Enameling of Functionalized Steel Surfaces

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Introduction

Enameling of steel surfaces has been done for many years on different types of steel, depending on the final application of the enameled pieces.

The first type of steel is hot rolled for silos and hot water tanks. Usually, hot rolled steel will be enameled on only one side to avoid any fish-scaling problem ; for silos, were two-sides enameling is essential, special technologies and selected steel-qualities are necessary.

The other type is cold rolled steel, which can be decarburized, depending on the enameling process. Steel containing less than 0.08% carbon (according to EN 10209) is used for conventional enameling (1 coat/1 fire or 2 coat/2 fire) for architectural panels, ovens cavities, or dripping pans/broiler pans. Decarburized steels with less than 0.004% carbon are mainly used for direct enameling (white) or 2 coat/1 fire application. Final pieces are used for the appliance market (hobs/cooktops or home laundry) or sanitary ware.

1. New Pre-Coated Steel

Steel suppliers have developed new types of steel which are pre-coated with different primers or bonding layers. These simplify the enameling process and save money by shortening the process time, increasing productivity, decreasing energy consumption, and increasing environmental friendliness by eliminating pickle-nickel. [1]

This paper presents the different types of coatings found on the market and their influence on the enameling process. Two types of coating were evaluated :

- "R2E Steel", which is a new pre-coated steel (ready-to-enamel),
- Pre-primed steel, which is steel coated with a bonding layer for direct white enameling.

2. Current Enameling of Steel

The normal composition of a ground coat is based on alkali borosilicate glass with metallic oxides NiO, CuO, and/or CoO added to create bond.

Due to the new REACH regulation, NiO is used less in enamel ground-coats in Europe because the final products have to labeled as carcinogenic if they contain more than 0.1% NiO. Acid resistant ground-coat also contains TiO_2, while the addition of ZrO_2 provides alkaline and water resistance. All these raw materials are smelted at around 1200°C to obtain a glass frit.

The glass frits are then milled to produce either a Ready-To-Use (RTU) product which will be blended with water before wet application under customers conditions, or an electrostatic powder which will be directly dry sprayed by the customer.

Regardless of the application process, adherence of enamel on steel is obtained during firing through both mechanical and chemical adherence as shown below :

- Mechanical adherence is due to micro-roughness developed at the steel surface as presented in Figure 1.

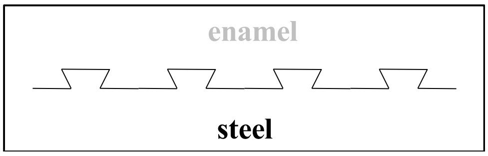


Figure 1 : Mechanical adherence

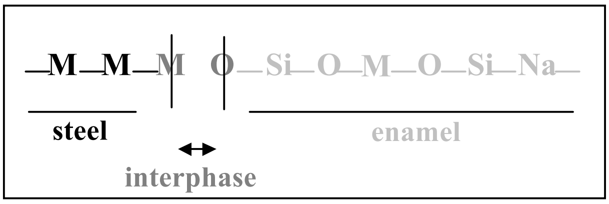


Figure 2 : Chemical adherence

- Chemical adherence is due to the oxidic-reduction reactions which take place at the enamel/steel interface during firing as shown in Figure 2. [2]

Before enameling , the steel needs to be pretreated by the appropriate process given in Table 1.

Conventional Enameling	Direct-on Enameling
1- Alkaline degreasing	1- Alkaline degreasing
2- Rinsing	2- Rinsing
3- Drying	3- Acid pickling
	4- Rinsing
	5- Nickeling
	6- Rinsing
	7- Neutralization
	8- Drying

Table 1 : Surface treatment of steel before enameling

Of course these pre-treatments take time, and are costly. Additionally, nickeling is increasingly prohibited because of hazardous waste from an environmental point of view.

To suppress these types of issues in production plants, the new grades of steel can be considered for all the enameling processes (conventional, 2 coat/1 fire, direct-on white) which require neither degreasing nor pickle-nickel.

3. Enameling Results - Ready to Enamel Steel for Ground Coat Enameling

3.1. Enameling Process

- Dry spray enameling : can be done directly on the pre-coated steel, without any degreasing step.
- Wet-spray enameling : as the coating applied to the steel shows an “oily” appearance, wet spraying with a conventional slip leads to tearing defects.

