} : Flux measured on Reference specular reflector







Gloss increases with enamel sintering
Gloss decreases with enamel crystallization

Gloss is an optical properties which indicates how well a surface reflects light. Measurement are standardized at 20 , 60 or 85°

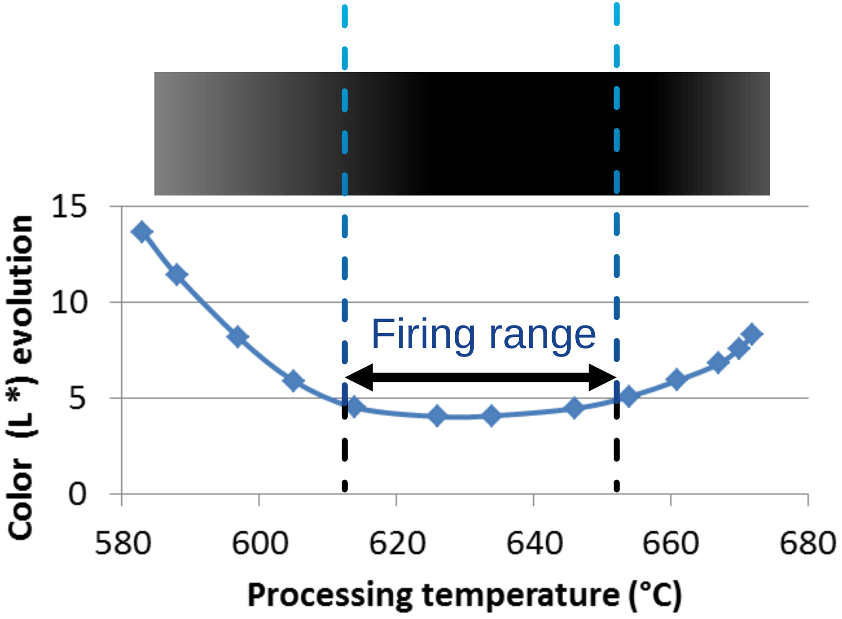
Ref: Optical Models for Material Appearance, M Hebert, Insitut d'Optique Graduate School Textbook

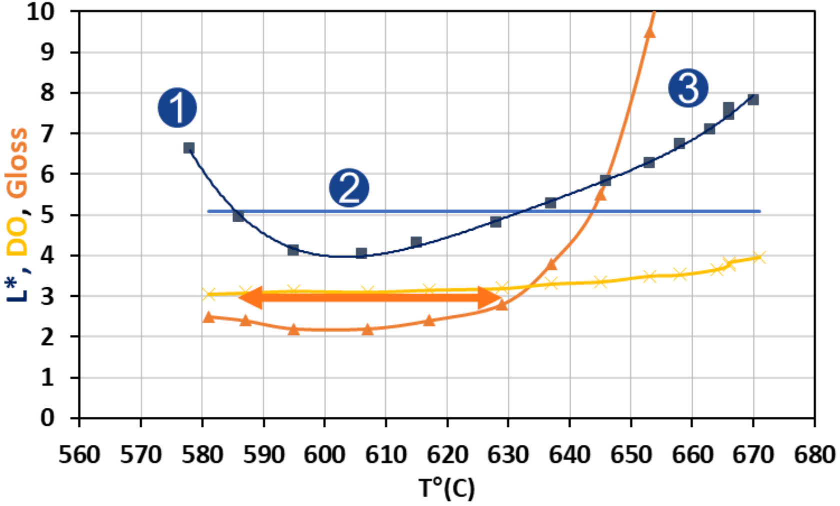
COLOR MEASUREMENT

COLOR AND ENAMEL PROCESSION AND APPLICATION

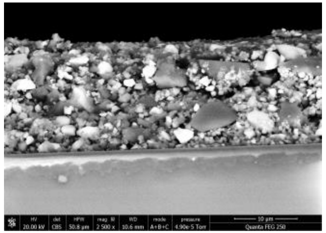
Color defines the firing range

Color (L*min < L* < L*min +1) => Firing range (T1, T2)





