



Universidad de Oviedo

TRABAJO FIN DE MASTER - MASTER THESIS  
**MASTER IN CHEMICAL ENGINEERING**

**BOTTOM UP APPROACH FINE  
TUNNING OF A THIN ORGANO-  
MINERAL PRIMER**

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## EXECUTIVE SUMMARY

This project is a part of a long-term project referred to enamel coatings, thin glass coating. The objective in this particular project is merging the knowledge obtained from two background projects. The first one obtained a primer formulation (J7) without adherence - produced using the "Solgel" idea. The second project used the idea of tuning formulations with metallic oxides to improve adherence and opacity.

This whole project works to introduce metallic oxides in the "Solgel" primer formulation (J7) to improve its properties (adherence, opacity, surface finish). Another objective was to improve firing temperature and time for the "Solgel" primer formulation (J7) improving efficiency, and also it could help to improve adherence. First step to perform was to find out colourless metallic oxides to get the desired finish. There were found some different metallic oxides with good surface finish (these results were part of a patent in July 2015). Next phase was the optimization of firing time and temperature for the original "Solgel" primer formulation (J7). Temperature reduction was found to be possible increasing firing times in a long range. The final adherence improves but it was not good enough. Once the temperature optimization of the primer formulation was done, next step was continued by working with metallic oxide addition. Different test were made changing the metallic oxides and the amounts.

The results confirmed that the metallic oxide addition increases adherence and also opacity but bubbles are trapped into the enamel producing a surface fault. The same results were analysed using optic microscopy, SEM microscopy, DSC, TGA. The main conclusion was the needing to use organometallics instead of metallic oxides to obtain the primer. This shift in the process is still in progress, showing interesting results.

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## RESUMEN

Este proyecto es parte del otro más amplio denominado *Thin glass coating* (Esmaltado fino cristalino), dedicado a la generación de esmaltes para proteger el acero del ataque tanto físico como químico. Los sistemas objeto de estudio están formados por un sustrato (acero), un *primer* o capa de imprimación para conseguir adherencia y una *top coat* o capa superior para conseguir el acabado superficial deseado.

El objetivo de este proyecto en concreto es unir los conocimientos o conclusiones obtenidos en dos trabajos previos. En el primer estudio se obtuvo una imprimación, utilizando la idea de un sistema "Solgel", que mostraba muy buenos resultados de adherencia con el acero, pero no con la capa superior. En el segundo trabajo se modificaron fórmulas de imprimaciones añadiéndoles óxidos metálicos para mejorar la adherencia con la capa superior y la opacidad.

Este proyecto modifica la composición de la imprimación obtenida mediante el sistema "Solgel" añadiéndole óxidos metálicos para mejorar su adherencia con la capa superior y la opacidad. También se trata de optimizar la temperatura de quemado del proceso para la fórmula "Solgel".

En primer lugar se llevaron a cabo experimentos para obtener óxidos metálicos incoloros. Se encontraron diferentes óxidos metálicos que respondían bien a las necesidades. A continuación se trabajó en la optimización de la temperatura y tiempo de quemado, consiguiéndose reducir la temperatura si se aumenta el tiempo para un amplio rango.

Una vez optimizados tiempos y temperaturas se trabajó con la fórmula "Solgel" introduciendo óxidos metálicos obteniendo una buena adherencia con el acero y la capa superior pero el acabado superficial no es lo suficientemente bueno. Analizando los resultados con microscopio óptico, SEM, GD-OES, DSC y TGA se llega a la conclusión que este defecto es debido a la producción de una reacción paralela, y a que la temperatura de vitificación es muy alta, por lo que la mejor opción es cambiar el proceso de obtención de la imprimación utilizando órgano-metálicos en lugar de óxidos metálicos.

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## **1. INTRODUCTION**

Enamelling consists of applying a thin layer of glass fused at high temperature on to the surface of a metal. Vitreous and porcelain enamels are the most industrially used. These enamels can be outlined as a glass-like material produced by the complete or partial smelting of primarily oxide materials. This inorganic preparation is applied with additives, in one or more coats, onto work pieces made of metal.

Enamelling is used industrially to protect metallic surfaces from physical damage and chemical attack. It is an economic way of protecting the steel, and other vulnerable products from corrosion.

It should not be confused with paint, which is sometimes called 'enamel'. Paint cannot compete with vitreous enamel. They do not have the hardness, heat resistance and colour stability that is only available with real vitreous enamel. Enamelled products are extensively used for such kitchen pots and pans, washing machines, drums, bathtubs, fridges, as facing for buildings, chemical apparatus, heat exchangers...

Enamelled products have to protect from corrosion, be compatible with usual manufacturing methods as cutting bending, forming operations...In addition to having a clean workshop and being environmental friendly.

Enamelling process can be divided in three fields:

- Enamelled aluminium alloys and steel working between 500 and 600 °C.
- Secondly enamelled iron at temperature about 750 °C and 820 °C.
- And finally the issue we are working about: enamelled steel with process temperature 760 °C to 860°C.

## **1.1. ENAMELLING PROCESS**

The enamel composition previously melted at high temperature and quenched in water or between cooled roll mills, is subsequently milled by conventional milling techniques in order to get a fine powder suitable for the application.

When a porcelain enamel is applied on a steel surface, the link between both materials is obtained after firing at high temperature, between 780°C and 860°C.

The steel surface is first cleaned to remove oils and all other impurities whose presence could disturb the enamel application as well as the reaction between both materials during firing.

The bonding mechanism between the oxide glass and the steel surface occurs in four overlapping stages.

As it was already explained the enamel layer, still in powder form, is porous and contains air. A superficial oxidation of the steel surface occurs between the room temperature and approximately 500°C. Around 450°C and up to 550°C the common ground coat enamel compositions found today on the market start to soften and become a viscous liquid. From porous, the enamel layer is thus progressively changed in a continuous film, impermeable to air. The superficial oxidation which takes place according to the reaction [1] is stopped.

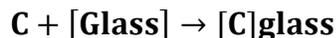
First step steel – glass adhesion mechanism



The second step of the mechanism starts then; the dissolution of the Fe-oxide layer previously formed on the steel surface is followed by a galvanic corrosion of the steel. This occurs progressively as both the viscosity and the surface tension at the glass decrease with the temperature and its chemical activity increases.

This second step [2] stops at about 750°C and 800°C, depending of the glass composition. It has to be noticed that in this temperature range  $\text{Fe}_2\text{O}_3$  is changed in FeO which is more stable within this temperature range. Summarized:

Second step of the steel mechanism – glass adhesion mechanism

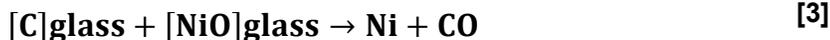


The third step consists of a global redox reaction [3] between the different species present near the interface. The galvanic corrosion of the steel surface by the melted glass enhances the presence of free iron and carbon truly “soubise” in the oxide glass. These elements reduce the thermodynamically most unstable oxides of the glass, i.e. the metallic oxides from the transition group previously melted in the glass composition. It can be seen in the **¡Error! La autoreferencia al marcador no es válida.** that within the elements constituting the glass, the only ones able to be reduced at “low temperature” are the oxides of the transition group. Here after a few examples of the possible reactions are given.

Combination Iron-Metallic oxide



Combination Carbon-Metallic oxide



Combination Iron oxide- Metallic oxides

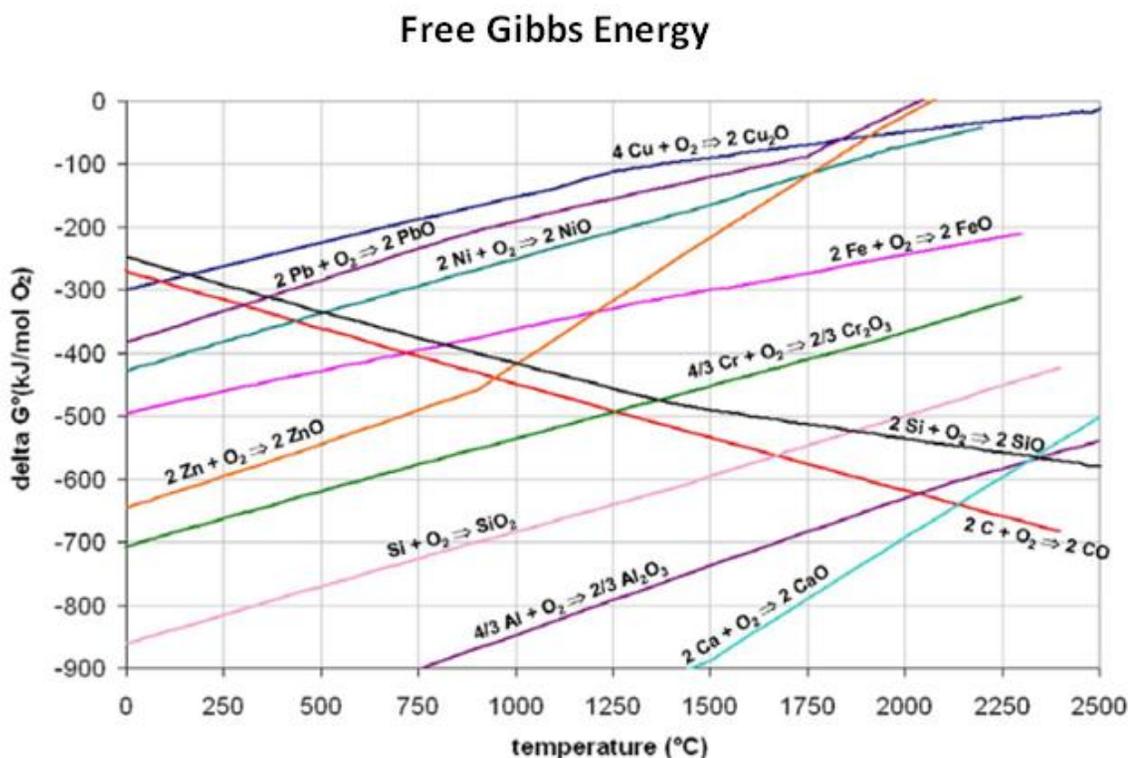


Fig. 1 Ellingham diagram of common oxides; Free Gibbs Energy for oxides

The reduced species (iron, cobalt, nickel, copper, manganese etc.) are diffusing towards the glass metal interface and precipitate on it in form of small irregular dendrites (Fig. 2), which compositions are complex and belong to the inter-metallic phase diagrams from the system Fe-Co-Ni-Cu-Mn depending of which oxides were previously melted in the glass. These redox exchanges occur mainly between 780°C and 860°C, depending of the glass composition, particularly on its capacity to corrode the steel and its content in metallic oxides (nature and amount).

The fourth and last step of the bonding mechanism occurs during cooling of the enamelled plate. The viscosity of the glass progressively increases until reaching the

softening point of the glass. So the precipitates are trapped in the solid glass, this fact gives the link between both materials. A kind of weld was build.

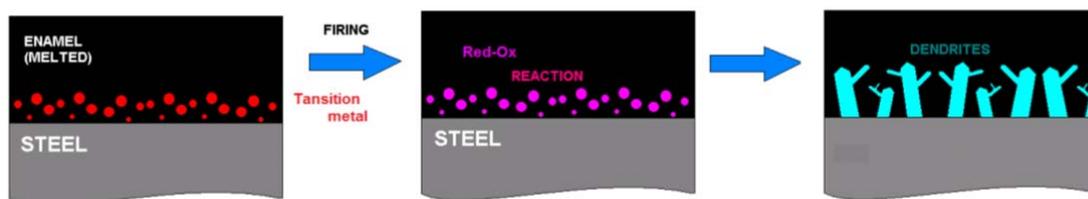


Fig. 2 Adhesion mechanism of en amel on steel (1)

The final enamel system, when it includes several layers applied on top of previous one(s), present also other interactions: diffusion reactions (for example of interaction of iron into the first layer, as previously detailed) might also happened between two enamel layers, and also redox reactions, when two glasses with different redox potential can react together.

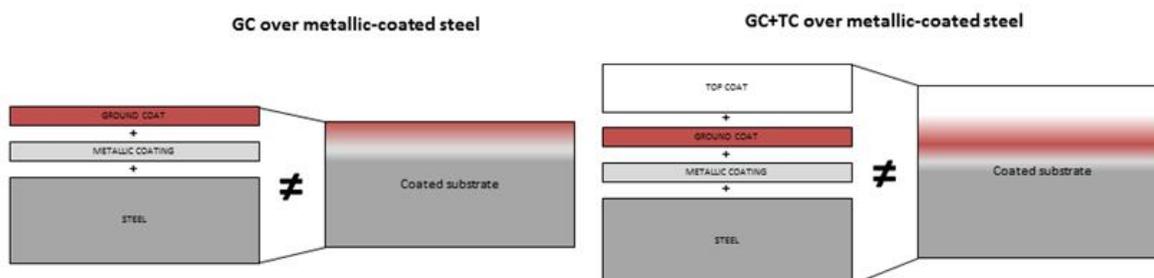


Fig. 3 Interfacial interactions

## 1.2. STRENGTHS AND WEAKNESSES

Production process of enamelling steel involves temperatures around 820°C. Consequently the risk of fish scale exists, which is a break with this typical shape due to accumulation of hydrogen on the steel -enamel interface during the enamelling. To avoid this problem specific steels capable of hydrogen trapping are used. Due to the use of high temperatures a strong annealing is produced which affects the final mechanical properties.

These high temperatures can produce surface defects in the enamel (carbon release) so the second specificity of enamelling steels is that they are all low carbon containing steels. All of these aspects limit the use of enamelled steel to a niche market (Table I).

In the enamel process a link is produced between the glass and the metal. It uses the diffusion and redox reaction of CoO and NiO (compounds with high price). Films from 80 to 200  $\mu\text{m}$  are needed to obtain a link. The glass-metal link produces warping the sheet steel when it is not thick enough. Steel sheets from 0.5 to 3 mm thickness are needed to avoid the warping. Nowadays thick enamel layers are used and this induces high material and process costs. This makes it less competitive and limits technical feasibility.

Table I. A few characteristics of the enamelling of steel and their impacts on the business

	Tips	Solutions // consequences	impact
Enamelling @ 820°C	risk of fish scale	specific steels for H trapping	limited offer in a niche market
	strong annealing	none // limited mechanical properties	
	surface defects in enamels (Carbon release)	ELC or ULC steel grades	
	energy cost	high	
Enamelling=post treatment	thick enamel layers on shaped steel	//(all) materials costs & process cost	lower competitiveness technical feasibility limit almost reached
		permanent deformations	
		limitation in steel thickness reduction	
	complex- multi steps	impact on cost and LCA	
Glass to metal link	Thick & based on diffusion/Redox of CoO,NiO	impacted by REACH?	Futur in EC
		cost of Critical Raw Materials	
		thick reactive interface	

It is also remarkable that enamel coatings can be tuned for very particular applications (Table II), thanks to very broad field of chemical compositions, all derived from glasses.

Table II. Possibilities offered by enamels for tuneable surface properties

durable-recyclable	>>20 years- like steel
Tunable surface properties	hardness –abrasion-ceramic like
	water & steam resistance
	acid and alkaline resistance
	hydrophilic-hydrophobic
	anti clogging-chemical resistance
	Corrosion resistance (chemicals)
	antibacterial
	anti graffiti
	food contact - ETC- drinking water
Temperature resistance	paints-plastics<E> ceramics
	thermochock resistance
Aesthetic bulk properties	mat/bright/colourable
	UV stable-luminescent-thermochrome

## **2. BACKGROUND**

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## 2.1. THIN GLASS COATING PROJECT

The Thin Glass Coating (TGC) project is a long term-breakthrough project at OCAS. The main objective is obtaining enamel coatings providing solutions to the existing limitations.

A new concept about enamelling manufacturing process is introduced in this project. It consists in:

- Reducing operation temperatures to avoid fish scales, to reduce deformations and to increase mechanical properties.
- Introducing a diffusion barrier towards the diffusion of iron & carbon into enamels, and if possible of hydrogen into steel.
- Trying to get a mechanical adherence instead of a chemical one. Co-Ni free system.
- Splitting the enamel in 2 layers. First one ensures the glass to metal link and is integrated to the substrate; a second one ensures aesthetic and functional aspects of the top surface of the new composite material.
- Ready to fire steel where the pre-enamelled steel is directly formed and fired (Fig. 4).

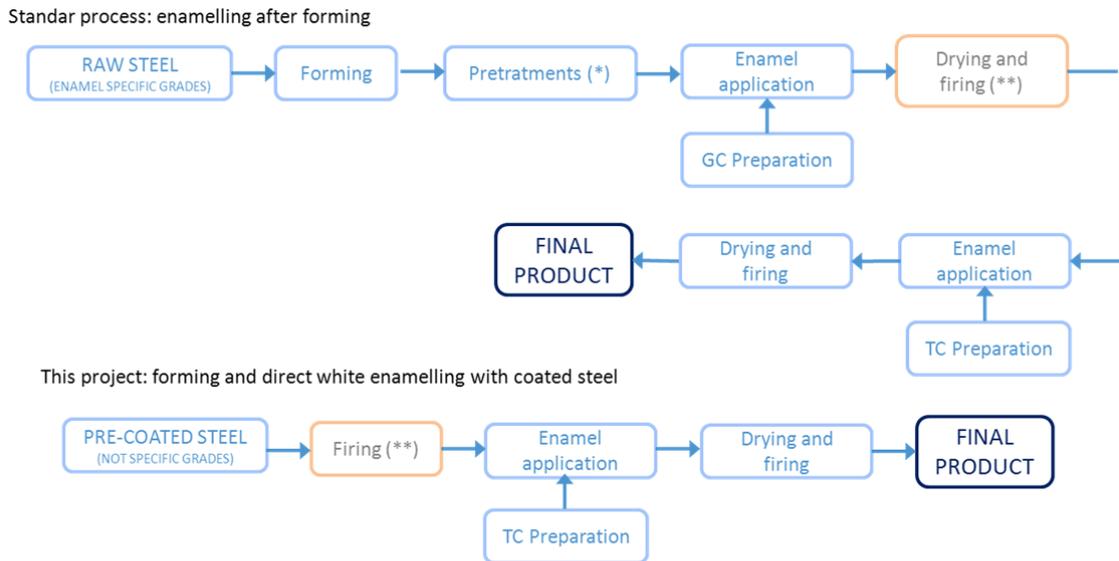
Using this new concept was found:

- By using metallic coated steel in place of steel suitable for enamelling.
- By reducing the enamelling temperature from 830°C (average) to about 720 °C.
- By substantially reducing thickness of the enamel layer(s) (Fig. 5)
- By REACH compliant system is developed.
- By transferring the glass to metal link onto the metallic coated steel substrate, in the form of an organic/glass or ceramic layer, glass ceramic layer, hereafter named primer.
- By using a cover coat enamels designed for further vitrification at about 720 °C applied on top of the primer, and able to be used at lower thickness than the state of the art.