Of course, it is possible to increase the substrate surface energy by degreasing it, but we can not use this process with this R2E (ready-to-enamel) steel as the goal is to enamel it without degreasing. So, it is better to add a wetting agent to the enamel slip to modify the surface tension and eliminate the tearing defect.

The wetting agent reduces the surface tension of the liquid phase. Wetting of solids by liquids is influenced by surface tension and surface energy of which typical values are given in Table 2. In general, the following applies :

- A substrate with high surface energy is easily wetted,
- A liquid with a low surface energy is good at wetting,
- Wetting is ideal if the surface energy of the liquid is significantly lower than the surface energy of the substrate.

Substrate	**Surface energy (mN/m)**
Steel	50
Aluminium	40
PTFE	20

Table 2 : Surface energies of different substrates [3]

Based on this theory, different wetting agents were tested in the enamel slip. One additive gave good results. Figures 3 and 4 show the dried enamel on steel, with and without the wetting agent ethoxylated alcohol blended at 1% into the enamel slip.

Figure 3 : Enamel without wetting agent (tearing defect)

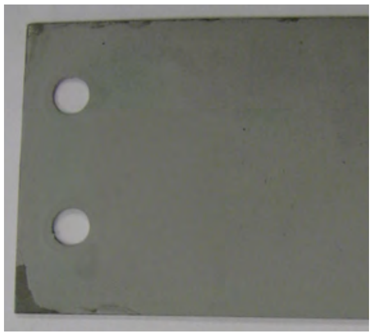


Figure 4 : Enamel with wetting agent (no surface defect)

3.2. Results with Conventional Enameling (1C/1F ground coat)

Enamel RM628A was applied at a rate of 420 g/m² to steel and fired with different times and temperatures. The standard firing conditions on conventional steel are 820°C at 0,56 m/min (5'30). The following table shows the adherence results per EN 10209 (1996), obtained versus decreasing firing temperature and/or time (1 corresponds to a very good adherence, 5 corresponds to a very bad adherence).

	820°C	**800°C**	**780°C**	**760°C**	**740°C**
0,56 m/min	1	1	1	1	5
0,60 m/min	1	1	1	1	5
0,65 m/min	1	1	1	1	5
0,70 m/min	1	1	1	1	5
0,78 m/min	1	1	1	1	5
0,83 m/min	1	1	1	2	5
0,88 m/min	1	1	1	3	5
0,93 m/min	1	1	1	3	5
0,99 m/min	1	1	1	5	5

Table 3 : Firing conditions of RM628A on R2E steel

As a comparison, the pictures of adherence impact of RM628A on degreased steel and pre-coated R2E steel are shown in Figure 5.

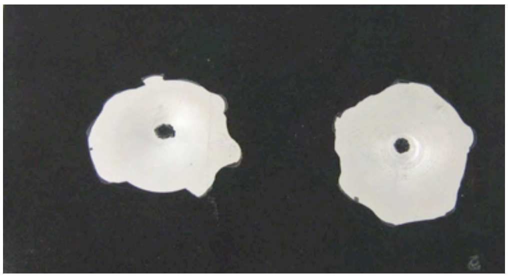
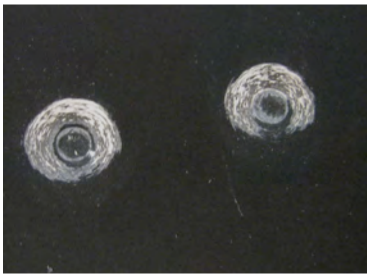



Figure 5 : RM628A on degreased steel – RM628A on R2E steel (760°C – 0,83m/min)

The adherence of the conventional ground-coat was developed on the pre-coated steel at 60°C lower than the standard firing temperature and with the conveyor speed increased about 50%. Without the pre-coated steel, no adherence was observed with the same firing conditions.

3.3. Results with 2C/1F Enameling (Ground Coat)

Three different ground coats currently used for 2C/1F process were evaluated with added wetting agent. Each ground coat was applied at a rate of 130 g/m² on steel and fired at different times and temperatures. The standard firing conditions were 820°C at 0,56 m/min. A conventional white cover-coat was used.