1



Dried State – Underfired enamel

Porous, heterogeneous

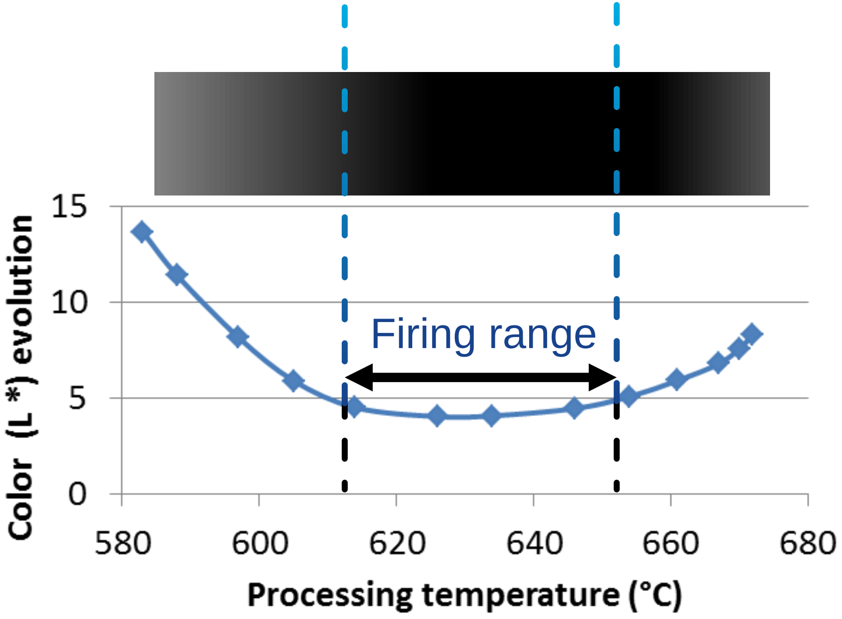
Low optical density

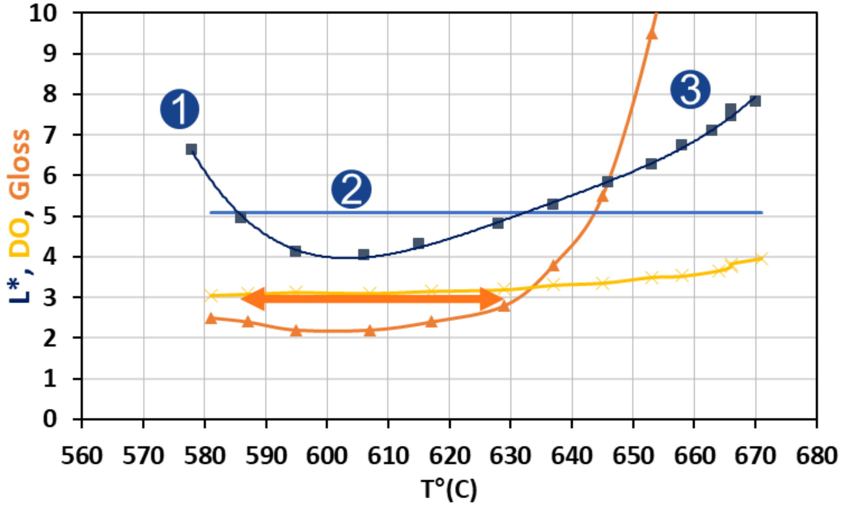
COLOR MEASUREMENT

COLOR AND ENAMEL PROCESSION AND APPLICATION

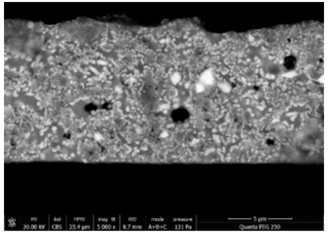
Color defines the firing range

Color (L*min < L* < L*min +1) => Firing range (T1, T2)