It was possible to use steel grades normally not suited for enamelling, not ELC (Extra low carbon) not ULC (Ultra Low Carbon) specific grades as defined in EN 10209, being carbon steel grades, micro alloyed steel grades, quenchable steel grades, bake hardenable steel grades, high strength steel grades, hot formable steel grades ... (no exhaustive list). This is possible because the metallic layer on top of the steel, in between the steel and the enamel(s) layer(s), acts as a barrier towards:

- Contact between the enamel layer(s), being an oxide, and carbon from the steel.

- Diffusion-absorption of hydrogen from the firing atmosphere onto the steel, known to have high affinity for this gas at high temperature



(\*) The surface treatments may induce: degreasing, rust removal, pickling, nickel deposition, activation, neutralization, several rising steps in-between, and draining/drying.

(\*\*) Firing of the formed piece after GC application is carried out if the process is 2C/2F

Fig. 4 Comparison between standard enamelling process and ready to enamel steel

A contact between an oxide glass and an iron/carbon alloy at high temperature would lead to initiate redox reactions, leading to the formation of gas—namely CO or CO<sub>2</sub>, which would form bubbles in the enamel layer(s).

The absorption of hydrogen in steel is known to increase with temperature, and to become important above AC1 transition temperature in the iron-carbon phase diagram, thanks to the transformation of ferrite into austenite at this temperature. Unfortunately, this phase transformation is reversible, so hydrogen would desorb from the steel matrix after cooling, in case of insufficient trapping capacity into the steel matrix.

So the metallic coating on top of the steel acts twice as a barrier and avoids contact or diffusion of carbon towards the enamel and avoids hydrogen to diffuse into the steel.

There is another benefit of combining any of the steels here above mentioned in a vitrification process (to get the enamel layer on top) at only about 720 °C. Beside the fact that the adsorption of hydrogen by the steel will remain low, whatever the steel grade is, one has to keep in mind that the enamelling process is – for the steel and whatever grade is, an annealing. So its own mechanical properties (yield strength and tensile strength) will lower. The fact that high carbon steel grades, alloyed steel grades can be used instead of low

alloyed low carbon grades (as defined in EN 10209), changes the figures. At the end, higher mechanical properties are obtained after enamelling, which allows reducing the thickness of the steel of enamelled parts, providing substantial earnings.

Last but not least, enamelling of steel consist to associate a ductile material, being the steel, to a brittle one, glass like, being the enamel. This association forces to configure the system in a particular way, fixing the thermal expansion coefficient of the enamel at a lower value than the one of the steel. So, by cooling down the system, compressive stresses are generated in the enamel layer, and tensile stresses into the steel, which is the unique way to keep integrity of the enamel coating. Otherwise, the enamel layer would crack and would not protect the steel from corrosion anymore, but this concept has a drawback: thin sheets of steel deform (are bended by the enamel), the phenomenon being increased by the fact that the enamel layer is rather thick (Fig. 5) (deformations are proportional to the thickness of the coating), and because of the strength of the steel is rather low, because it is a low allowed and low carbon steel grade, moreover annealed.

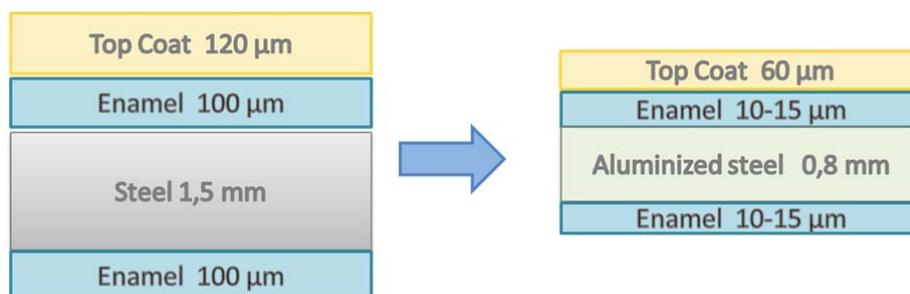


Fig. 5 Thickness of substrate coatings today and the expected evolution.

These innovations will lead to get a more sustainable process. All this improvements increase added value for ArcelorMittal with a product integrating glass metal link design and coating-substrate compatibility.

## 2.2. DEVELOPMENT PROJECT APPROACHES

OCAS launched two parallel development projects: Firstly Top Down approach, modifying prepared enamel compositions. Secondly Bottom up approach, using a pseudo Solgel process to obtain enamels from salts and nano dispersions. Both projects were launched to develop a new glass to metal link, using Metallic coated steel instead of steel.

### 2.3. ENAMEL TOP DOWN PRIMERS

This project was tuning compositions of primers in a top down process, starting from commercial enamel compositions and modifying them, if necessary, by mixing other enamels or pure oxides. Main objectives were obtaining good adherence between the steel and layers and achieving an acceptable surface quality when top coat is applied on top of it. Main characteristics of this study are:

- Metallic coated steel (aluminized or galvanized) was used as substrate, replacing steel to easily get adherence by creating a mechanical interlock between the glass and the metal. The glass penetrating the roughened metal, if its viscosity and surface tension are correctly chosen.
- During the study the temperature range of 675 to 740°C was used to obtain the vitrified glass
- In this temperature range, it was demonstrated that it was not necessary to use specific (enamelling) steel grades.
- Thickness of the glass layer was reduced improving the life cycle assessment and obtaining lower deformations.
- Thin glass layers are free of Co and Ni and other components forbidden by REACH.
- Final thin glass layer precursor can be optionally integrated to metallic coated steel in a polymer matrix to get better control of thickness on the first primer layer.

The main problem was that primer and top coat showed bad compatibility at the beginning. Chemical resistance of the layer was not good and the layer was not opacifying during vitrification. Two hypotheses were made and subsequent experimental programs were launched

1. White top layer is a metal stable glass composition in which  $\text{TiO}_2$  recrystallizes during firing. It was supposed that the recrystallization of  $\text{TiO}_2$  during the second firing was disturbed by further inter-diffusion of some elements from primer into the top coat
2. The recrystallization of  $\text{TiO}_2$  during second firing was disturbed by a displacement of equilibrium. Oxygen partial pressure decreases and it produces  $\text{TiO}_2$  recrystallizes in a sub stoichiometric manner and changes the refractive index of the glass, lowering its opacity.

The results of the study show that adding transition metallic oxides in the phosphate glasses and after also alkaline borosilicate enamels, they adhere onto Alusi above 700°C (Table III). All compositions allow getting opacification of white top coat but:

- × Formulations B9 and C15 did not form a glass, and release colouring oxides (Cu, Cr...) into the top coat during the second vitrification step.
- × Formulation I8 is, as such:
  - Too soft
  - Not fitting with rules recently implemented in REACH about enamels. Its own CuO content has to be at maximum 3% and silica content needs to be at least 30% weight.
- × Formulations G10 and G11 are kept temporarily for further optional use as hardeners. Both cannot be commercialized as such (because of REACH rules), and will force to make one more iteration if they are employed.

Table III. Primer compositions finalized in the Top Down study by mixing enamels and pure oxides

W%	B9	I8	C15	G5	G9	G10	G11
Al <sub>2</sub> O <sub>3</sub>	15 << 20	< 2	2 << 5	< 2	< 2	< 2	< 2
B <sub>2</sub> O <sub>3</sub>	5 << 10	>> 20	10 << 15	10 << 15	>> 20	>> 20	>> 20
Cr <sub>2</sub> O <sub>3</sub>	< 2	< 2	10 << 15	< 2	< 2	< 2	< 2
CuO	15 << 20	2 << 5	10 << 15	5 << 10	10 << 15	10 << 15	5 << 10
Fe <sub>2</sub> O <sub>3</sub>	< 2	15 << 20	< 2	>> 20	>> 20	>> 20	>> 20
K <sub>2</sub> O	5 << 10	2 << 5	2 << 5	10 << 15	5 << 10	5 << 10	5 << 10
MnO <sub>2</sub>	< 2	< 2	< 2	< 2	< 2	< 2	< 2
MoO <sub>3</sub>	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Na <sub>2</sub> O	5 << 10	>> 20	10 << 15	10 << 15	10 << 15	10 << 15	15 << 20
P <sub>2</sub> O <sub>5</sub>	>> 20	2 << 5	5 << 10	2 << 5	2 << 5	< 2	< 2
SiO <sub>2</sub>	2 << 5	20 <<	>> 20	15 << 20	15 << 20	10 << 15	15 << 20
TiO <sub>2</sub>	< 2	10 << 15	5 << 10	10 << 15	5 << 10	5 << 10	5 << 10
ZrO <sub>2</sub>	2 << 5	< 2	< 2	< 2	< 2	< 2	< 2

It was also found that the thickness of the primer (ground coat) layer plays an important role, especially when it is very thin.

The introduction of “unstable” metallic oxides, such as CuO, MnO<sub>2</sub> leads to the formation of small metallic precipitates onto Alusi. It seems possible to match the bonding

mechanism of enamels onto steel combining adequately Alusi, low temperature and specific oxides trying in a further step to melt them into a glass matrix.

## 2.4. BOTTOM UP APPROACH

The aim of the project is to obtain a final product formable, ready-to-enamel pre-coated steel. It makes a simplified process allowing a direct forming and easy, integrated firing (Fig. 4). The concept is based on a coating comprising an organic (polymer) matrix in which the enamel precursor is embedded (Fig. 6).

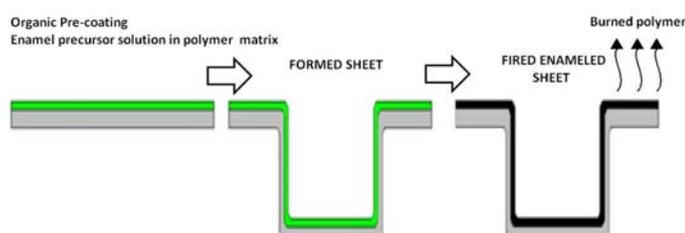


Fig. 6 Ready to Fire Pre-Coating

This study focuses on a bottom-up approach which relied on the use of solubilized “enamel precursors” (Metal salts/ nano-powder suspensions) in order to build a glass in-situ and therefore obtain a coating with thicknesses as low as 5 to 10  $\mu\text{m}$ . The general idea of the **Solgel process** was considered for this purpose but **using metal salts and nano powders instead of organo-metallic precursors**.

### 2.4.1. Solgel process

Solgel synthesis is a method used for the fabrication of metal oxides in material science. “Sol” part means the process to convert monomers into a colloidal solution. This colloidal solution acts as precursor for the “gel” part that is an integrated network formed by either discrete particles or network polymers. The precursor “sol” is deposited on a substrate to form a film by bar coating and cast into a suitable container. The Solgel approach is a cheap and low-temperature technique that allows for the fine control of the product’s chemical composition.

Solgel process is used to obtain a very pure composition, and perfectly fits for bulk materials as well as for coatings. This technology is often used since the 80’s in many fields including optics, electronics, biomaterials, sensors, etc.

The main principle of the Sol-gel synthesis relies on the transformation of organo-metallic precursors into metal oxides or glasses by means of hydrolysis and condensation processes (Fig.7). Highly pure materials are obtained in a lower sintering temperature in comparison with no-chemical processes such as solid-state reaction.

Organic compounds and water of the process are removed by heating. In addition to being suitable for various macroscopic shapes (bulks as monoliths or powders, films, fibers), this method allows for a precise control of the microstructure (fiber or sphere-like) of the material, through the parameters of synthesis like the pH (1).

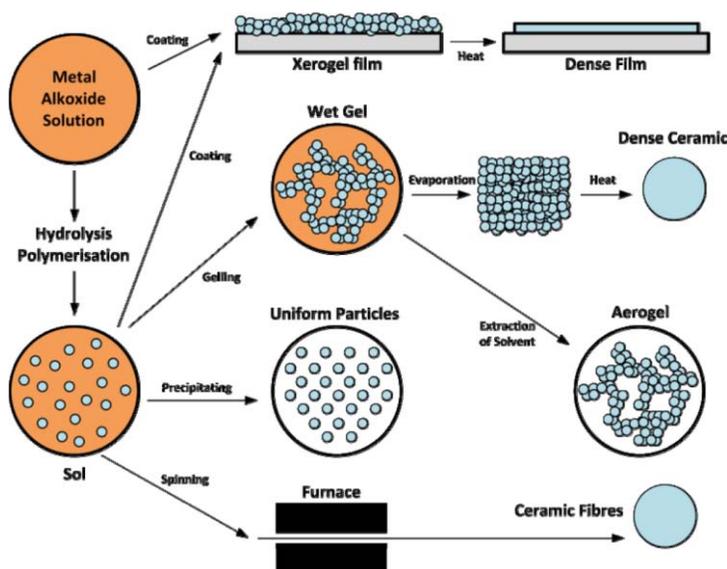
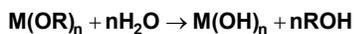
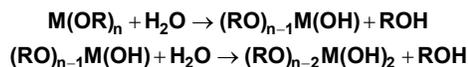


Fig. 7 Scheme of the sol-gel process

## 2.4.2. Reaction mechanisms

### Hydrolysis

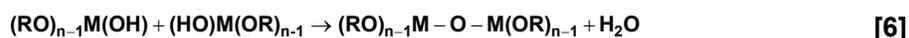
Hydrolysis is the first step of the sol-gel process: it is the activation reaction, where the precursors are partially or fully hydrolysed to form a reactive monomer MOH, and alcohol, where M represents the non-organic element and R an organic radical [4]



[4]

*Condensation: sol information*

The monomers' condensation allows the carbon chains to grow within the sol. Two different mechanisms are involved, Alcoxolation [5] and Oxolation [6], to create an M-O-M bond.



Hydrolysis and condensation reactions occur rather simultaneously once the hydrolysis reaction has been initiated. However the kinetic of one or the other can be sped up through parameters such as the acidity. Indeed, Solgel syntheses can be achieved in neutral pH or catalysed by acidic or basic conditions that favour hydrolysis and condensation, respectively (2).

*Cross-linking: gel formation*

The gelation results from the cross-linking, which occurs when the condensation has reached a certain level; it leads to the formation of a 3-dimensional network.

**2.4.3. Results**

At the end of the first phase of the work a phosphate aluminium glass coating was obtained from a hybrid powder suspension/precursor salt solution. The ground coat is fully covering as thin as 10  $\mu\text{m}$  at 710°C (3). Under these conditions a perfect adhesion is obtained.

First step was obtaining a solution between all main salts at an acid pH (5, 5 - 6). Thereafter nanoparticles dispersions were chosen to be compatible with the previous solution.

The hybrid system (using powder and salts during the most of the study) has the disadvantage of forcing the use of a complex system involving colloidal stability on a high ionic strength media. In Table IV different compounds tested are shown.

The main problematic sources were that of aluminium and that of silicon.

- × For aluminium it was decided to work with aluminium oxide powder with a  $d_{50}$  of 60 nm due to the highly oxidative nature of other substances or the difficulty to obtain a homogeneous mix.
- × Silicates were considered at first as silicon precursors but finally Levasil 200/40% pH 10.5 was used.

Different formulations were prepared with those precursors (Table IV). The best formulation obtained has the composition shown in Table V:

Table IV: Overview of precursor formulations

	J1	J2	J2-Bis	J4	J6/J7
$B_2O_3$	$H_3BO_3$				
$K_2O$	$K_2SiO_3$	$K(OH)$			
$MoO_3$	$(NH_4)_6Mo_7O_{24}$				
$CuO$	$Cu(NO_3)_2$	$CuSO_4$		$CuO$	
$P_2O_5$	$NaH_2PO_4$				
$Na_2O$	$NaH_2PO_4 + Na(OH)$				
$SiO_2$	$K_2SiO_3$	Colloidal $SiO_2$			
$Al_2O_3$	$Al(OH)_3$			$Al_2O_3$ (nano)	

Table V: At the left precursor mass % composition at the right  
j7 oxide composition

Oxide composition	
Oxide	% w
$Al_2O_3$	>> 20
$B_2O_3$	10 << 15
$MoO_4$	<< 2
Na + K	>> 20
$P_2O_5$	>> 20
$SiO_2$	5 << 10

The main mechanism of adhesion was identified as the growth of Fe-Si-Al ternary phase in the Alusi coated steel; making the Alusi-enamel interface rougher and leading to increased mechanical interlocking. It is not clear yet whether Redox reactions are occurring to precipitate dendrites and therefore play a role in adhesion.

Once precursor is ready next step remains to have a final product comprising a formable polymer coating. It was found that an acrylic polymer currently applied onto Alusi or galvanized steel provided the more stable system. The objective here is to achieve a stable paint formulation including both the polymer and the precursor electrolyte.

Requirements for the polymer are (see in Table VI the available polymers for this purpose):

- Compatible with the salt/powders system

- Relatively low Tg will lead to increase formability but tackiness is expected when very low Tg is used.
- Film forming temperature and time required for optimal curing.
- Polymer must be readily burned at lower temperatures than the melting point of the glass.