3.3.1. One side Enameling

Enameling on one side of the steel was evaluated first. The results are summarized in Table 4.

	Degreased steel						Pre-coated R2E steel				
	800°C	**780°C**	**760°C**	**740°C**	**720°C**		**800°C**	**780°C**	**760°C**	**740°C**	**720°C**
0,56 m/min	1	1	1	4	5		1	1	1	1	5
0,60 m/min	1	1	1	4	5		1	1	1	1	5
0,65 m/min	1	1	2	4	5		1	1	1	4	5
0,70 m/min	1	1	2	4	5		1	1	1	4	5
0,78 m/min	1	1	3	5	5		1	1	1	5	5
0,83 m/min	1	1	3	5	5		1	1	1	5	5
0,88 m/min	1	1	4	5	5		1	1	1	5	5
0,93 m/min	1	1	4	5	5		1	1	1	5	5
0,99 m/min	1	1	4	5	5		1	1	1	5	5

Table 4 : Adherence of a 2C/1F ground coat on conventional degreased steel compared to pre-coated steel (one side enameling process)

On degreased steel, the adherence was good from 800°C to 780°C at 0,56 to 0,99 m/min and acceptable for a firing at 760°C at 0,56 to 0,70 m/min. As a comparison, on the new pre-coated steel, the adherence of the same enamel was good even for firing at 740°C at 0,56 to 0,60 m/min. No change in the color was observed versus the firing temperature or time ($\Delta E<1$). The surface of the white cover-coat showed some orange peel and boiling defects when fired at 760°C or lower. However, this issue can be solved by the use of a softer white cover-coat.

3.3.2. Enameling on Both Sides

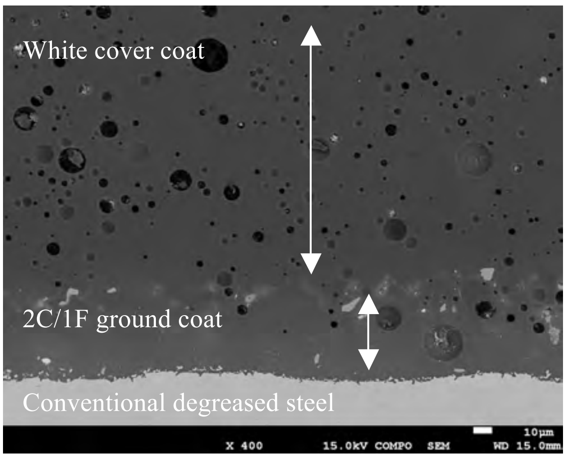
In order to confirm the previous results, enameling on both sides of the steel was tested, which is used for industrial production of cooktops. The pre-coated steel again provided adherence at a firing temperature 20°C lower than the standard conditions as shown in Table 5 and Figure 6.

	Degreased Steel						Pre-coated R2E Steel				
	800°C	780°C	760°C	740°C	720°C		800°C	780°C	760°C	740°C	720°C
0,56 m/min	1	1	4	5	5		1	1	1	4	5
0,60 m/min	1	2	4	5	5		1	1	1	4	5
0,65 m/min	1	2	4	5	5		1	1	2	5	5
0,70 m/min	1	2	4	5	5		1	1	2	5	5
0,78 m/min	1	2	5	5	5		1	1	3	5	5
0,83 m/min	1	3	5	5	5		1	1	3	5	5
0,88 m/min	1	3	5	5	5		1	1	3	5	5
0,93 m/min	1	3	5	5	5		1	1	3	5	5
0,99 m/min	1	4	5	5	5		1	1	3	5	5

Table 5 : Adherence of a 2C/1F ground-coat on conventional degreased steel compared to pre-coated steel (both sides enameled)

Figure 6 : Adherence of a 2C/1F enamel on degreased steel compared with pre-coated R2E steel (760°C at 0,56 m/min)

Scanning Electron Microscopy (SEM) and Electron energy Dispersive Spectroscopy (EDS) observations and analysis were done to examine the difference in adherence between degreased and pre-coated steel. SEM micrographs are shown in Figures 7 to 10.