2



Continuous glassy phase

Pigments encapsulation

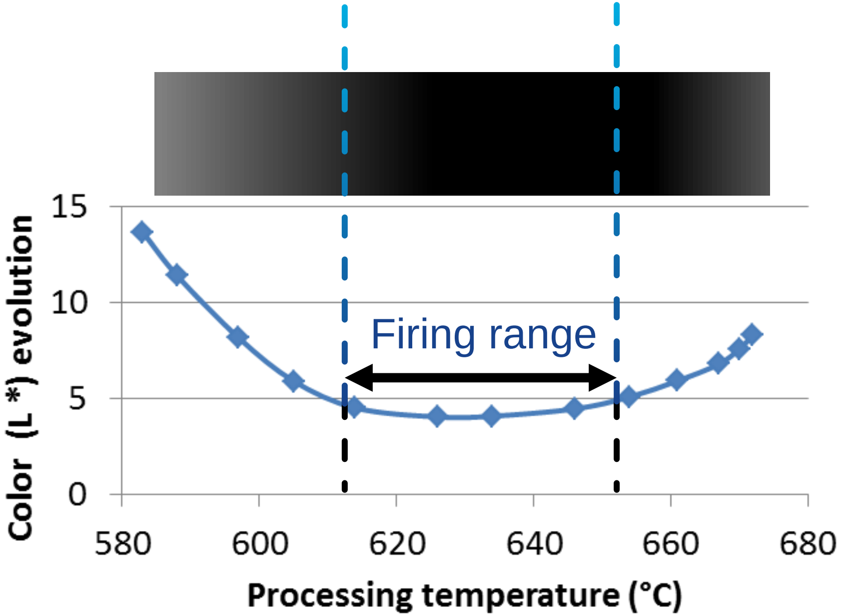
SAINT-GOBAIN

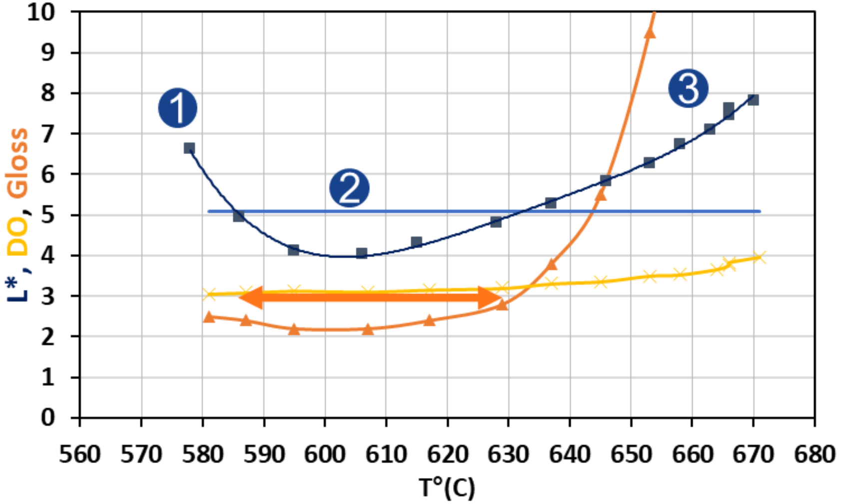
COLOR MEASUREMENT

COLOR AND ENAMEL PROCESSION AND APPLICATION

Color defines the firing range

Color (L*min < L* < L*min +1) => Firing range (T1, T2)