Table VI: Available polymers and their properties

Binder	Tg (°C)	Tform (°C)	pH	wt. %	Property
Acrylic Thermoset AM185	28	180 PMT	8	50	Anionic
Acrylic Thermoplastic AM355	12	180 PMT	9,5	46	Non Ionic
Polyurethane (Beetafin)	145	210	9	35	Anionic
Gardobond	-	90 PMT	-	30	-
Texicryl Acrylic TD17-093	-	210	3,5	45,5	Acrylic-Epoxy
Acrylic copolymer (Thermoplastic)	45	70-85 PMT	3	50	-

Among the polymers tried there were found polymers completely incompatible with the salts/powders system. Acrylic copolymer showed the most promising results in terms of compatibility as very limited limping and quite promising stability. The pH plays a role in the stability of the powder suspension. The pH of the current salt solution is suitable for suspending alumina powders (It is done by a specific mixing protocol.)

### **3. OBJECTIVES**

This study is a natural follow up to the previous ones here before described. In the top down approach, phosphate glass and then soft borosilicate glass compositions were modified by adding transition metal oxides.

In the bottom up, a simplified phosphate glass composition was first obtained.

At this point, it looks interesting to think in merging both tracks in order to try to answer to the following questions:

- Is the Solgel glass compatible with Top Coat enamel layers?
- If not, is the addition consisting of adding transition metal oxides to enamels, helpful for the Solgel track?
- Solgel technology is known to provide ceramic coatings at rather low temperature of the Solgel solution?
- Further reduction of curing temperature (as option to be checked).

The objectives of this study are:

- **A vitrified glass layer should be obtained at temperatures below 700 °C** which eliminates the need of a specific steel grade. The use of higher temperatures induces the requirement of using specific steel grades able to afford hydrogen. Starting with J7 composition reduces curing temperature as far as possible keeping in mind the consequent time increase.
- **The precursor of the ground coating should be able to support steel forming process** in order to obtain a ready to fire steel to induce the glass layer. Furthermore the ground coating should act as a precursor of the final glass layer.
- **Compatibility with top coats (TC) and substrates:** The obtained composition should be compatible with different substrates (different metallic coated steels) and commercial top coats.

### 3.1. FOREWORD – COMBINATION SOLGEL PRIMER-TOP COAT ENAMEL

In Fig.8 at the left, the Top down I8 composition with top coat enamel after firing at 710°C during four minutes is shown. At the right side Solgel layer curing at 710°C during 4 minutes is shown. On the left side is smooth and white opacified layer on the right side peeling, cracks bubbles...



Fig. 8 White top coat applied onto I8 composition the left and white coat applied onto J7 (Solgel) at the right T: 710°C t: 4'

### 3.2. POSSIBLE INTERPRETATION

A possible hypothesis to explain these results is that compositing salts do not have enough time to recombine and achieve a stable state.

One objective of the present study is to reduce curing temperature. Due to that and the previous hypothesis we will try to reduce firing temperature increasing firing times. This provides the opportunity to reach the stable state.

The opacifying during vitrification had bad outcomes. It is known that applying the white Top Coat on another glass was leading to opacification (Fig. 8) even by firing at around 700°C. It was known too that TiO<sub>2</sub> (rutile) was crystallizing into the glass matrix. The hypothesis made for this phenomenon is that the recrystallization of TiO<sub>2</sub> during second firing was disturbed by a displacement of equilibrium, more particularly, by a reduction of the partial pressure of oxygen in the system (Fig. 9). It is known that when TiO<sub>2</sub> recrystallizes in a sub stoichiometric manner, its refractive index is affected.

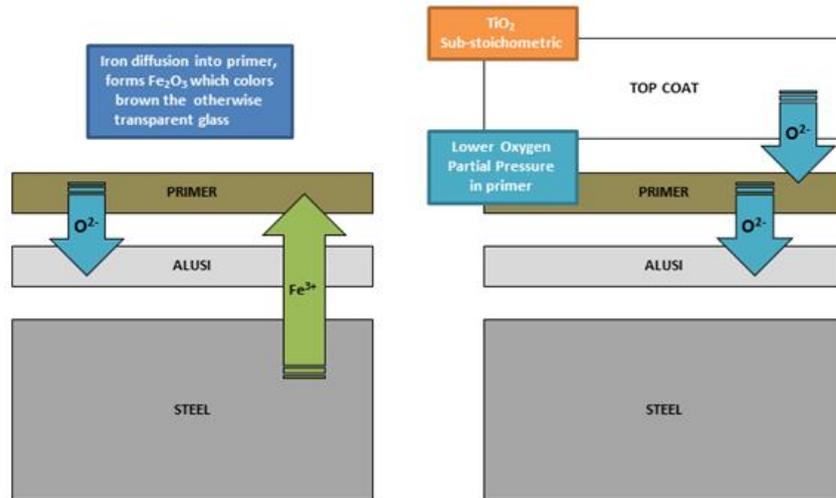


Fig. 9. Opacification hypothesis: lower oxygen partial pressure on interface primer-top coat

## **4. MATERIALS AND METHODS**

## 4.1. CHOICE OF MATERIALS

### 4.1.1. Substrate

In this study 0.5 mm thick cold rolled steel coated with 20  $\mu\text{m}$  of Alusi (Aluminium with 10wt% Silicium) for corrosion protection has been used. The Alusi coating (Fig. 10) maintains corrosion protection of the steel sheet before and after the application of the primer and up until firing of the material. The Alusi coated steel is designed to sustain temperatures up to 800°C (depending on steel-grade). Therefore it is used when resistance to corrosion is needed at elevated temperatures such as in exhaust systems, heating equipment and boilers.

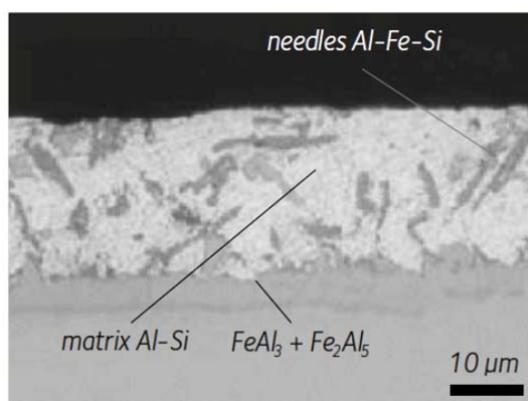


Fig. 10 Micrographic cross-section of Alusi coating illustrating its microstructure.

In this project, the choice of Al based metallic coating is motivated by the fact that:

- 1- The use of Zn based metallic coated steel is covered by a patent owned by Pemco.
- 2- It is known that in enamelling of aluminium alloys, inter-diffusion between metal and glass occurs only on a very few microns.

The silicon in Alusi has strong affinity with iron and therefore acts as a diffusion barrier during hot dip process. In order to obtain adherent thin enamels and to conserve their properties, it is capital to allow iron diffusion but to limit it as well so as not to solubilize too much iron in the glass. This justifies the use of Alusi coated steel for the purposes of this project. However around 700°C iron diffusion through the Alusi leads to the growth of an Al-Fe-Si ternary phase (Fig. 11).

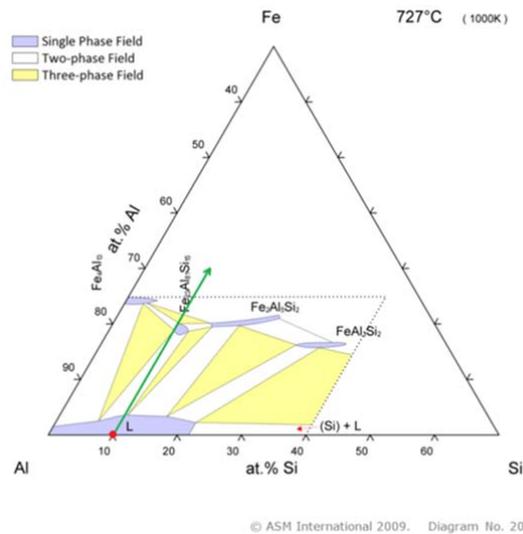


Fig. 11 Solid-Liquid phase equilibrium in the Al-Fe-Si System at 727°C

This phase grows chaotically and generates a rough surface, it is expected that this phenomenon will further increase enamel adhesion, but it also requires a good wettability of the melted glaze.

These intermetallic compounds have a tendency to render the surface rough and brittle when the coating is annealed at too high temperature or for too long (Fig. 12.). Part of this study will therefore focus on the growth of these phases in the substrate during firing and its influence on coating adhesion.

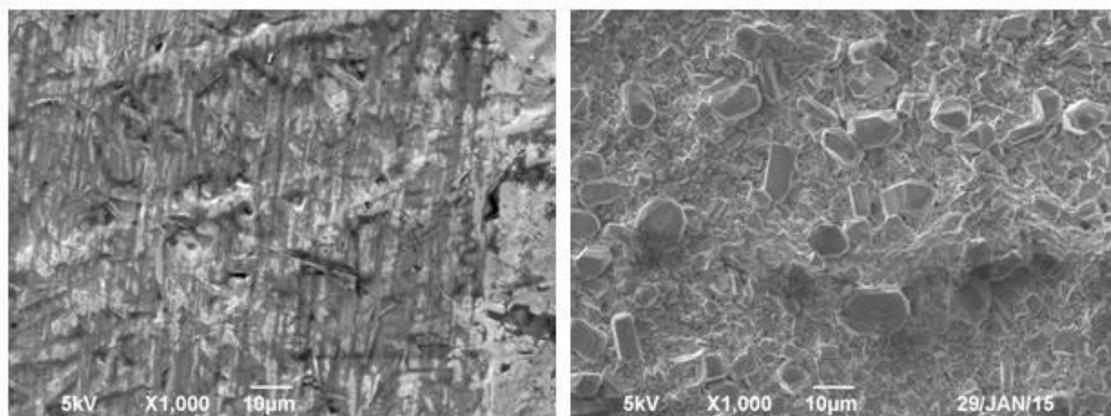


Fig. 12 SEM surface image of Alusi before (left) and after (right) firing at 740°C.

#### 4.1.2. Primer composition

In the previous study in our system invest reference (3) was found a chemical composition named J7 (Fig. 13). This primer formulation has very good adherence properties. During the study of the solution it was shown that:

- Aluminium salts have a tendency to crystallize or generate precipitates.
- Aluminium nano-powders can be used but need to be put into suspension with proper product or additives.
- Some polymers are completely incompatible with the salts/powder system.
- The pH plays a role both in the stability of the powder suspension and the pH of the current salts solution is suitable for suspending alumina powders.

Solutions in H2O		
Salts	47	wt. %
Vol H2O	50	mL
Total mass of precursors	44,3	g

Mix	m (g)/25 mL
Al <sub>2</sub> O <sub>3</sub>	5,1
H <sub>3</sub> BO <sub>3</sub>	0,0
HeptaMolybdate	0,3
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	13,7
K(OH)	0,0
SiO <sub>2</sub> Levasil	3,1



1. Pour 50 mL H <sub>2</sub> O in plastic cup.	Stirrer : 8000 rpm	
2. Add H <sub>3</sub> BO <sub>3</sub>		
3. Add K(OH)		
4. Add HeptaMolybdate		
5. Add NaH <sub>2</sub> PO <sub>4</sub>		
6. Add Levasil 200/40		
8. Add Alumina Powder (Disperal)	Stirrer during 30 minutes	
9. Add polymer	18,9	g
11. Prepare for Bar coating		
13. Bar coat + Fresenberger	90 sec - 95°C	
14. Firing and quenching in air	5 min - 710°C	g

Fig. 13 Protocol for J7 + polymer (Example for 50 mL of H<sub>2</sub>O) (3)

The sample preparation has to be done following a specific protocol to avoid the precipitation of some compounds, as Alumina Nano-powder.

The mixing parameters bellow has been proven with the following *modus operandi*:

- Mixing Vessel Size: Ø85mm/Blade Size: Ø20mm.
- When G60/3 is added softly stirring with a spoon is required.

The final oxide composition of the glass obtained is shown in Table VII.

Table VII: Oxide composition of J7 mixture in weight percentage (%) [3]

Oxide composition	
Oxide	% w
Al <sub>2</sub> O <sub>3</sub>	>> 20
B <sub>2</sub> O <sub>3</sub>	10 << 15
MoO <sub>4</sub>	<< 2
Na + K	>> 20
P <sub>2</sub> O <sub>5</sub>	>> 20
SiO <sub>2</sub>	5 << 10

To understand the influence of the composition of the glass on its properties, it is necessary to define its main components.

The glass theory designates three types of oxide compounds depending on their influence on the glass:

- **XO<sub>2</sub>/X<sub>2</sub>O<sub>5</sub> compounds:** These are the glass formers, the materials responsible for the glassy skeleton. There is 1-2 ratio with oxygen. This is the main compound, and the others are to modify its properties. SiO<sub>2</sub> is the main glass former in this case, but there are more compounds as TiO<sub>2</sub>, SnO<sub>2</sub> or ZrO<sub>2</sub>.
- **X<sub>2</sub>O<sub>3</sub> compounds:** These are used as stabilizers which increase the melting point of the glass and hardening the glass. They are in 2-3 ratio with oxygen. Some stabilizers examples are Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub>.
- **XO/X<sub>2</sub>O compounds:** There are called fluxes and its main property is reducing the melting point of the glass allowing to flow better when are molten to achieve a better wetting of the surface. The main fluxes are K<sub>2</sub>O, Na<sub>2</sub>O, ZnO or BaO.

## 4.2. EXPERIMENTAL PROCEDURE

The experimental procedure carried out is composed of 7 different steps in our case as it is a 2 coats 2 firing process (2C/2F) as is shown in Fig. 14.

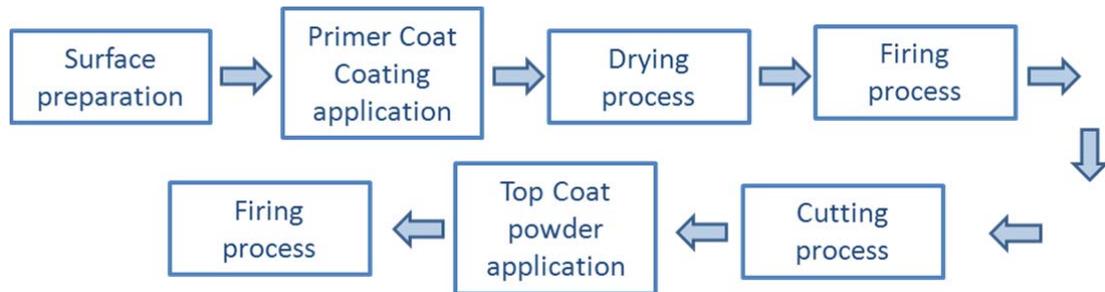


Fig. 14 Two coats two firings process

### 4.2.1. Surface preparation of the substrates

Before being coated, the substrates have to be prepared and cleaned. It is a very important step in the coating process because it influences covering and adherence (chemical exchange). Indeed, if the substrate is not perfectly clean the coating cannot properly adhere. As substrate is used 0.5 mm steel sheet coated with Alusi which size is 20x10 cm. The different steps of the sample preparation are given in Fig. 15.



Fig. 15 Substrate preparation

Deburring consists in smoothing the substrate edges. It is necessary to avoid damaging the bar coater, and to achieve a uniform coating and a good control of thickness. In addition, the substrate has to be perfectly flat to use the bar-coating method. The steel samples are vapour-degreased, then light alkaline-degreased to remove the oil applied on those substrates, fingerprints and oxide layer before application of the coating enamel.

#### 4.2.2. Coating Application: Bar coating

The choice of a coating method depends, among other things, on the density and the viscosity of the solution. The bar coating technique is suitable for materials with a viscosity from 1 to 1000 centipoises. Furthermore thicknesses ranging from a few nanometres to 150 $\mu$ m can be obtained with this method.

The bar-coater is pressed against the top of the substrate and slipped along its length to apply the solution on the whole surface (Fig. 16).

A magnetic coating bed is used to keep the substrate flat. The thickness of the applied film is approximately given by the number of the bar-coater.



Fig. 16 Hand bar-coating technique

To obtain a good repeatability by the bar-coating technique constant pressure and speed have to be applied during the bar coating procedure. It can be done automatically, but in our case it has been done manually.

#### 4.2.3. Drying process

Once samples have been coated with the Solgel mixture as it is described in **¡Error! No se encuentra el origen de la referencia.**, they are dried in a hot air oven (FRESENBERGER) (Fig. 17). Depending on the polymer used the Peak Metal Temperature (PMT) and the duration of curing is selected. Longer times may be used depending on water content of solution and the thickness of the film. The regular temperature is around 105°C and the time around 3 minutes, in such conditions the polymer is cured and the solvent is fully removed. Coatings obtained at the end of this step are called “raw coatings”.



Fig. 17 "FRESENBERGER" oven

#### 4.2.4. Cutting

Steel sheets covered with the primer after bar coating are cut (Fig. 18) to obtain pieces which size is 10x5 cm.



Fig. 18 "DE TOLLENAERE" Cutting machine

#### 4.2.5. Firing

The pre-coated sample is fired in a box oven (Fig. 19) at selected time and temperature requirements. At this point, the aim is to provoke pyrolysis of the polymer, evaporation of possibly remaining water and oxidation of the metal ions and subsequent melting of the glass. This parameter was studied trying to reduce the temperature parameter as much as possible elongating firing times. Temperature range goes from 550°C and times up to 5 hours to 740°C and times in the order of minutes.



Fig. 19 "Nabertherm" curing oven

#### 4.2.6. Top coat powdering

A second coat is applied on the sample after firing. This top coat is provided by an external company. Ferro is a company that develops enamels. This top coat is verifiable at 700°C and provides the required surface and aesthetics properties such as white colour, acid and alkaline resistance, gloss and smooth surface.

This Top coated is applied on top of the sample as a powder using an electrostatic gun (Fig. 20). The parameter used to measure the amount of powder added is the weight. Samples are supported by a wire linked to a scale. The amount added to the sample is around 0.08 g/cm<sup>2</sup>.



Fig. 20 Left: Electrostatic gun "GEMA VOLSTATIC" and right: extractor to trap the powder

#### 4.2.7. Second firing

After Applying the second coat the sample is fired in the same oven as the first time at 740°C during 4 minutes. This induces the melting of the two coats and the link between both layers.