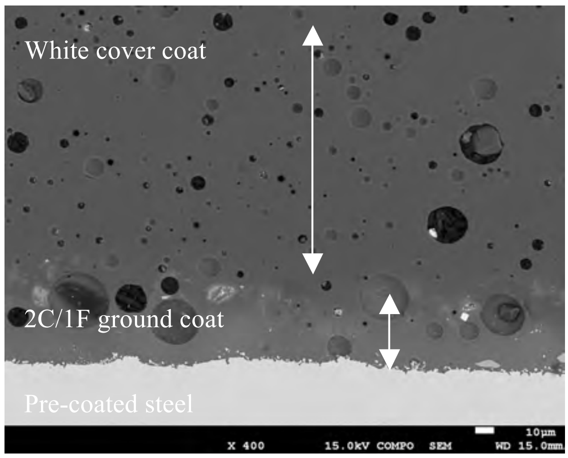


Fig 7 : Cross-section of 2C/1F on conventional steel (760°C at 0,56 m/min)

Fig 8 : Cross section of 2C/1F on pre-coated R2E steel (760°C at 0,56 m/min)

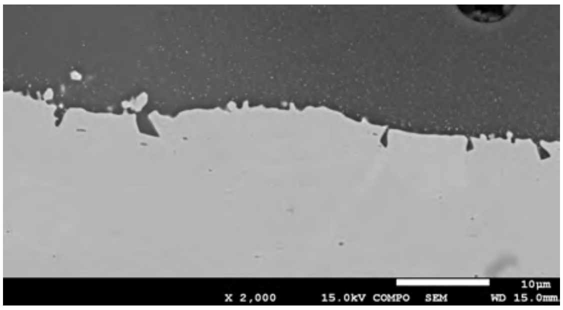


Figure 9 : Cross-section of 2C/1F on conventional steel (760°C at 0,56 m/min)

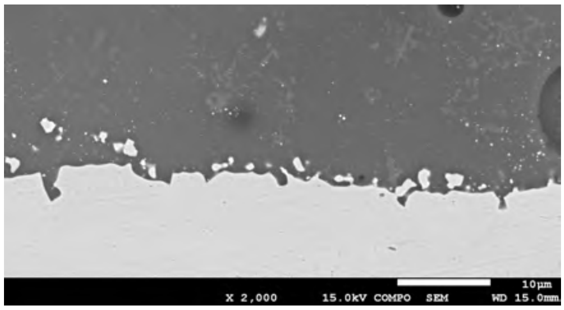


Figure 10 : Cross-section of 2C/1F on pre-coated R2E steel (760°C at 0,56 m/min)

The enamel/steel interface appeared smooth on the conventional steel while it was rougher on the R2E steel : the oxidic-reduction reactions were accelerated. Figure 11 shows the many metallic alloy particles that are similar to those seen with conventional enameling [4], [5] at 820°C at 0,56 m/min.

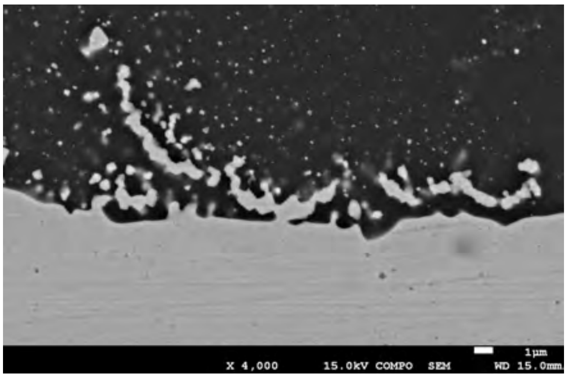


Fig 11 : Cross-section of 2C/1F on pre-coated R2E steel (760°C at 0,56m/min)

The metallic particles observed on the R2E steel consist of two parts. One is iron and the other one is rich in copper. EDS spectra are shown in Figures 13 and 14 for the SEM micrograph in Figure 12.