3 Over-fired fired enamel :

Crystalization

Chemical interaction with glass substrate

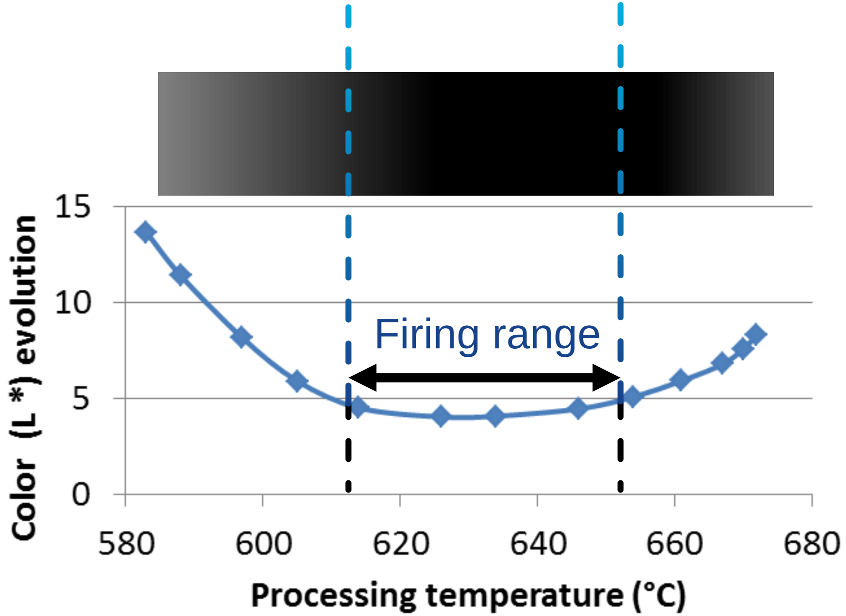
SAINT-GOBAIN

COLOR MEASUREMENT

COLOR AND ENAMEL PROCESSION AND APPLICATION

Color defines the firing range

Color (L*min < L* < L*min +1) => Firing range (T1, T2)



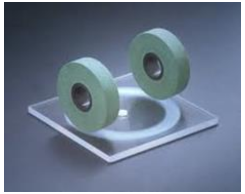
But also ageing resistance :

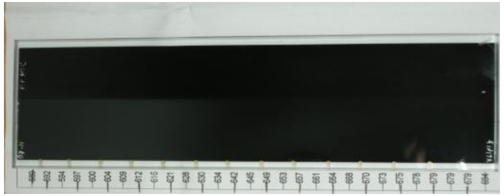
(L_i^*, a_i^*, b_i^*) => (L_f^*, a_f^*, b_f^*)

$$\Delta E = \sqrt{(L_i^* - L_f^*)^2 + (a_i^* - a_f^*)^2 + (b_i^* - b_f^*)^2}$$

Accepted range $\Delta E < 1$

Normalized abrasion Taber test





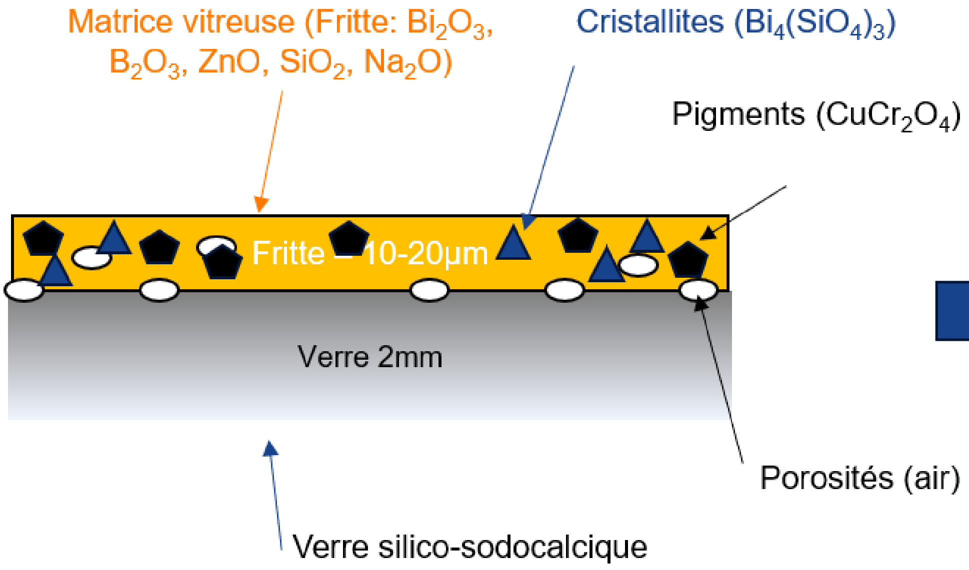
Acid immersion test

FROM MICROSTRUCTUE TO OPTICS

04

FROM ENAMELED GLASS MICROSTRUCTURE TO OPTICS

HOW DOES THE MICROSTRUCTURE TUNE FINAL COLOR ?