### 4.3. MATERIAL CHARACTERIZATION TECHNIQUES

#### 4.3.1. Adherence

The main tested characteristic of the coating is its ability for deformation and its adhesion to the substrate after the vitrification step. These were tested using impact testing according to EN10209: a ball indenter of 2 cm diameter is dropped with a 2 Kg weight from a 50 cm height. The resulted impact was then observed for delamination or cracks in the coating.

Typical impact test results are shown in Fig 21. For good results, coating follows the deformation of the substrate and there is no chipping off. For Medium results, some dots are removed, for Bad results, the enamel is removed below the impact (4).

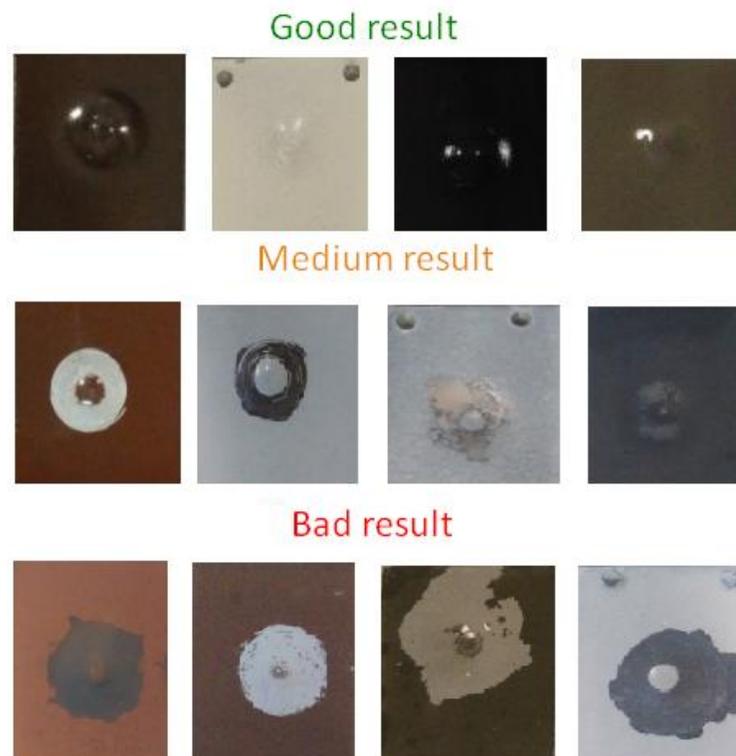


Fig. 21 Adherence test results, showing good medium and bad results obtained

#### 4.3.2. Compatibility between primer and top coat

By compatibility between enamel primer and enamel top coat it is understood that in a two coat two fire process the two layer system needs to adhere to the metallic coated steel and the top coat needs to have a smooth surface with the desired glossy and finish / transparency or opacity.



Fig. 22 Visual evaluation on samples where is shown a bad result at the left side, a medium result in between and a good result at the right.

## **5. RESULTS**

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This project aims at merging knowledge of both background projects. Metallic oxides are introduced in the formulation, increasing adherence with top coat -Conclusion in Top down approach (5). This needs to be checked into the Bottom up project formulation (3), J7. It is also necessary to search for colourless metallic oxides that will be introduced in I8 formulation

Enamel compositions are shown as the weight percentage of the final oxide composition. Each element is expressed in the most stable oxide.

### **5.1. METALLIC OXIDES ADDITION INTO PRIMER COMPOSITION IN TOP DOWN PRIMERS**

A previous step before to start working with the J7 composition found in (3) consists in fine tuning of top down primer compositions. Some metallic oxides tested as CuO are limited by REACH regulation. CuO content has to be 3% at maximum. Previous results obtained in this study showed sometimes higher CuO concentrations except for I8 (see Table III). Besides, other metallic oxides tested are colouring top coat. Another “unstable” oxide would be of interest to find. It should improve the adherence onto Alusi and also play a role on the redox of the system being “colourless” and REACH compatible. In glasses such an oxide might be antimony oxide ( $\text{Sb}_2\text{O}_3$ ), cerium oxide ( $\text{CeO}_2$ ), tin oxide ( $\text{SnO}_2$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ), and Tungsten oxide ( $\text{WO}_4$ ).

The two enamel primers selected to introduce transition metallic oxides are shown in Table VIII.

Sample preparation was done on 50 grams of primer basis. Transition oxide amount is shown in weight percentage respect to the primer amount. These compounds are introduced into a mill. A mix of chemical additives (Perkasil, Bentone and KG25) is added to the mill. These are added to keep compounds in suspension after the water addition. Between 15 to 50 mL of water are added to the mill. Mixture is ground during three minutes obtaining a homogeneous mixture.

These primers were applied onto Alusi® using BC 30 and BC 100 and a few times BC140 because it is important to know how thickness affects the primer adherence, the adherence between primer and top coat and the opacity obtained after firing.

Firing temperatures were 680°C during 6 minutes; 710°C during 4 minutes and 740°C during 4 minutes. Second firing is after applying the top coat at 740°C during 4 minutes.

Table VIII: Oxidic composition in Weight % for selected formulations from enamel top down primer study

Oxide composition	Primer enamel	
	18	G10
W%		
Al <sub>2</sub> O <sub>3</sub>	< 2	< 2
B <sub>2</sub> O <sub>3</sub>	>> 20	>> 20
Cr <sub>2</sub> O <sub>3</sub>	< 2	< 2
CuO	2 << 5	10 << 15
Fe <sub>2</sub> O <sub>3</sub>	15 << 20	>> 20
K <sub>2</sub> O	2 << 5	5 << 10
MnO <sub>2</sub>	< 2	< 2
MoO <sub>3</sub>	< 2	< 2
Na <sub>2</sub> O	>> 20	10 << 15
P <sub>2</sub> O <sub>5</sub>	2 << 5	< 2
SiO <sub>2</sub>	20 <<	10 << 15
TiO <sub>2</sub>	10 << 15	5 << 10
ZrO <sub>2</sub>	< 2	< 2

G10 composition does not satisfy minimum requirements for CuO (< 3%) and SiO<sub>2</sub> (>30%) but it shows good adherences and opacity (5). G10 is a hard primer what means it has a high vitrification temperature. Adding metallic oxides, its melting point might increase. G10 was mixed with 5549 frit, a soft glass composition supplied by Ferro. This 5549 primer does not contain CuO and it contains 33% SiO<sub>2</sub>.

A new primer was produced mixing both products obtaining a formulation with less than the 3% CuO and more than 30% SiO<sub>2</sub>. Results obtained in Table IX show bad primer adherence because primer does not adhere onto steel. Results are better with lower bar coater, but it is still poor. A new attempt was tried adding quartz. Some improvement was found in the primer adherence, opacity is good too but adherence between primer and top coat is poor (Table X). This composition was most probably overloaded with refractory filler.

Table IX: G10 + 5549 composition % W and results obtained

G10 + 5549					
G10 (%)	5549 (%)	BC	T (°C)	time (min)	Primer adh.
84	16	30	680	6	
84	16	30	710	4	
84	16	30	740	4	
84	16	100	680	6	
84	16	100	710	4	
84	16	100	740	4	

Table X: G10+5549+H224 composition (%) and results obtained

G10+5549+H224								
G10	5549	H224	BC	T (°C)	time (min)	Primer adh.	TC + Primer adh.	Opacity
50	16	34	30	680	6			
50	16	34	30	710	4			
50	16	34	30	740	4			
50	16	34	100	680	6			
50	16	34	100	710	4			
50	16	34	100	740	4		740° 4'	

I8 formulation complies REACH regulation for CuO. This composition is a very soft primer; this means that it might become possible to add other mineral fillers to it such as quartz, and transition metallic oxides, without affecting too much its melting range.

Metallic oxides tested are tin oxide, antimony oxide, cerium oxide and tungsten oxide. Results are shown in Table XI. Primer adherence is perfect for all assays except for antimony. It is probably because the oxide was not integrated into the glass. Antimony is known to decompose at low temperature, the decomposition disturbing glass film formation.

Table XI: I8 + different metallic oxides or/and SiO<sub>2</sub>

I8 + 20% W. SnO <sub>2</sub>					
BC	T (°C)	Time (min)	Primer adh.	Top coat adh.	Opacity
30	710	4			
30	740	4		740° 4'	
100	710	4			
100	740	4		740° 4'	
140	710	4			
140	740	4		740° 4'	
I8 + 20% W. Sb <sub>2</sub> O <sub>3</sub>					
BC	T (°C)	Time (min)	Primer adh.	Top coat adh.	Opacity
30	710	4			
30	740	4			
100	710	4			
100	740	4		740° 4'	
140	710	4			
140	740	4		740° 4'	
I8 + 10%W. WO <sub>3</sub>					
BC	T (°C)	Time (min)	Primer adh.	Top coat adh.	Opacity
30	680	6			
30	710	4			
30	740	4		740° 4'	
100	680	6			
100	710	4			
100	740	4		740° 4'	
I8 + 12% W. H <sub>2</sub> T <sub>2</sub>					
BC	T (°C)	Time (min)	Primer adh.	Top coat adh.	Opacity
30	680	6			
30	710	4			
30	740	4		740° 4'	
100	680	6		740° 4'	
100	710	4		740° 4'	
100	740	4		740° 4'	
I8 + 10 %W. H <sub>2</sub> T <sub>2</sub> + 10%W. SnO <sub>2</sub>					
BC	T (°C)	Time (min)	Primer adh.	Top coat adh.	Opacity
30	680	6		740 °c 4'	
30	710	4		740 °c 4'	
30	740	4		740 °c 4'	
100	680	6		740 °c 4'	
100	710	4		740 °c 4'	
100	740	4		740 °c 4'	
I8 + 10%W. H <sub>2</sub> T <sub>2</sub> + 10%W. CeO <sub>2</sub>					
BC	T (°C)	Time (min)	Primer adh.	Top coat adh.	Opacity
30	680	6		740° 4'	
30	710	4		740° 4'	
30	740	4		740° 4'	
100	680	6			
100	710	4		740° 4'	
100	740	4		740° 4'	

- I8 + 20% weight SnO<sub>2</sub> shows good top coat adherence for BC100 samples and good opacity too. BC30 is not thick enough and top coat adherence and opacity are poor. Top coat adherence is better using BC100 than using BC30 for the same temperature and time. This means that thickness affects adherence of bilayer system as well as opacification of top coats.
- I8 + 20 % weight Sb<sub>2</sub>O<sub>3</sub> adherence is not obtained anyway, but opacity is good. It confirms that introduction of unstable oxide in primer composition is modifying the recrystallization of TiO<sub>2</sub> in top layer.
- I8 + 10 % weight WO<sub>3</sub> primer adherence is perfect. BC100 samples shows good top coat adherence but for BC30 top coat adherence is poor. As shown in SnO<sub>2</sub> test, when the primer layer is not thick enough the top coat adherence is not obtained. Opacity is not obtained for BC30 and for BC100 it is even not perfect. Top coat shows bubbles trapped inside, this procures poor glossy finish.
- I8 + 12% weigh quartz (SiO<sub>2</sub>) shows perfect or acceptable adherence in both cases but opacity is not good enough. Surface finished does not look glossy in examples fired at lower temperature.
- I8 + 10% H224 (SiO<sub>2</sub>) + 10% SnO<sub>2</sub> primer adherence is perfect. After top coat is applied and fired, BC30 samples shows poor adherence. The same happen using BC100 for 680°C and 710 °C too. The only good result is obtained after firing 740°C. Opacity is poor in BC30 and perfect in BC100 samples. Bubbles are trapped in the top coat for all samples except for BC100 fired at 740°C.
- I8 + 10% H224 (SiO<sub>2</sub>) + 10% CeO<sub>2</sub> primer adherence is perfect and top coat adherence is good enough in our temperature range. Opacity is poor for BC30 but for BC100 is perfect. Surface finished shows bubbles in assays with BC30 but with increasing thickness bubbles disappear and a glossy surface is obtained.

The addition of metallic oxides into I8 affects the effectiveness on the primer adherence, top coat adherence and opacity as follows:

**Primer adherence: Ce > W > Sn > Sb**

**Top coat adherence: Sn > Ce > W > Sb**

**Opacity: Ce > Sn > W > Sb**

Best results in terms of amount addition are **20% w. metallic oxide** (when only is added the metallic oxide), and **10% w. metallic oxide – 10 % w. quartz** (when also Silicium is added).

**Best thickness: 100 > 30**

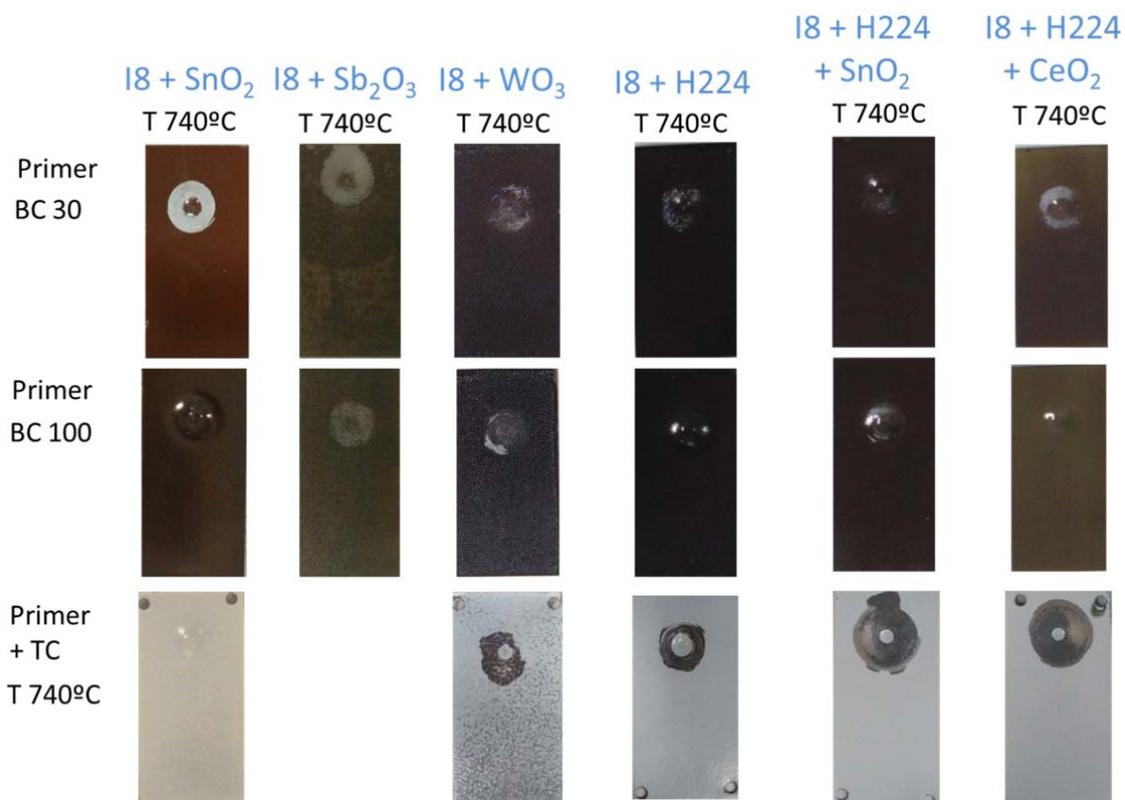


Fig. 23 Results for after metallic oxide addition and/or SiO<sub>2</sub> in I8 formulation

## 5.2. ENAMEL COMPOSITION: J7

Our starting point is the composition shown in Table V. A glass layer is easily obtained from a simple mixture of salts and oxides. A perfect primer adherence was obtained at 710°C and 4 minutes firing time, but when the top coat is applied and fired a reaction occurs between both layers. It seems that both layers are mixing at high temperature also that gas reaction takes place leading to peeling and decohesion (Fig 24).

One hypothesis is that a composition based on salts does not have time enough to recombine itself and find a stable state and when the sample is removed from the oven after first firing the synthesis was not finished.

Nevertheless the decomposition into oxides of this mixture is achieved at about 400°C approximately as is shown in the Thermo Gravimetric Analysis (TGA) curve in Fig 25.

The green curve represents the weight lost produced in the sample. The first drop in the green curve is due to water loss, and the second downturn is due to the weight lost produces by the glass forming process of the salts.

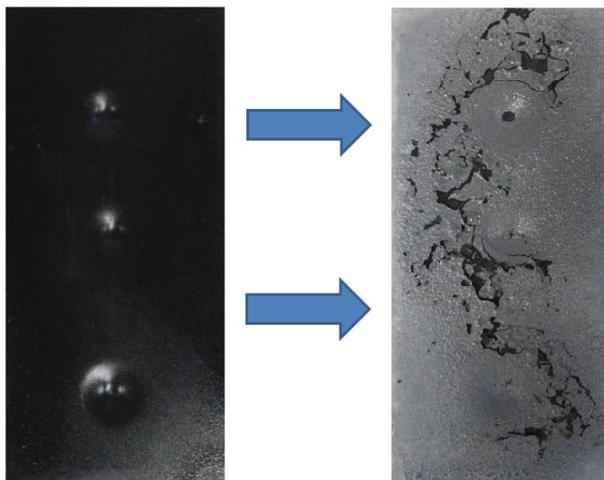


Fig. 24 J7 before and after applying Top Coat

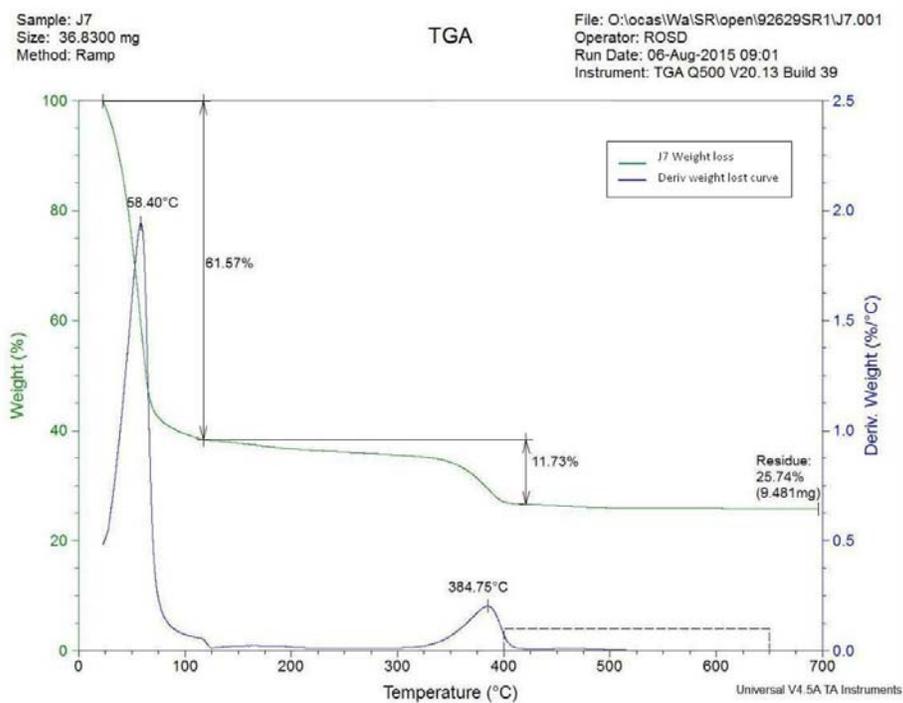


Fig. 25 TGA curve of J7 + G60 polymer at 10°C/ min

So, the bad aspect obtained is not due to a decomposition providing gases at high temperature but to something else.