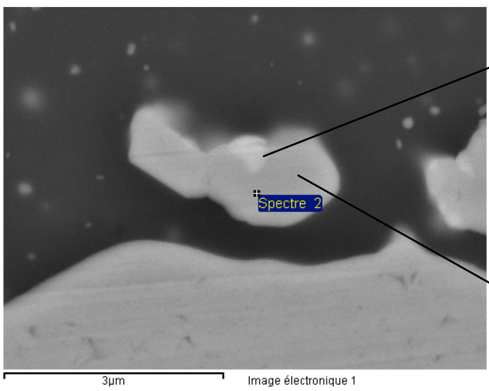


Figure 12 : R2E steel/enamel interface (760°C at 0,56m/min)

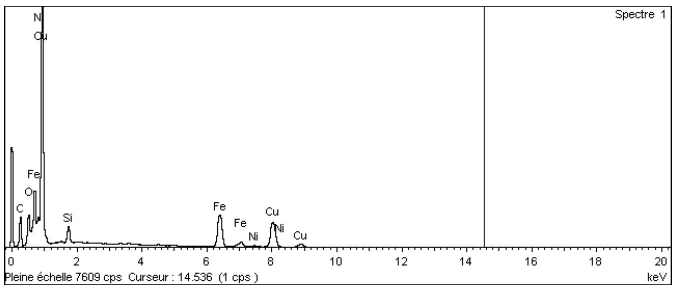


Figure 13 : EDS spectrum of metallic particle (white part)

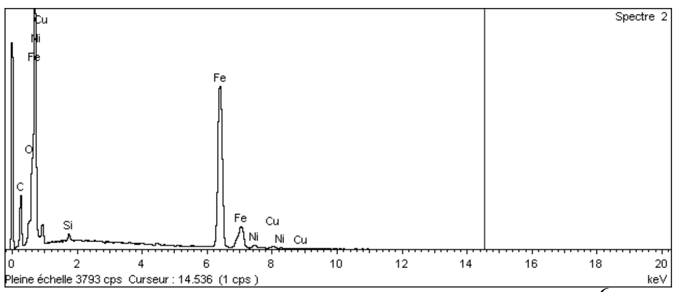


Figure 14 : EDS spectrum of metallic particle (grey part)

3.4. Results with Low Cost Ground Coat

Because the R2E coating applied on steel accelerated the adherence reactions at a lower temperature and shorter firing time, it should be possible to develop adherence with a low cost ground coat containing a lower metallic oxide content.

The trials done are summarized in Table 6 for firing at 0,70 m/min.

	Steel (C<0,06%)		Steel (C<0,004%)		Pre-coated steel	
	780°C	820°C	780°C	820°C	780°C	820°C
Low cost GC	2	1	2	1	1	1
90% Low cost GC + 10% glaze	3	1	3	1	1	1
80% Low cost GC + 20% glaze	3	1	3	1	1	1
70% Low cost GC + 30% glaze	5	2	5	5	2	2

Table 6 : Adherence of a low cost ground coat on conventional degreased steel compared to pre-coated steel

As already known, adherence is better on steel containing more carbon, but a low cost ground coat does not develop enough adherence at 780°C, even if used alone. On the other hand, if this specific ground-coat is applied on pre-coated R2E steel, good adherence is observed even at 780°C as shown in Figure 15.

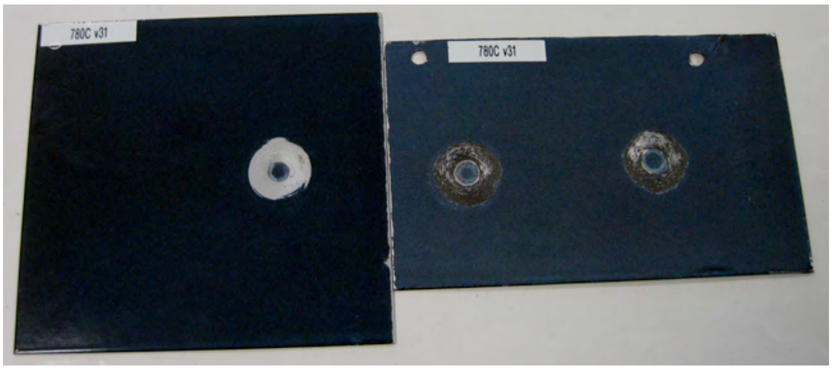


Figure 15 : Adherence impact of low cost ground-coat of uncoated steel (left) and coated steel (right)

Results showed that even with a low metallic oxide content, adherence was good on pre-coated steel, where it is very poor on conventional degreased steel as presented in Figure 16.