$$n_{tot}(\lambda) = n(\lambda) + iK(\lambda)$$

Refractive index

$$n(\lambda) = A + \frac{B}{\lambda^2} \quad (Cauchy)$$

$$= A + B\lambda^2 + \frac{C}{\lambda^2} \quad (Herzberger)$$

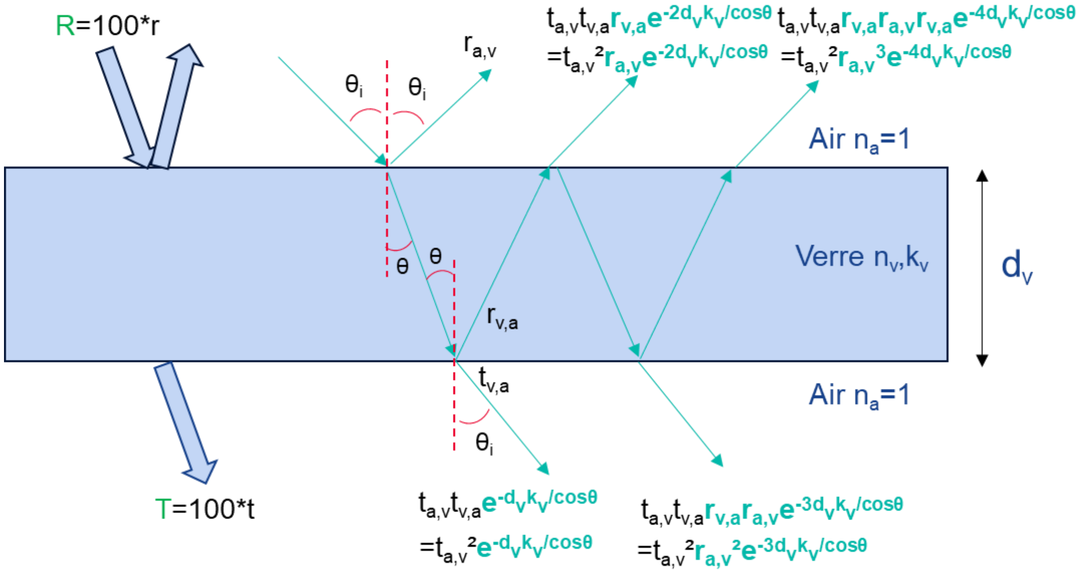
Extinction index

$$k(\lambda)\ [cm^{-1}] = \frac{4\pi\, K(\lambda)}{\lambda}$$

$$\frac{I}{I_0} = e^{-k(\lambda)*x}$$

FROM ENAMELED GLASS MICROSTRUCTURE TO OPTICS

OPTICAL DESCRIPTION OF CLEAR GLASS



$$r = r_{a,v} + t_{a,v}{}^2 \frac{r_{v,a} * e^{-2d_vk_v}}{1 - r_{v,a}{}^2 e^{-2d_vk_v}}$$

$$t = (1 - r_{a,v})^2 \frac{e^{-d_vk_v}}{1 - r_{v,a}{}^2 e^{-2d_vk_v}}$$

SAINT-GOBAIN

FROM ENAMELED GLASS MICROSTRUCTURE TO OPTICS

OPTICAL DESCRIPTION OF CLEAR GLASS

- Calcul de k_v par mesure en Transmission (Beer Lambert)

$$T = 100 * t = 100 * (1 - r_{a,v})^2 \frac{e^{-d_v k_v}}{1 - {r_{a,v}}^2 e^{-2 d_v k_v}}$$

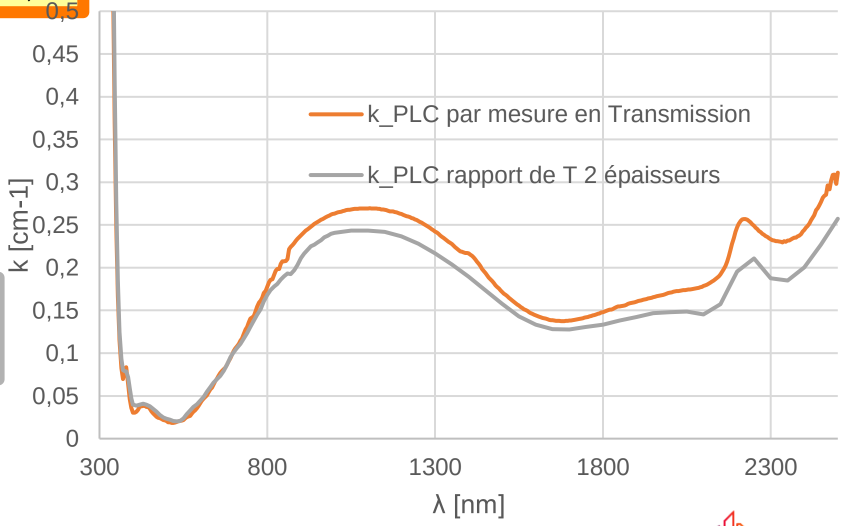
$$k_v[cm^{-1}] = -\frac{1}{d_v} \ln \left(\frac{-100^2 (1 - r_{a,v})^2 + \sqrt{100^2 (1 - r_{a,v})^4 + 4*(T)^2*(r_{a,v})^2}}{2*T*(r_{a,v})^2} \right)$$