This means that theoretically it should be possible to reduce the firing temperature of the formulation for obtaining the thin glass coating. That is why it was tried first to reduce firing temperature and increase firing time. It was expected to obtain good adherence and bad opacity result due to a reduction of the partial pressure of oxygen in the system (Fig. 9). Time necessary to counter the temperature decreasing is unknown. The experiment was carried out at 650°C and 15 minutes and from that point times were progressively increased and temperatures were decreased as far as possible. Fig. 26 shows the scheme of assays progress.

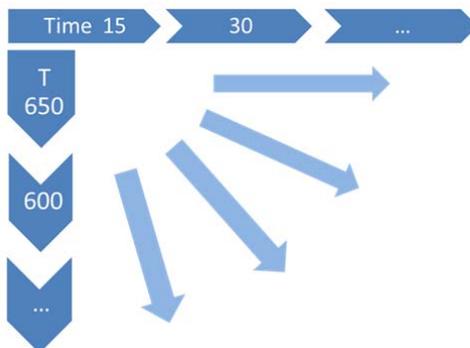


Fig. 26 progress assays function of obtained results

Assays were performed applying different thickness using bar coater 30, 50 and 100 at different temperatures and times as shown in Table XII. These times were selected as function of the previous results, in an iterative mode. In the Table XII adherence is worse for short times because it seems the glass does not have time enough to be formed. The thicker is the layer, the longer time is needed to form the layer.

Ideally, it would have been necessary to verify afterwards by XRD that all crystallized forms had reacted with phosphate and other soft compound to form a glassy layer. This was not done at this stage and will be done after fine tuning.

After firing the aspect of the samples is shown in Fig 27. With the naked eye it can be seen that when temperature decreases the final aspect of the samples goes greenish and having mat finish. Curing conditions don't allow forming a glass film. Samples need longer firing time; another possibility is that it is maybe not possible to carry out the full sintering at such low temperature. Adherence is perfect, except for 500°C.

Table XII: Results obtained for adherence in J7 mixture at different firing T and time.

Time (min)	Temperature (°C)							
	650		600		550			500
	BC 30	BC 50	BC 30	BC 50	BC 30	BC 50	BC 100	BC 50
3	Good	Good						
5	Perfect	Good						
9	Perfect	Good						
15			Perfect	Good				
20	Perfect	Perfect						
30	Perfect	Perfect	Perfect	Perfect			Good	
45	Perfect	Perfect	Perfect	Perfect	Perfect	Good		Perfect
60			Perfect	Perfect	Perfect	Good	Good	Perfect
75			Perfect	Perfect	Perfect	Good		
90					Perfect	Good		Perfect
100			Perfect	Perfect	Perfect	Good		
120							Neutral	Good
130			Perfect	Perfect	Perfect	Good		
150							Neutral	Perfect
180								Good
200								Perfect
220								Good

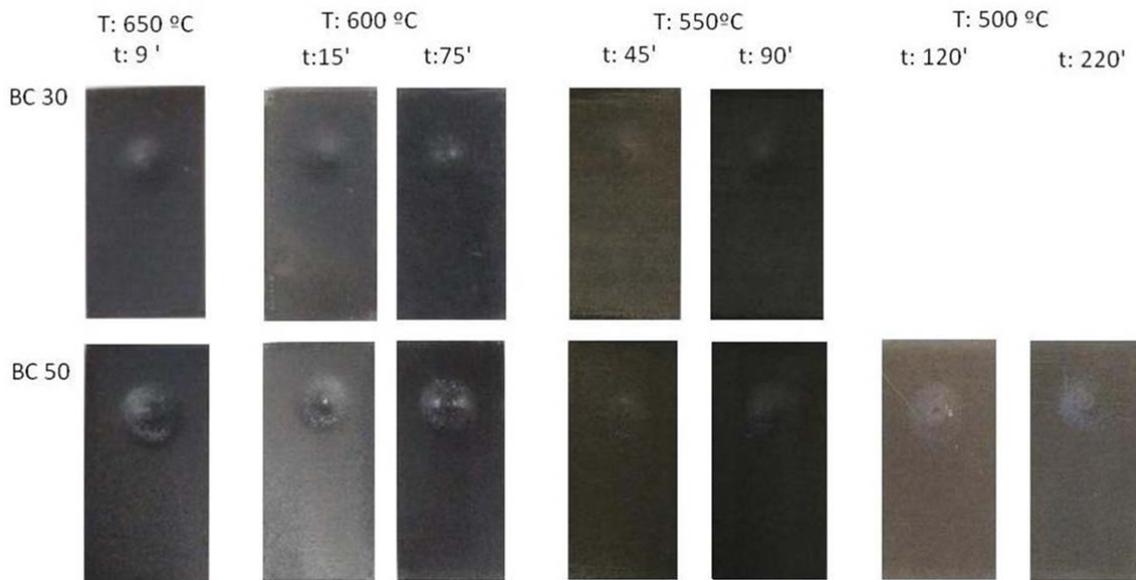


Fig. 27 From left to right samples fired at 650, 600, 550 and 500°C at BC 30 and 50

After the adherence test the top coat was applied on samples fired 60 minutes at 550 °C to see if the proposed hypothesis (reaction does not have time enough to be finished) is fulfilled. That temperature was selected because it is the middle of tested range, bar coater chosen were BC50 and BC100. Two different bar coater were used to see the influence of the primer thickness on the final result. Top coat applied were fired at 710 °C during 4 minutes.

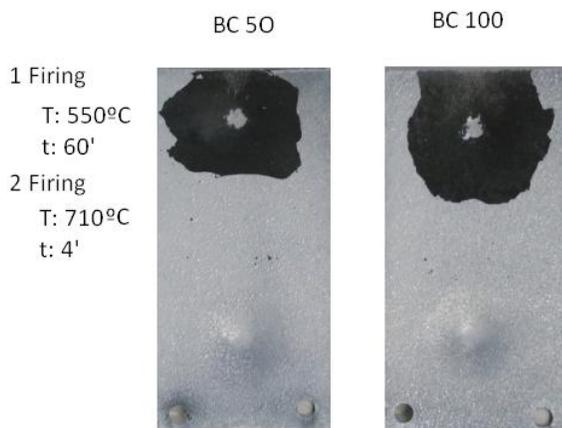


Fig. 28 J7 Samples after top coat is applied and adherence exam is done.

Adherence test shows bad results for top coat while primer still sticks onto Alusi®. Opacity is obtained but surface finish is very poor. Compared to the starting point (Fig. 8) can observe an improvement, but adherence, opacity and finish are not acceptable. The Alusi melting point is around 615 °C what means that iron diffusion across the Alusi takes hours instead of minutes when firing temperature is below the melting point. The bad adherence of top coat and the way it chips off is characteristic, bubbles are trapped between primer and top coat.

### 5.3.ADDITION OF TRANSITION METAL OXIDE

Different transition metallic oxides were added to improve adherence. In previous work (5) it was confirmed that the addition of transition “metallic” oxides increases adherence with top coat and opacity.

“Metallic” oxides such as copper, cerium, zinc, and tin... oxides have been introduced to try to obtain better final results.

Oxides were introduced in form of nano particles (Table XIII). Introduction of particles in nano size helps getting better stability of the suspension and better reactivity. All sample

compositions were applied onto Alusi with BC50. Different amounts were tested and combinations thereof.

Table XIII: Oxidic composition: % weight

Oxide composition	J7	J7 + Fe <sub>2</sub> O <sub>3</sub>	J7 + Fe <sub>2</sub> O <sub>3</sub>	J7 + CuO	J7 1/3 Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> + CuO	J7 1/3 Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> + ZnO	J7 NO Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> + ZnO
		S22	S30	S29	S33	S35	S37
Al <sub>2</sub> O <sub>3</sub>	24,1	22,44	19,4	23,6	7,1	6,6	0,0
B <sub>2</sub> O <sub>3</sub>	10,4	9,79	8,5	10,3	9,3	8,5	8,8
CuO				4,3	3,9		
Fe <sub>2</sub> O <sub>3</sub>		7,01	21,4		23,6	21,1	25,3
K <sub>2</sub> O	8,4	7,77	6,7	8,2	7,4	6,8	7,0
MoO <sub>4</sub>	1,0	1,02	0,9	1,1	1,0	0,9	0,9
Na <sub>2</sub> O	14	13,55	11,7	14,2	12,9	11,9	12,2
P <sub>2</sub> O <sub>5</sub>	36,0	31,02	26,8	32,6	29,5	27,1	28,0
SiO <sub>2</sub>	6,0	7,4	4,74	5,8	5,2	4,9	5,0
ZnO						12,3	12,7
%	100,0	100,0	100,0	100,0	100,0	100,0	100,0

Sample S22 and S30 contain different amounts of iron oxide (Fe<sub>2</sub>O<sub>3</sub>). As it is seen in Fig 29, S22 and S30 primer adherence looks good. The top coat has a good adherence in both cases. In S30, containing higher iron oxide amount, opacification is better. These test leads to conclude that both hypotheses are correct. For S30 opacity is obtained but the surface finish is not good enough.

In a previous report (5) it was found that copper oxide helps obtaining good opacity in the top coat. Main problem of this compound is that its use is limited by REACH regulation. REACH limits copper oxide concentration up to 3% w. Some tests were done with low concentration of copper (S29 and S33) but no improvements were found. Primer adherence is perfect, as in previous ones, but after applying top coat the result is worse. Top coat adherence in sample S29 is very poor. In S33 adherence obtained is worse than in S35 (which has a similar composition except for copper). Opacity is bad also (), none of the formulations provides opacity. As result copper is discarded as metal oxide added in our composition due to the complications related.

In S30 there is iron oxide (Fe<sub>2</sub>O<sub>3</sub>) addition, replacing alumina (Al<sub>2</sub>O<sub>3</sub>) proportionally. X<sub>2</sub>O<sub>3</sub> compounds increase vitrification temperature and they have to be limited in formulations. When Iron oxide (Fe<sub>2</sub>O<sub>3</sub>) is introduced Alumina (Al<sub>2</sub>O<sub>3</sub>) is reduced or removed. In sample S35 one third of the original alumina (Al<sub>2</sub>O<sub>3</sub>) amount was introduced, and in S37 alumina (Al<sub>2</sub>O<sub>3</sub>) was removed. In order to reduce vitrification temperature ZnO (a flux

component) was introduced to help to reduce melting range of the formulation. ZnO amount was selected from previous studies (6) (7).

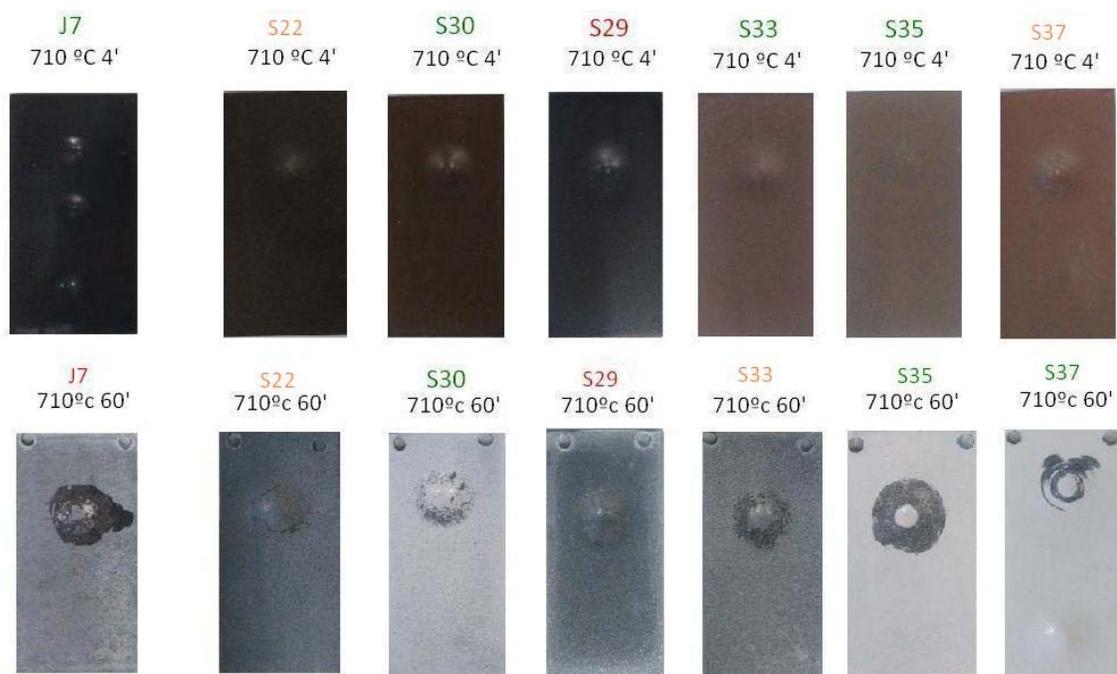


Fig. 29 Samples shown in Table XIII, on the top the primer and below after top coat is applied, labelling green for good, orange for medium and red for bad result.

Results obtained using formulas S35 and S37 are good. Both of them have a good primer and top coat adherence, opacity is obtained and applying enough top coat powder ( $4 \text{ g/dm}^2$ ), white is obtained (Fig 30).



Fig. 30 Sample 35 at the left and sample 37 at the right after 2 coats and 2 fires

In this formulations adherence in primer and top coats and opacity have been obtained but the surface finish still shows a few wrinkles.

As is shown in Fig. 31, the rough surface seems to be due to the presence of big bubbles trapped in the top coat.

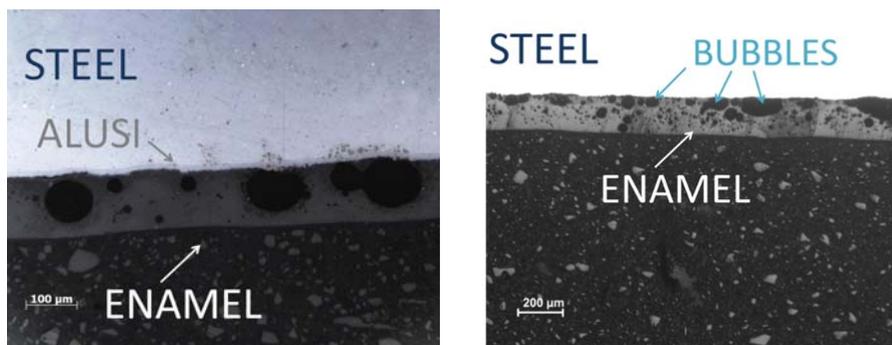


Fig. 31 Cross section observation by optical microscope

This can be due to three hypotheses:

- Too high vitrification temperature: when the vitrification temperature is too high the too much redox exchange is produced leading to bubbles. After the first firing the reaction has not finished. During the second firing the reaction continues and produces bubbles. These bubbles rise up mixing both layers and are trapped in the top coat.
- Second theory proposed is that secondary reaction(s) is (are) produced. During the first firing the parallel reaction takes place and it does not end when the sample is removed from the oven. During the second firing the secondary reaction continues producing bubbles trapped into the top coat and also mixing both layers. A differential scanning calorimetry (DSC) study was launched to try to identify all evolutions of the formulation during the first thermal treatment.
- Another possible explanation is that density on top coat is higher than the one of primer which produces mixture of both (Fig. 32 a). If superficial tension of the top layer is lower than the surface tension of the ground coat mixture is producing between both and this is impossible to predict. This study was not engaged due to the complexity to measure density and surface tension at high temperatures.