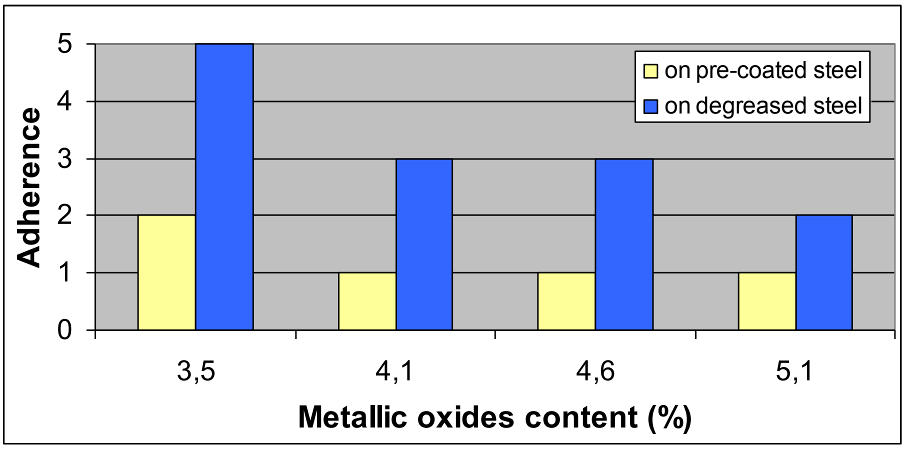


Figure 16 : Influence of metallic oxides content (in a low cost ground-coat) on adherence

SEM/EDS observations comparing the enamel applied to coated or uncoated steel after firing at 780°C at 0,70 m/min are shown in Figures 17 to 19.

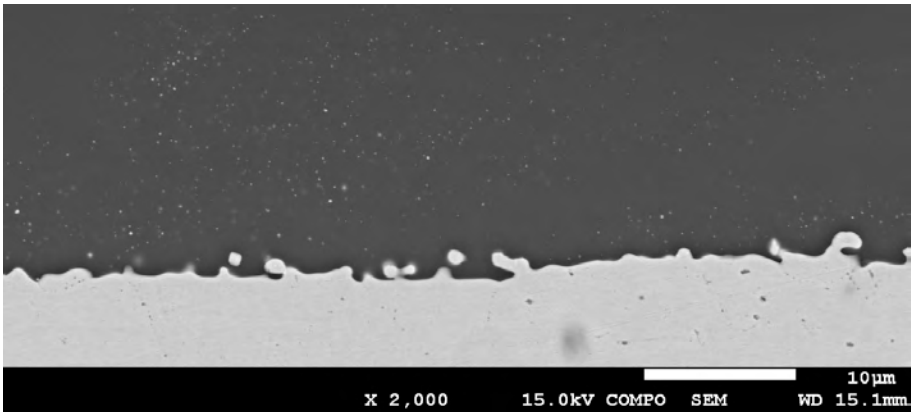


Figure 17 : SEM cross-section of low-cost ground coat on uncoated steel

Smooth steel surface with some metallic alloy due to oxidic-reduction reaction between the ground coat (low metallic oxide content) and steel.

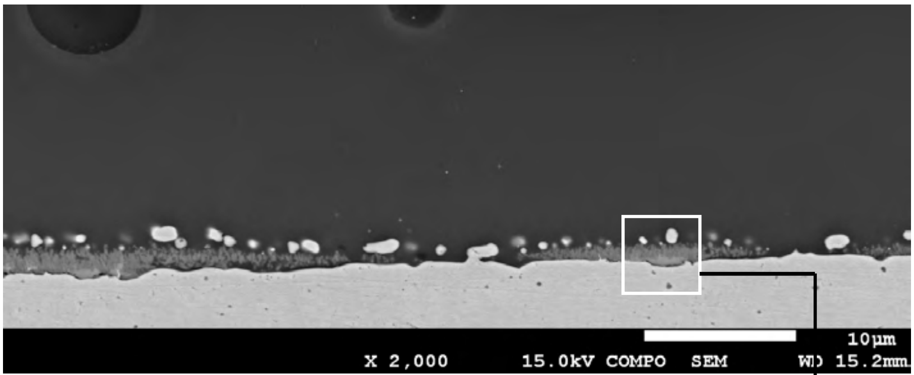


Figure 18 : SEM cross-section of low-cost ground coat on coated steel

Smooth steel surface with much metallic alloy due to oxidic-reduction reaction between ground-coat (low metallic oxide content) and steel. Iron silicate is also present at the steel surface.