$$Avec: r_{a,v} = \frac{R}{(200 - R)} \; ; T$$

- Calcul de k_v par rapport de T à 2 épaisseurs différentes

$$k_v = \frac{1}{d_b - d_a} \ln \left(\frac{T_a}{T_b} \right)$$

$$Avec: {r_{a,v}}^2 e^{-2 d_v k_v} << 1 \rightarrow T = 100 * t = 100 * (1 - r_{a,v})^2 e^{-d_v k_v}$$



SAINT-GOBAIN

FROM ENAMELED GLASS MICROSTRUCTURE TO OPTICS

OPTICAL DESCRIPTION OF CLEAR GLASS

Formule polynomiale (Herzberger) $n_v(\lambda) = A - \lambda^2 * B + \frac{C}{\lambda^2}$

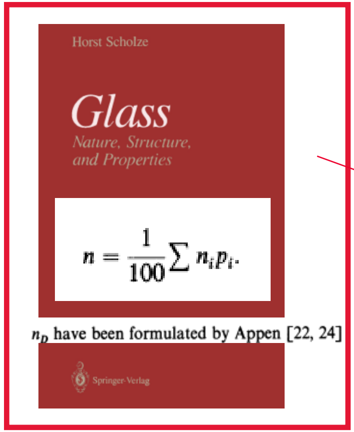
-Calcul de $R_{calculé}$ - à partir de $n_v(\lambda)$ et $k_v(\lambda)$:

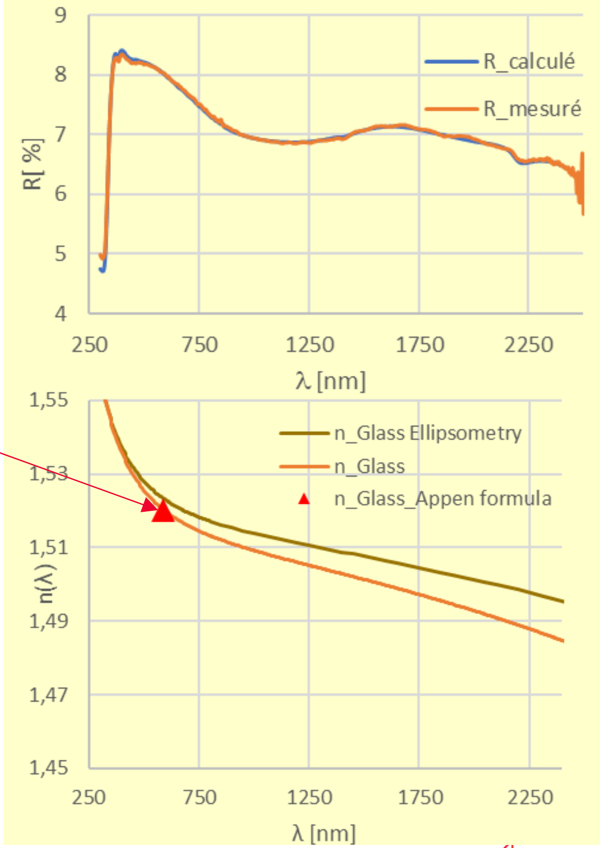
Relation de Fresnel à l'interface Air-verre

$$r_{a,v} = \frac{(1 - n_v)^2}{(1 + n_v)^2}$$

$$r = r_{a,v} + {t_{a,v}}^2 \frac{r_{a,v} * e^{-2 d_v k_v}}{1 - {r_{a,v}}^2 e^{-2 d_v k_v}}$$