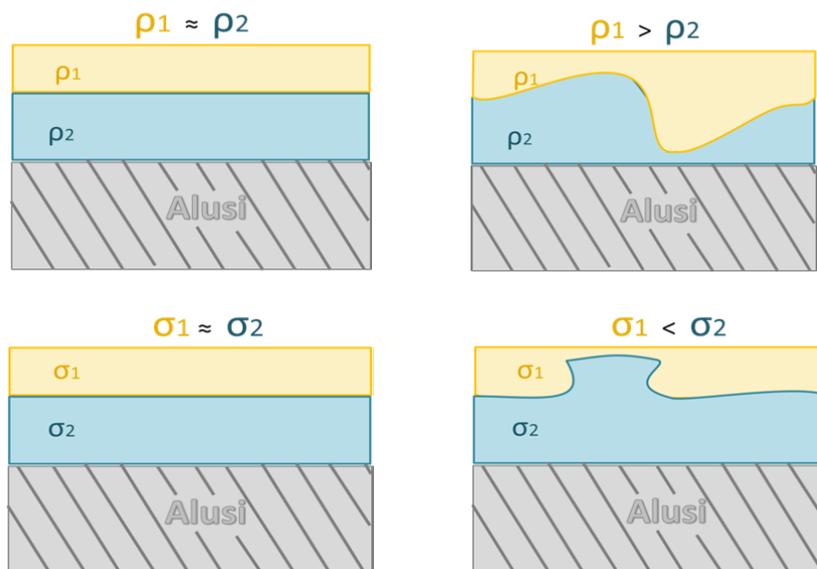


Fig. 32 Scheme of Alusi primer and top coat at the left (a) about different density and (b) about superficial tension

#### 5.4.INPUT OF SALTS TO REDUCE VITRIFICATION TEMPERATURE (T<sub>g</sub>)

According to previous hypothesis it has been tried to decrease vitrification temperature to avoid bubbles get caught. A literature study was launched (7) (6) to see how phosphate glasses could be modified. Analysing those results it is right to conclude:

- Glass transition (T<sub>g</sub>) and dilatometric softening temperature (T<sub>s</sub>) are higher in glasses containing iron and alumina than glasses containing only one of both
- Addition of iron increases density and vitrification temperature in Sodium phosphate glasses (Na-FP) and in Zinc Phosphate glasses (Zn-FP) vitrification temperature (T<sub>g</sub>) decreases.
- Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO SiO<sub>2</sub> compounds increase vitrification temperature (T<sub>g</sub>).
- K<sub>2</sub>O P<sub>2</sub>O<sub>5</sub> ZnO decrease vitrification temperature (T<sub>g</sub>).

Some formulations have been prepared based on these ideas in order to get low vitrification temperature.

IDEAS			
[5]	Tg 480 °C	Tg 474 °C	Tg 470 °C
	<b>% mass</b>	<b>% mass</b>	<b>% mass</b>
	Al <sub>2</sub> O <sub>3</sub> 17,1	Al <sub>2</sub> O <sub>3</sub> 3,8	Al <sub>2</sub> O <sub>3</sub> 20,7
	Na <sub>2</sub> O 11,7	P <sub>2</sub> O <sub>5</sub> 72,0	P <sub>2</sub> O <sub>5</sub> 69,3
	P <sub>2</sub> O <sub>5</sub> 71,2	Fe <sub>2</sub> O <sub>3</sub> 15,0	ZnO 9,9
		ZnO 9,2	
[6]	Tg 212 °C	Tg 313 °C	Tg 303 °C
	P1	P6	P5
	<b>% mass</b>	<b>% mass</b>	<b>% mass</b>
	Na <sub>2</sub> O 15,6	Al <sub>2</sub> O <sub>3</sub> 6,7	Fe <sub>2</sub> O <sub>3</sub> 7,7
	K <sub>2</sub> O 21,0	K <sub>2</sub> O 26,1	K <sub>2</sub> O 28,7
	P <sub>2</sub> O <sub>5</sub> 63,4	P <sub>2</sub> O <sub>5</sub> 67,2	P <sub>2</sub> O <sub>5</sub> 63,7
	Tg 305 °C	Tg 475 °C	
	P15	P18	
	<b>% mass</b>	<b>% mass</b>	
	P <sub>2</sub> O <sub>5</sub> 50,7	P <sub>2</sub> O <sub>5</sub> 46,3	
	ZnO 17,4	ZnO 40,4	
	PbO 31,9	Al <sub>2</sub> O <sub>3</sub> 5,4	
		B <sub>2</sub> O <sub>3</sub> 7,9	

Fig. 33 Phosphate glass formulations with low vitrification temperature

New formulations (Fig. 34) have been made, merging formulations S37 and S35 with the formulas found in the literature (23).

H<sub>2</sub>O: 50 mL

J7 1/3 Al <sub>2</sub> O <sub>3</sub> no Na		J7 NO Al <sub>2</sub> O <sub>3</sub> no Na	
Amounts	Oxidic Composition	Amounts	Oxidic Composition
Al <sub>2</sub> O <sub>3</sub> 3,54	Al <sub>2</sub> O <sub>3</sub> 13,46	Al <sub>2</sub> O <sub>3</sub> 0,00	B <sub>2</sub> O <sub>3</sub> 21,94
H <sub>3</sub> BO <sub>3</sub> 7,96	B <sub>2</sub> O <sub>3</sub> 16,55	H <sub>3</sub> BO <sub>3</sub> 9,20	K <sub>2</sub> O 36,08
HeptaMolybdate 0,54	K <sub>2</sub> O 31,69	HeptaMolybdate 0,60	MoO <sub>3</sub> 2,16
H <sub>2</sub> KO <sub>4</sub> P 20,00	MoO <sub>3</sub> 1,63	H <sub>2</sub> KO <sub>4</sub> P 20,00	P <sub>2</sub> O <sub>5</sub> 27,44
K(OH) 4,28	P <sub>2</sub> O <sub>5</sub> 27,34	K(OH) 5,00	SiO <sub>2</sub> 12,38
SiO <sub>2</sub> Levasil 6,32	SiO <sub>2</sub> 9,33	SiO <sub>2</sub> Levasil 7,30	
Total amount 42,65		Total amount 42,10	

Fig. 34 From left to right S35 Amounts, S35 oxidic composition, S37 Amounts, S37 oxidic composition replacing Na salt by K salt

Assays were done replacing partial or totally sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>; H<sub>2</sub>O) by monophosphate potassium (H<sub>2</sub>KO<sub>4</sub>P). Changing alumina (Al<sub>2</sub>O<sub>3</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>) and Zinc amounts also. Different Oxidic compositions are shown below (Fig. 35):

K1			K2			K3		
S35	OXIDIC COMPOSITION		S37	OXIDIC COMPOSITION		S35	OXIDIC COMPOSITION	
P6	Al <sub>2</sub> O <sub>3</sub>	6,40	P5	B <sub>2</sub> O <sub>3</sub>	9,4	P1	Al <sub>2</sub> O <sub>3</sub>	4,1
	B <sub>2</sub> O <sub>3</sub>	8,25		Fe <sub>2</sub> O <sub>3</sub>	7,8		B <sub>2</sub> O <sub>3</sub>	4,7
	Fe <sub>2</sub> O <sub>3</sub>	17,79		K <sub>2</sub> O	30,0		Fe <sub>2</sub> O <sub>3</sub>	22,1
	K <sub>2</sub> O	23,96		MoO <sub>3</sub>	1,0		K <sub>2</sub> O	14,1
	MoO <sub>3</sub>	0,76		P <sub>2</sub> O <sub>5</sub>	35,4		MoO <sub>3</sub>	0,9
	P <sub>2</sub> O <sub>5</sub>	27,26		SiO <sub>2</sub>	5,5		Na <sub>2</sub> O	6,6
	SiO <sub>2</sub>	4,89		ZnO	10,8		P <sub>2</sub> O <sub>5</sub>	31,6
	ZnO	10,46		No Al <sub>2</sub> O <sub>3</sub> No Na-P less Fe <sub>2</sub> O <sub>3</sub>			SiO <sub>2</sub>	3,1
	S35 with K-P Al <sub>2</sub> O <sub>3</sub> no Na-P						ZnO	13,0
							50Na-P - 50K-P with Al <sub>2</sub> O <sub>3</sub>	
K4			K5			K6		
S37	OXIDIC COMPOSITION		S35	OXIDIC COMPOSITION		S35	OXIDIC COMPOSITION	
P1	B <sub>2</sub> O <sub>3</sub>	7,3	P6	Al <sub>2</sub> O <sub>3</sub>	7,05	P1	Al <sub>2</sub> O <sub>3</sub>	5,8
	Fe <sub>2</sub> O <sub>3</sub>	19,9		B <sub>2</sub> O <sub>3</sub>	9,23		B <sub>2</sub> O <sub>3</sub>	7,3
	K <sub>2</sub> O	16,1		K <sub>2</sub> O	29,45		K <sub>2</sub> O	22,5
	MoO <sub>3</sub>	1,1		MoO <sub>3</sub>	1,01		MoO <sub>3</sub>	0,8
	Na <sub>2</sub> O	7,0		P <sub>2</sub> O <sub>5</sub>	34,81		Na <sub>2</sub> O	10,1
	P <sub>2</sub> O <sub>5</sub>	32,4		SiO <sub>2</sub>	5,21		P <sub>2</sub> O <sub>5</sub>	49,4
	SiO <sub>2</sub>	5,3		ZnO	13,24		SiO <sub>2</sub>	4,1
	ZnO	10,4		S35 with Al <sub>2</sub> O <sub>3</sub> no Na-P no Fe <sub>2</sub> O <sub>3</sub>			35 50 Na-P - 50 K-P No Fe <sub>2</sub> O <sub>3</sub>	
	50 Na-P - 50 K-P no Al <sub>2</sub> O <sub>3</sub>							
K7								
S37	OXIDIC COMPOSITION							
	B <sub>2</sub> O <sub>3</sub>	10,4						
	Fe <sub>2</sub> O <sub>3</sub>	22,8						
	K <sub>2</sub> O	8,3						
	MoO <sub>3</sub>	1,0						
	Na <sub>2</sub> O	12,9						
	P <sub>2</sub> O <sub>5</sub>	35,1						
	ZnO	8,5						
	S37 No SiO <sub>2</sub>							

Fig. 35 Formulas to reduce vitrification temperature

Compositions were tested onto Alusi using bar coater 50 and then fired at 740 °C during different times (4, 15, 30 and 60 minutes).

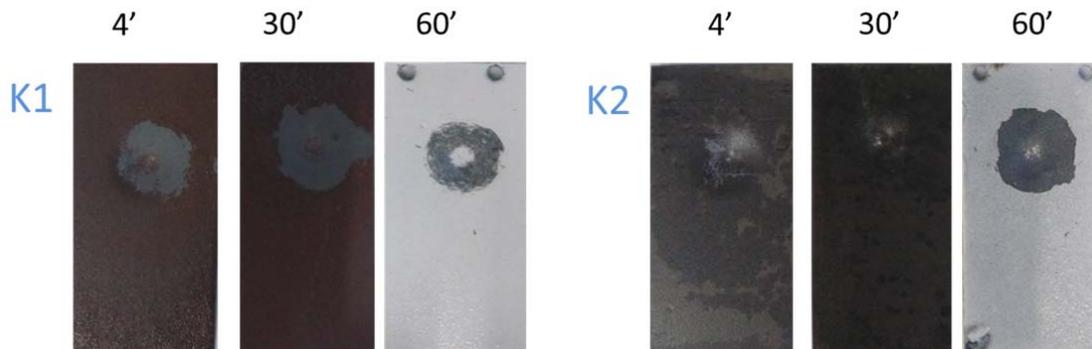


Fig. 36 Results obtained with total substitution of  $\text{Na}_2\text{PO}_4:\text{H}_2\text{O}$ . Fired at  $740^\circ\text{C}$

K1 and K2 (Fig. 36) are S35 and S37 compositions replacing  $\text{Na}_2\text{PO}_4:\text{H}_2\text{O}$  by  $\text{H}_2\text{KO}_4\text{P}$ . This is done to reduce vitrification temperature and to test how this salt works in our formulation. We want to improve surface finish. Results obtained in Fig. 36 show lower adherence of primer in K1 while in K2 primer adherence is perfect. On the other hand adherence between Top coat and primer is better in K1 than in K2. Opacity is obtained in both samples, but surface finish is poor, there are bubbles trapped inside. Glossy aspect is not obtained. This formulation doesn't upgrade results obtained for S35 and S37.

K3 and K4 formulas (Fig. 37) are based on S35 and S37 compositions replacing half part of  $\text{Na}_2\text{PO}_4:\text{H}_2\text{O}$  by  $\text{H}_2\text{KO}_4\text{P}$ . Results obtained show reducing primer adherence and bad adherence between primer and top coat. Opacity is obtained but no glossy aspect. Bubbles are trapped inside the layer.

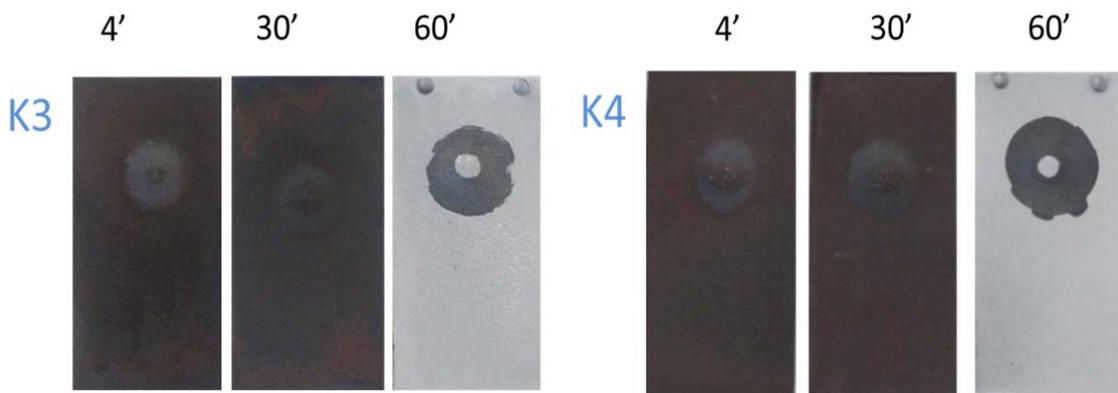


Fig. 37 Results obtained with partial substitution of  $\text{Na}_2\text{PO}_4:\text{H}_2\text{O}$ . Fired at  $740^\circ\text{C}$

K5 formula is based in S35 replacing  $\text{Na}_2\text{PO}_4\cdot\text{H}_2\text{O}$  by  $\text{H}_2\text{KO}_4\text{P}$  and removing iron oxide ( $\text{Fe}_2\text{O}_3$ ). In K6 iron oxide is removed but formulation contains half amount of  $\text{Na}_2\text{PO}_4\cdot\text{H}_2\text{O}$  and half of  $\text{H}_2\text{KO}_4\text{P}$  (Fig. 38). Primer adherence obtained in both samples is perfect. Opacity is obtained, but Top coat adherence and finish surface are bad.

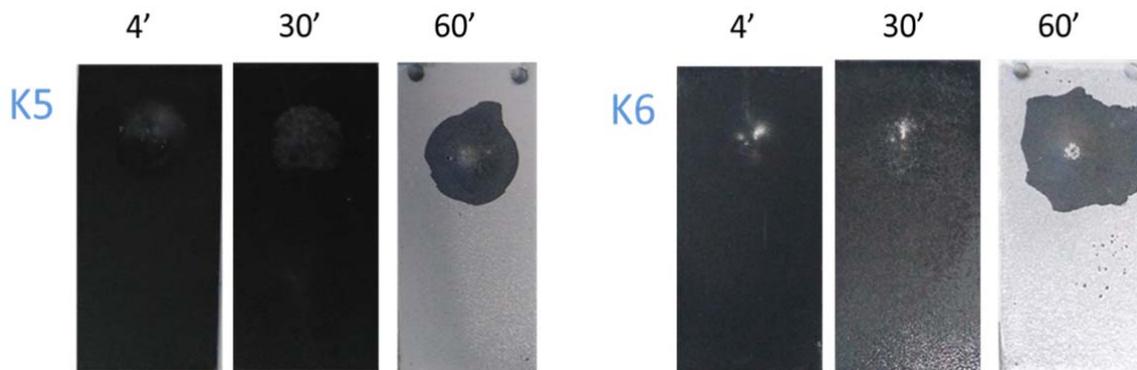


Fig. 38 Results obtained with substitution of  $\text{Na}_2\text{PO}_4\cdot\text{H}_2\text{O}$  and removing iron oxide. Fired at  $740^\circ\text{C}$

K7 (Fig. 39) is the same composition as S37 but removing silica ( $\text{SiO}_2$ ). Primer adherence is obtained, adherence between primer and top coat is obtained also. Opacity is good but the surface defect persists.

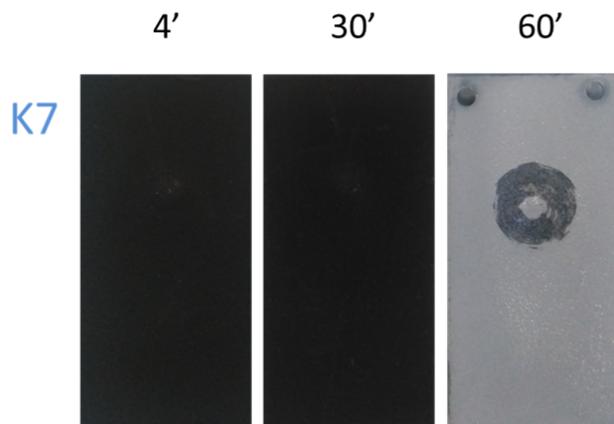


Fig. 39 S37 without silica

After these experiments bubbles inside the enamel persist. It can be due to the fact that we are not decreasing vitrification temperature enough, and/or a secondary reaction is produced

## 5.5. S37 ANALYSIS DIFFERENTIAL SCANNING CALORIMETRY

Differential Scanning Calorimetry (DSC) analysis is done on the S37 formulation. This analysis is done during heating up to 800 °C and after cooling. Results are shown in Fig. 40 and Fig. 41.

Fig. 40 shows cooling down starting at 800 °C. The graph shows two peaks that could be characteristics of the vitrification temperature (760°C) and glass transition temperature (654 °C). If this is the case, a vitrification carried out at 740°C is too low. To answer definitely, it would be necessary to superpose DSC to XRD to verify that a glass (no crystalline phase) is formed.

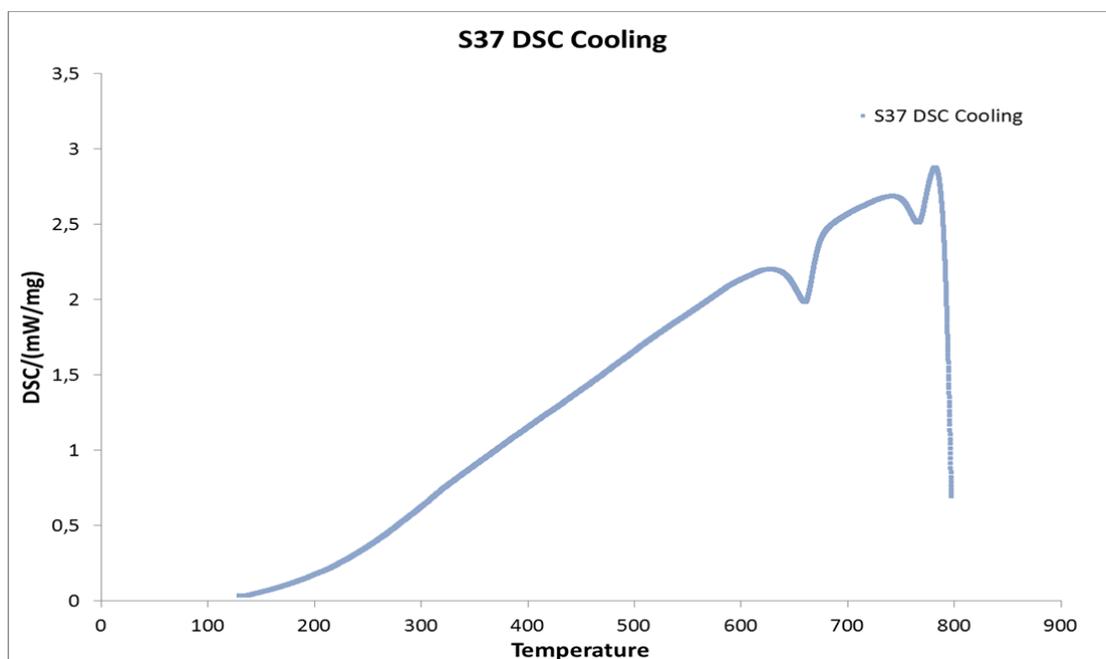


Fig. 40 S37 formulation DSC cooling

Fig. 41 shows results obtained heating up to 800°C. This graph shows five different peaks because of reactions occurring during heating. At 100°C it is known that water loss is produced. The other peaks are due to unknown reactions. Different components of S37 formulation are analysed separately to try to better understand this curve. DSC is done on single compounds.

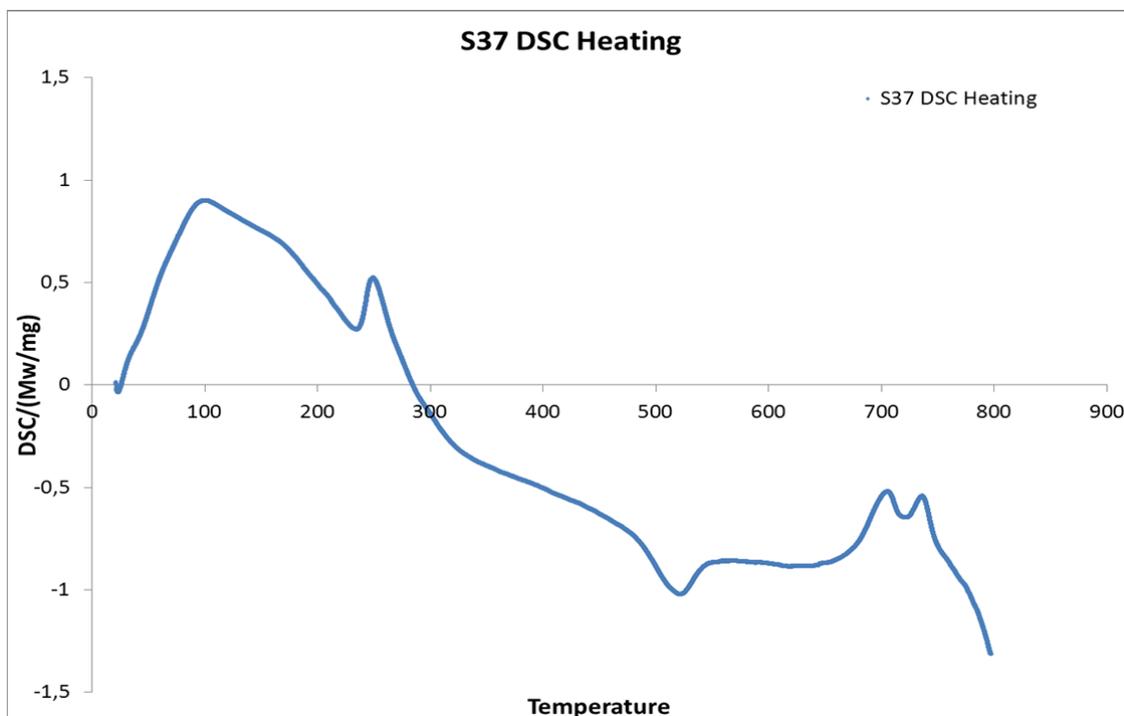


Fig. 41 S37 formulation DCS Heating

The most interesting results obtained analysing each compound separately was found for potassium hydroxide -K(OH)- (Fig. 42) and for the sodium dihydrogen phosphate monohydrate - $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ -.

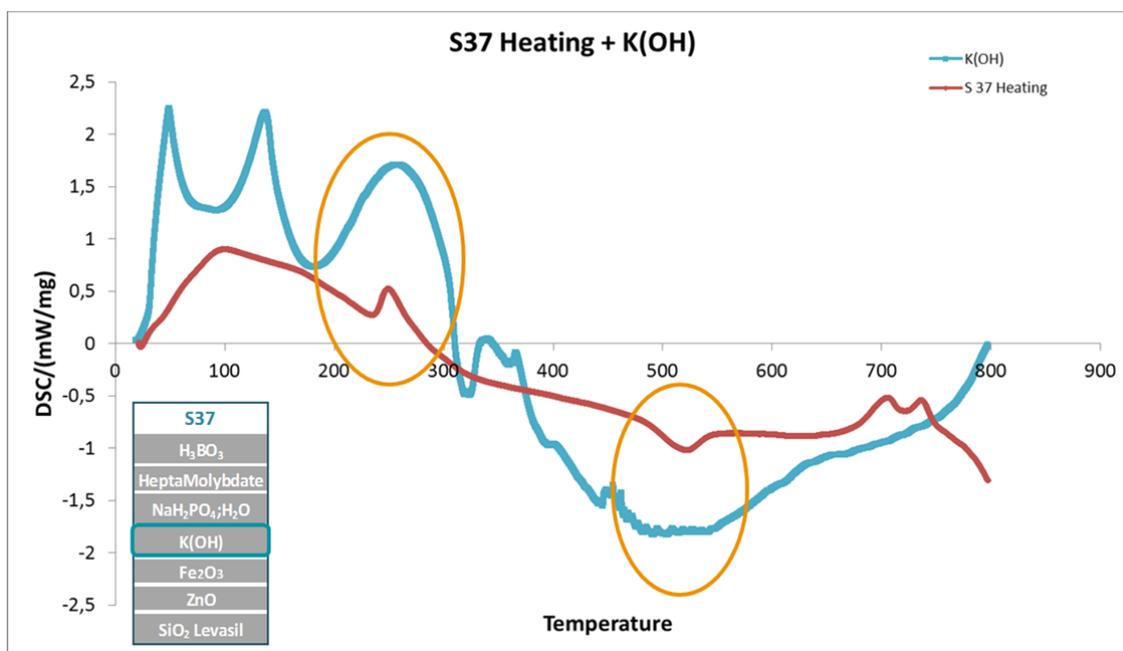


Fig. 42 DSC results for S37 Heating curve and K(OH)

Comparing S37 curve with K(OH) curve (Fig. 42) a coincidence is found with two peaks.

DSC results for NaH<sub>2</sub>PO<sub>4</sub> are interesting because they show many different peaks. This is because it is a complex salt with many intermediate states (Fig. 44) previous to the melting point (8). These instable intermediates can react easily with other compounds contained in the mixture; furthermore this possibility increases after the melting point, at 625°C.

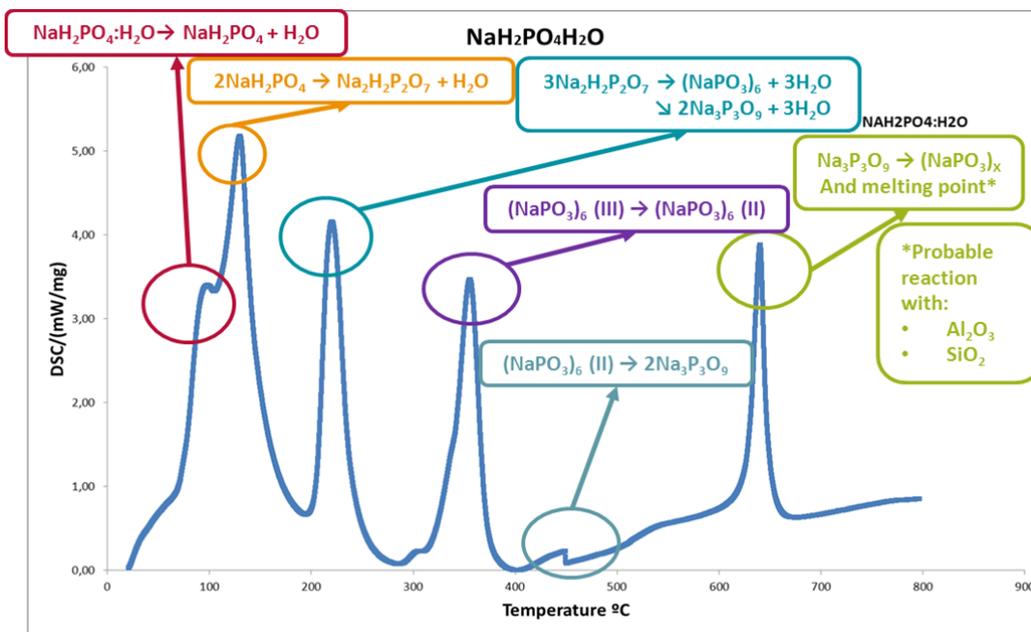


Fig. 43 NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O DSC results + explanation

Oxyphosphorus Compounds

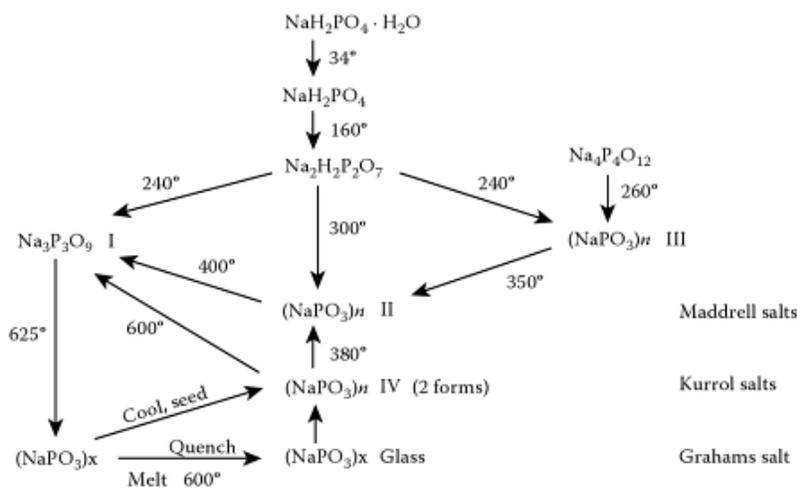


Fig. 44 Relationship of condensed phosphates (Na salts) (8)

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In Fig. 41 at around 700°C a reaction is occurring, probably between an unstable intermediate of the sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) and another compound in the S37 formulation.

Main conclusions are:

- Vitrification temperature is too high (760°C), what obliges to increase firing temperature and time. This is because the project drifted away from the original Solgel concept. Increasing metallic oxide concentration producing a salt percentage reduction.
- Secondary reaction is produced. This reaction is produced due to the instable intermediates generated by heating in our system.

A fresh approach is necessary to continue improving results.

## **5.6. NEW APPROACH: TRUE SOLGEL SYSTEM**

In different patents (9) (10) (11) (12) (13) a process was found to obtain an aluminium phosphate by curing at only 500°C. This is possible using a true Solgel system. The experimental procedure carried out in this process is shown in Fig. 45.

Two solutions are prepared dissolving each organo-precursor in ethanol. After both solutions are mixed and heated at 65°C during 16 hours. Following step is an evaporation to increase concentration. Coating and curing are done in a temperature range between 250°C to 450°C firing during 2 minutes to one hour. After this procedure an Aluminium phosphate coating, of a few micrometres thickness, by vitrification is obtained.

Intermediate steps are introduced sometimes. Ethanol is added again after the evaporation, reducing again concentration to slow down the condensation and formation of a gel. To have a coating it is necessary to form the aluminium phosphate onto the steel during the firing. If it condenses, an Aluminium phosphate powder is obtained onto the steel instead of a coating.

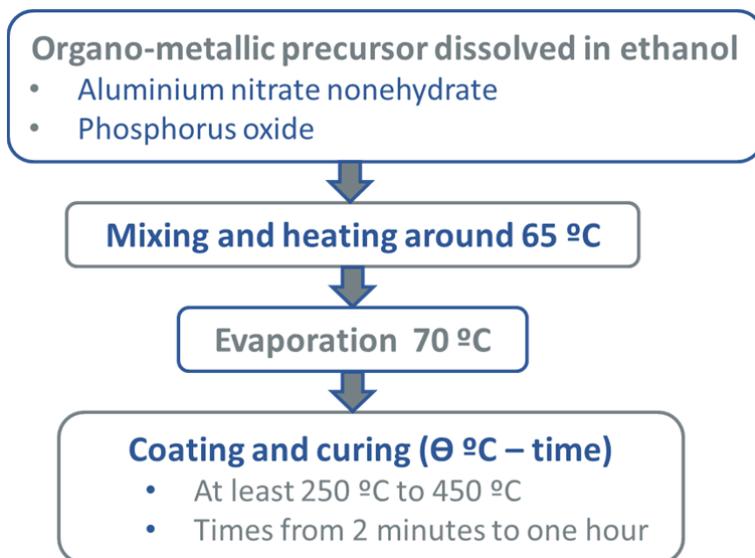


Fig. 45 ATFI Solgel experimental procedure to obtain  $\text{AlPO}_4$

The product obtained by this experimental procedure is an aluminium phosphate ( $\text{AlPO}_4$ ) that shows perfect resistance in terms of:

- Oxidation resistance
- Scratch resistance
- Chemical resistance
- Fingerprint/ fish scale resistance

When this coating is applied onto SOLFER® steel (specific steel grade for enamelling) perfect surface finish and opacity of the top layer are obtained, but no adherence (Fig. 46).

### Primer + Top coat

1st Firing:  
T: 500  
time: -

2nd Firing:  
T: 740 °C  
T: 4 min



Fig. 46 ATFI composition applied onto SOLFER® steel

### 5.6.1. First screening

A first set of experiments was performed, with two objectives:

1. To check the feasibility described in the patents filed by ATFI, in order to obtain an aluminium phosphate coating, alkaline and boron free. This represents a big difference with OCAS coating formulations developed in 2013 and in the first part of the present study
2. To try to “merge” again both approaches- Solgel and top down , introducing chemical elements such as copper oxide or Iron oxide, into the concept described by ATFI

To obtain a coating with a lower vitrification temperature and without introducing softeners ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{B}_2\text{O}_3$ ) it is necessary to use a true Solgel system. The use of organometallic precursors is necessary to obtain the final composition.

Selected organo precursors to introduce transition metallic oxides are:

- Iron nitrate nonehydrate
- Copper nitrate trihydrate

### 5.6.2. Preparation of the coating formulations

Following the process proposed by ATFI and described in Fig. 45, 2 formulations were prepared (see Table XIV). The first one is our reference, and corresponds too many examples described in the literature, as previously mentioned. The second one is a modified version that includes “key elements” of the top down approach of the development of OCAS primers (14).

Table XIV: Organometallic mixtures and final oxide compositions

	Formula	ATFI	S37
precursor 1	P2O5	25	25
	ethanol	100	100
precursor 2	Al Nitrate	264	97,5
	Cu Nitrate		10,045
	iron Nitrate		157,6
	ethanol	300	300
final coating	P2O5	58	58
	Al2O3	42	15
	Fe2O3		33
	CuO		5

### 5.6.3. Application of coatings

Coating formulations were applied by dipping on small strips of stainless steel and of Alusi, previously degreased. The operation was repeated 5 times with intermediate dryings.

### 5.6.4. GDOES surface analyses

After drying and curing all coatings were checked by GDOES. As it can be observed in Fig. 47 the coating with the formulation S37 applied on stainless steel is rather thin, with a sputtering time of only approximately 5 seconds. It still contains some carbon, and present all elements included in the master batch: Al, P, Fe, Cu.