$$R_{calculé} = 100 * r$$





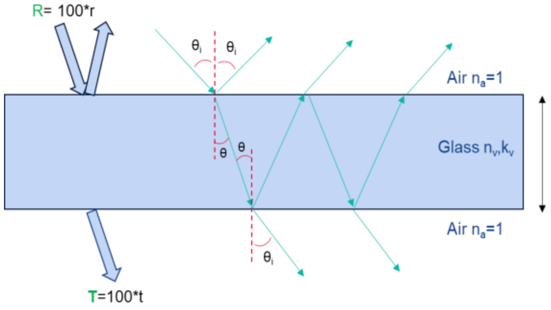
-Minimisation de l'écart $R_{calculé}$ -$R_{mesuré}$

N. G. Sultanova, I. D. Nikolov, and C. D. Ivanov, "Measuring the refractometric characteristics of optical plastics," Optical and Quantum Electronics, vol. 35, no. 1, pp. 21–34, Jan. 2003,

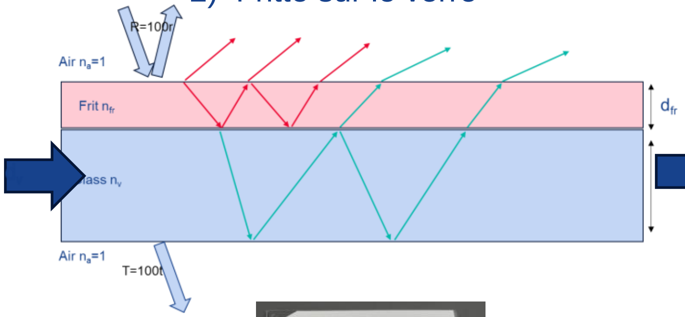
FROM ENAMELED GLASS MICROSTRUCTURE TO OPTICS