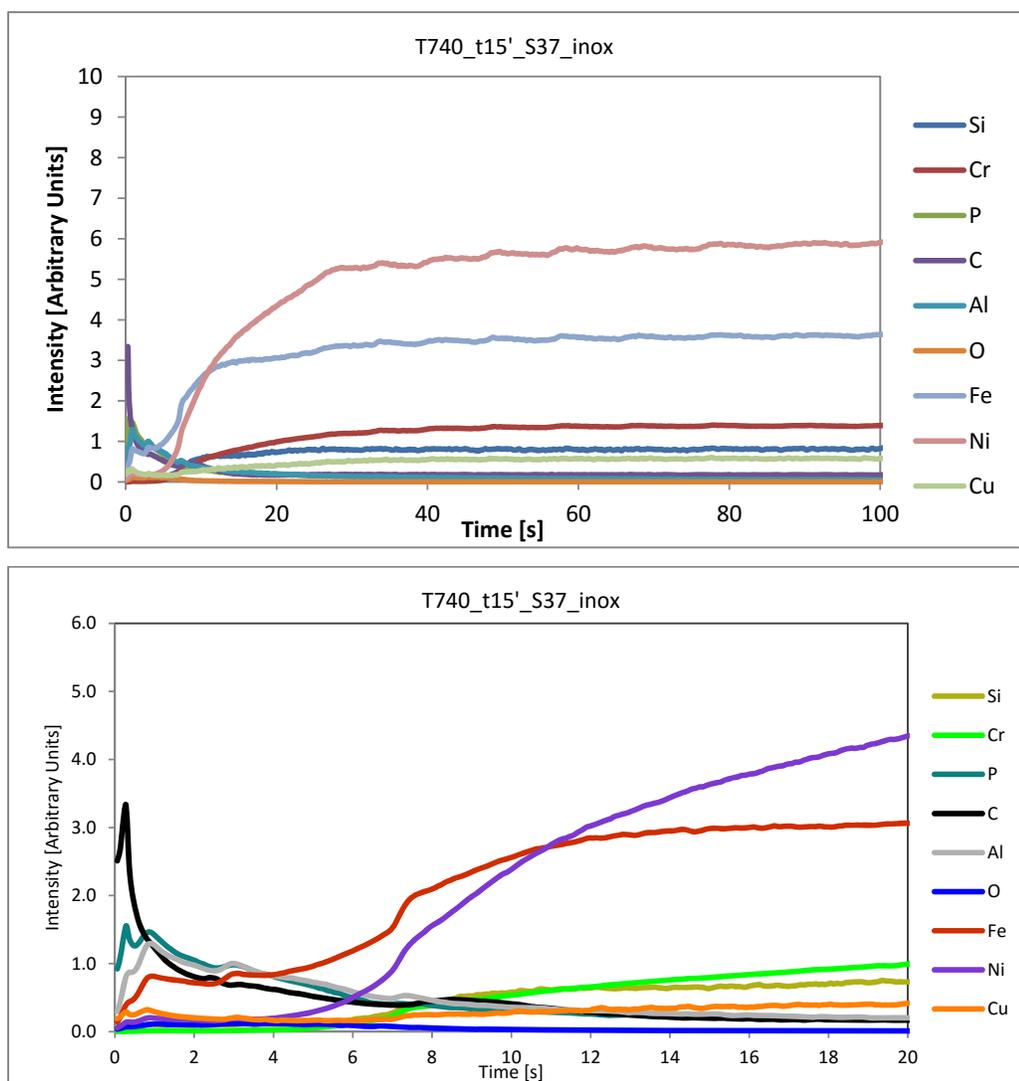


Fig. 47 GDOES profiles of S37coating formulation on stainless steel

The true aluminium phosphate coating patented by ATFI looks the same on the same substrate, as shown on . Compared to S37, it seems that aluminium and phosphorus interact more with the substrate, if we consider the overlap with Ni and Fe signals.

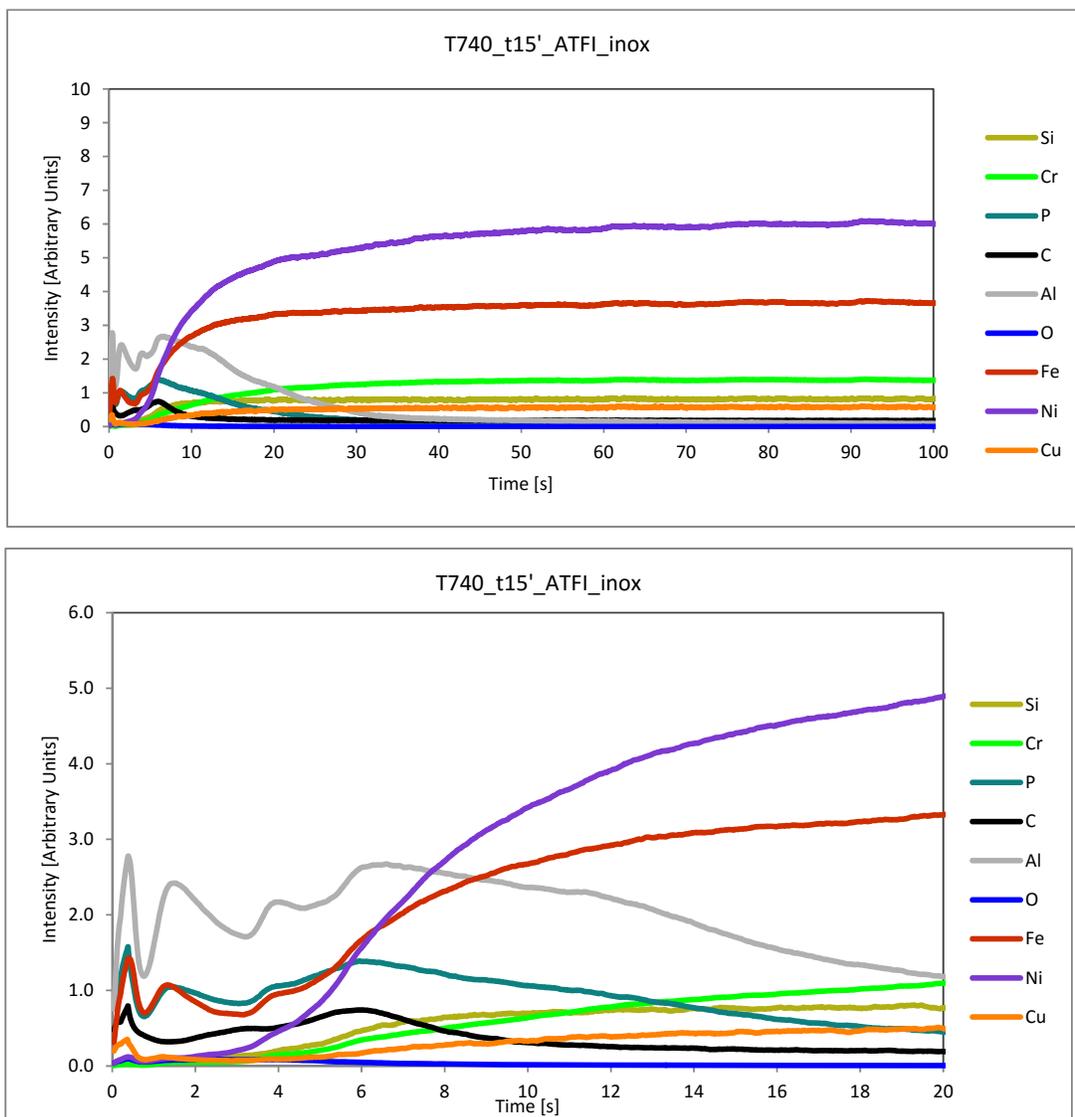


Fig. 48 GDOES profiles of ATFI coating formulation of stainless steel

S37 applied onto alusi (Fig. 49) in the same conditions as for stainless steel (dipping solution, dipping time) is even thinner than on stainless steel. What is remarkable is that a deposition of copper can be observed: the intensity of the signal, relatively to the ones of aluminium or phosphorus in the coating, is more important than the one observed on

stainless steel with the same solution. This result is known and used already in the enamelling of aluminium. Pemco patented an enamel system including copper oxide for further ruse on specific aluminium alloys (15)

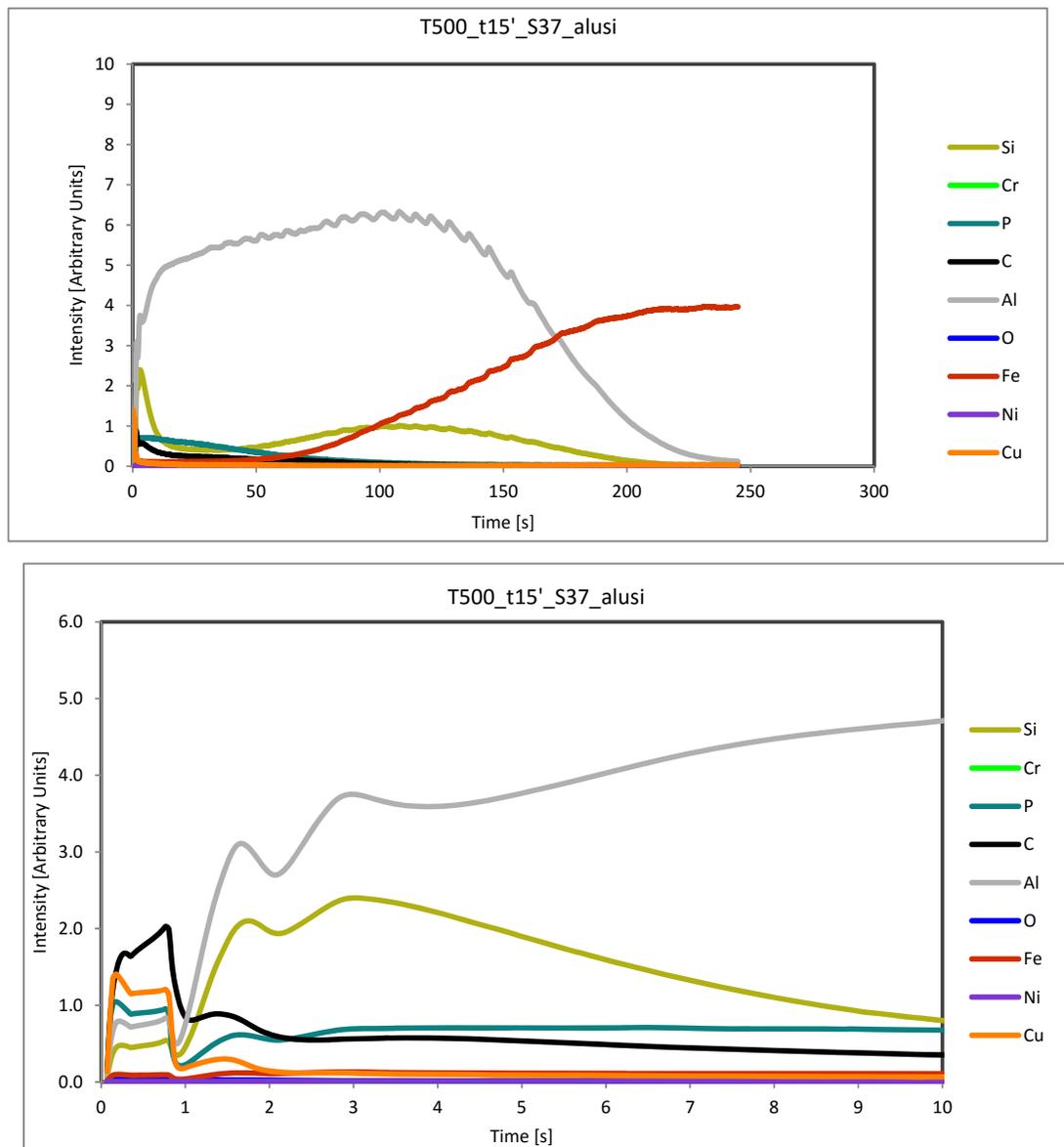


Fig. 49 GDOES profiles of S37 coating formulation on stainless Alusi

Aluminium phosphate applied onto Alusi (Fig. 50) is, as well as on stainless steel, very thin. It also contains some carbon which presence into the Alusi coating is strange. The possibility to slightly “carburize” the surface of Alusi thanks to the decomposition of the

organics during curing of the Solgel could be an option, to be further checked Fig. 50  
 GDOES profiles of ATFI coating formulation on Alusi

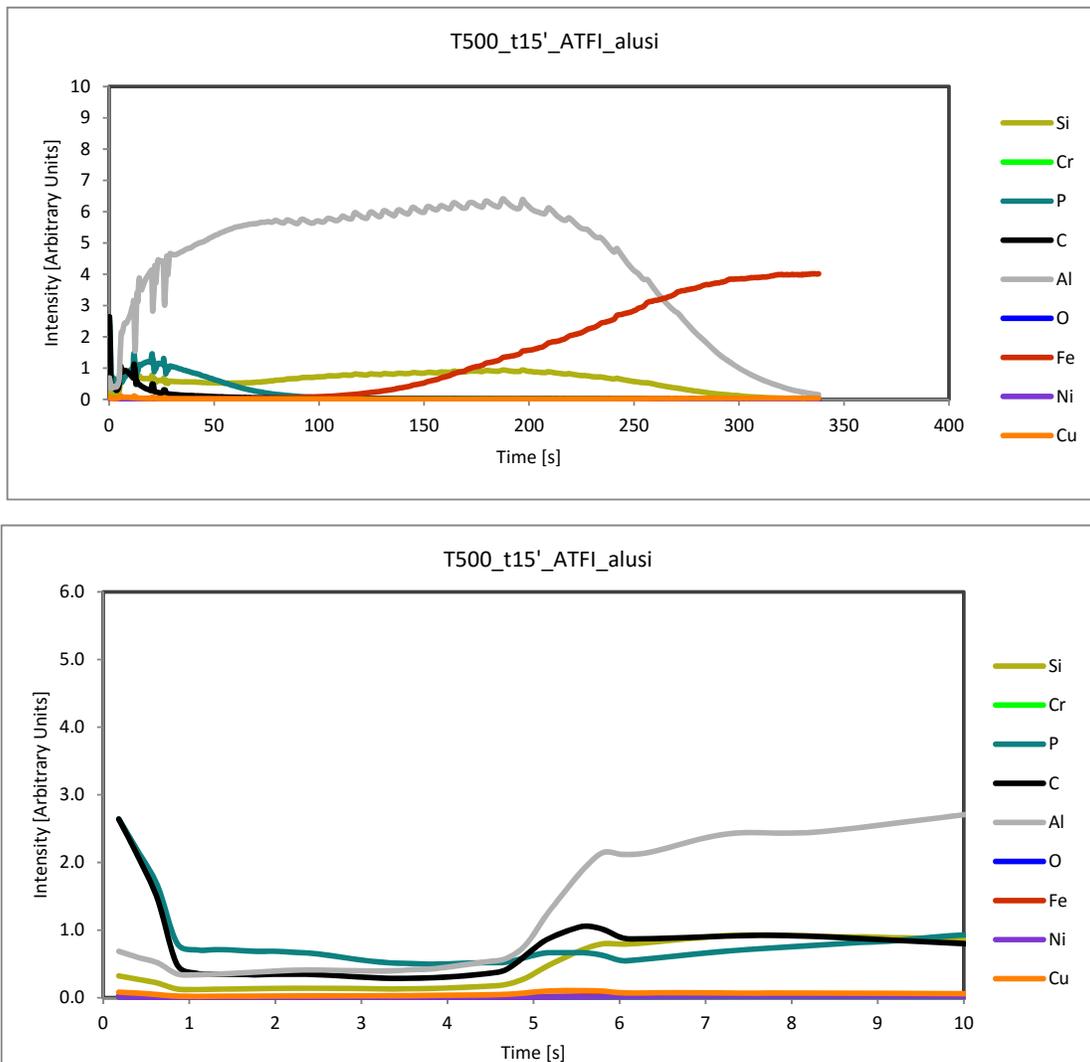


Fig. 51 GDOES profiles of ATFI coating formulation on stainless Alusi

## **6. CONCLUSIONS**

- Top down primer composition I8, described in (14), was further positively modified by adding colourless oxides, with a metallic character: tin oxide ( $\text{SnO}_2$ ) and cerium oxide ( $\text{CeO}_2$ ). Both were found to provide good adherence for enamel primer composition (on Alusi) and allowed getting opacification of white top coat enamel. This result is in line with the ones previously obtained by playing with transition metal oxides, easily reducible. Cerium and tin oxides are also known, in glass compositions to be capable of exchanging oxygen with their environment. Both were integrated to the claims of the patent application (pending)
- For the solgel composition J7, based on salts, previously developed in the Bottom up approach of TGC concept in 2013 (3), it is possible to reduce firing temperatures and times obtaining a smooth primer coating. Detailed results are shown in Table XII. Firing temperature can rather easily being reduced to  $650^\circ\text{C}$ , and even down to  $550^\circ\text{C}$  id long firing time, of an order of magnitude of one hour, are taken into account.
- Even if curing temperature of the primer J7 was reduced, the compatibility and a fair adherence of a bilayer system (primer+ top coat) wasn't obtained. A light improvement for longer firing times was observed, but it is still poor.
- To improve the adherence of 2 layers system, it was found that the addition of iron oxide and zinc oxide in J7 had a positive impact (S35 and S37 samples). But this modification didn't bring any improvement of surface quality of top white layers. A rough surface was obtained, bubbles being trapped in between primer( low viscous) and topcoat (more viscous) enamel layer
- Addition of metallic oxides in J7 composition increases adherence but it also increases vitrification temperature
- Detailed investigations of the sintering process of J7 formulation by TGA and DSC between RT and  $700^\circ\text{C}$  showed that the use of alkaline phosphate salt, very soft, doesn't allow getting a homogeneous single glass layer at the end of the process. Like for smelting of enamels, phosphate reacts with the other components of the composition, and might lead to form a single glass, but not in the time frame that is considered in this study. Phosphate decomposes in a multi stage process and recombine with other ingredients. This could lead too to secondary redox exchanges it was impossible to check, because DSC and TGA were conducted separately

- Bottom up formulation J7 and any of its derivative can anyway be valorised as such, not covered by any other enamel, to provide a long term corrosion protection onto Alusi
- In a second step, a true Solgel system was tested, being a true aluminium phosphate  $\text{AlPO}_4$ , obtained from organo-metallics, and according to recipes developed and patented by an American company, ATFI. Coatings were obtained onto stainless steel (as described in the patents) and also onto Alusi, although for both we still face practical issues at Ocas. Our methodology needs to improve.
- Original aluminium phosphate coating of ATFI obtained by Solgel was modified, merging the knowledge capitalized in the project on the top down concept. Transition metal oxides were added, namely  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$ . Only a few tests were made, that seem to be in line with the literature (15) : a galvanic coupling can be obtained between  $\text{CuO}$  and Alusi
- Coatings that were obtained are still thin and discontinuous, but this is linked only to the impossibility to get more concentrated solutions because of technical problems (Ocas); this should be solved when it will be possible to follow exactly the process described by ATFI.
- To improve the "Solgel" approach in this project, 2 tracks can be opened.
  1. A study using XRD at high temperature on any of the formulations tested, in order to see more easily phases disappearing and/or appearing during heating. This will be possible at Ocas only in 2016, after installing a new diffractometer.
  2. Compared to the start point J7, a new and simplified formulation was found. It can be tried to smelt a few ones in order to get a stable glass that could be used afterwards as primer. If the results are positive then a work can be engaged to try to get the same through a true Solgel process.

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