OPTICAL DESCRIPTION OF CLEAR GLASS

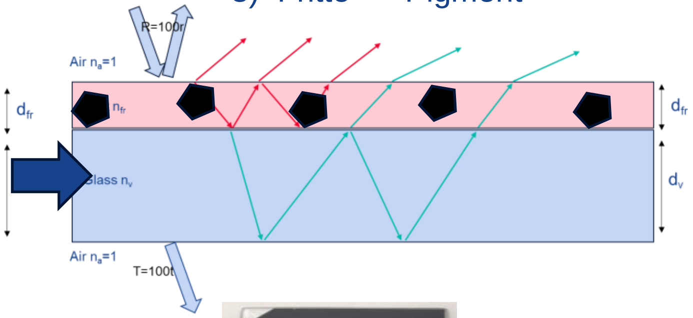
1) Echantillon de verre nu

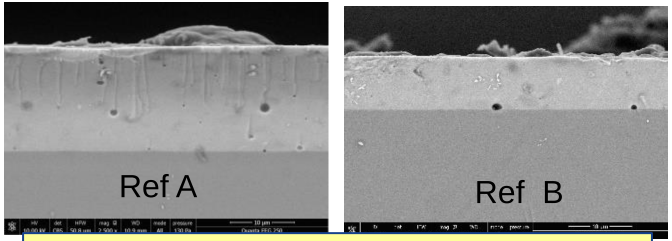


2) Fritte sur le verre



3) Fritte + Pigment



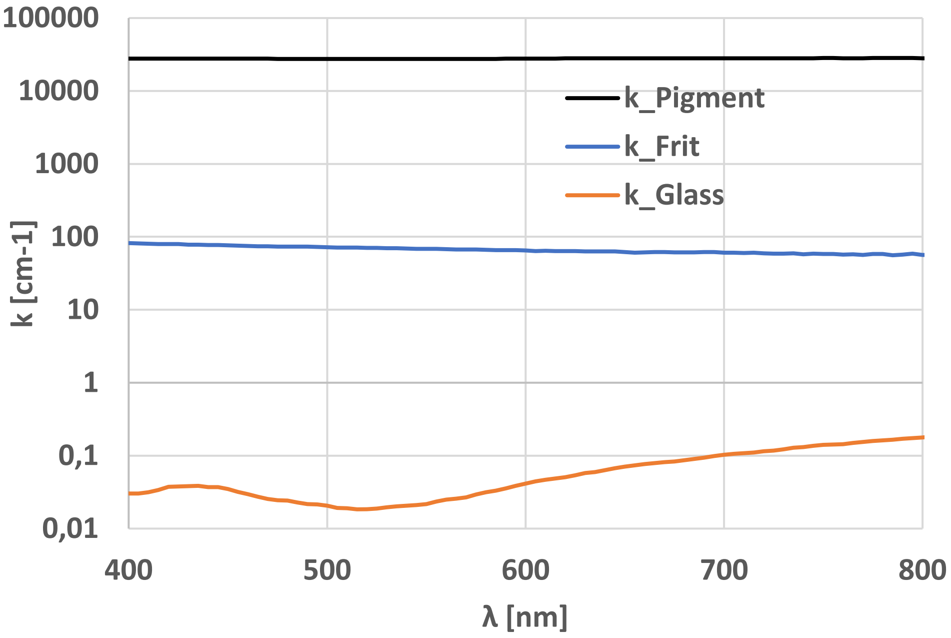


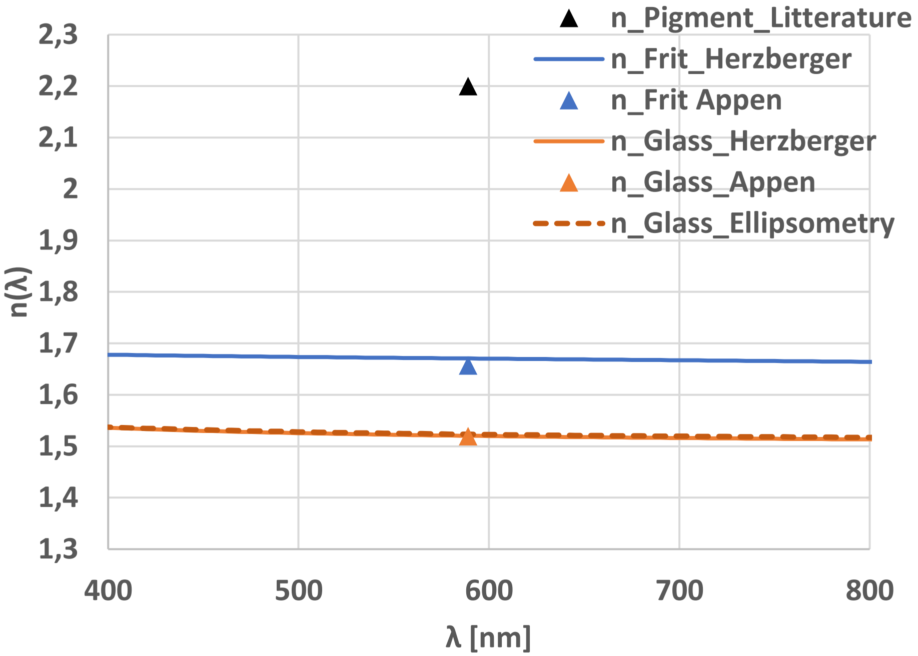
Microstructure dense, homogène et épaisseur contrôlée après cuisson du verre

Application aux frittes et pigments	
k	n
• Ratio Beer-Lambert de 2 mesures de transmission à 2 épaisseurs différentes	• Méthode d’Appen • Méthode d’Herzberger

FROM ENAMELED GLASS MICROSTRUCTURE TO OPTICS

OPTICAL DESCRIPTION OF CLEAR GLASS





Détermination de n, k = f(λ) pour chaque composant de l'émail :
=> Contribution principale des pigments ✓

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CONCLUSION

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CONCLUSION - THANKS

- Enamel Color and absorption are mainly driven by the pigment material

=> Highly absorbing pigments embedded in glassy matrix
=> Room for independent formulation of the frit material achieving functional requirements

Thanks to the entire ACE group lead by Juliette Jamart at SGR Compiègne for reference sample preparation, correlation with standard microstructure and fruitful discussions. Optical investigation of enamel sub-systems was investigated in collaboration with Pr. Ch. Andraud (MNHN).

MERCI

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THANK YOU

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