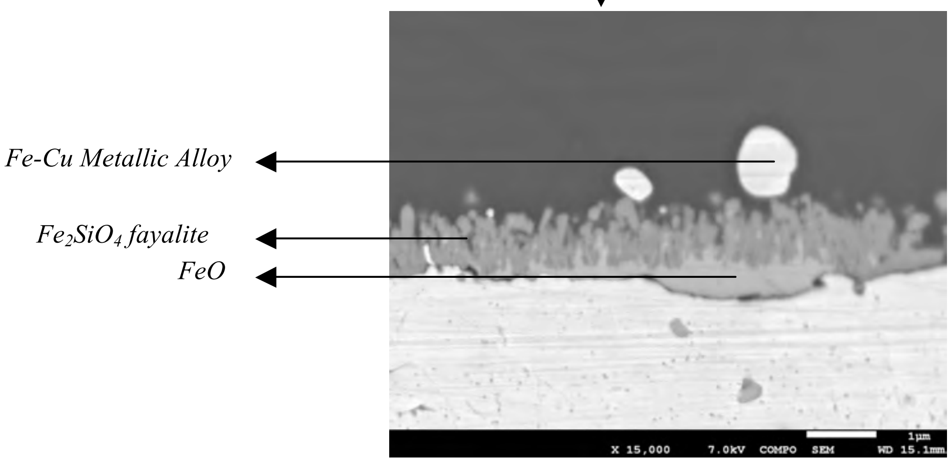


Figure 19. SEM cross-section of low-cost ground coat on coated steel

The chemical elements identified at the steel/enamel interface are metallic particles observed with ground coat enamel applied on steel but also two other compounds: (1) iron oxide FeO (due to the oxidation of steel) not yet dissolved by the enamel and (2) an iron silicate Fe_2SiO_4, which exists at the steel/enamel interface [6,7,8] when the enamel is saturated with iron oxide. This type of interface was already reported in the case of the adherence of transparent enamel GL1000 (enriched in 15% Fe_2O_3 wt%) applied on degreased steel as shown in Figure 20. [2].

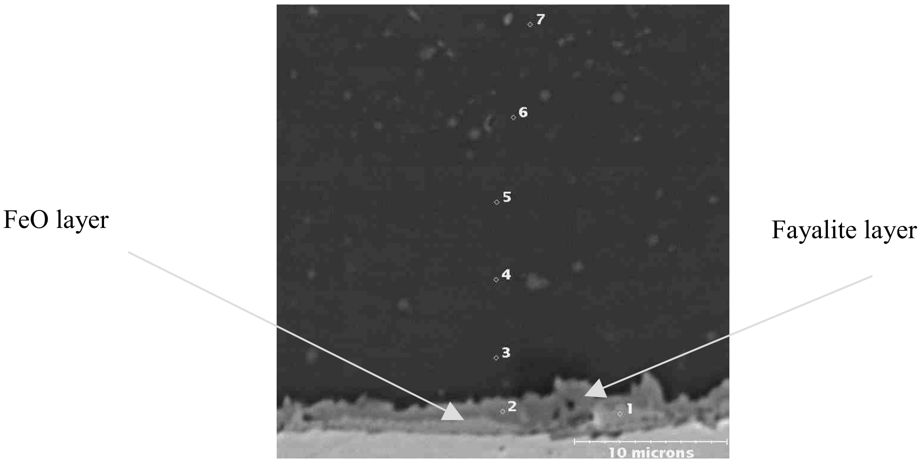


Figure 20 : SEM cross-section of GL1000+15% Fe_2O_3 on degreased steel at 800°C for 15 min

High oxidation of steel and therefore a high rate of dissolution of iron oxide in the enamel in the case of the pre-coated steel was confirmed by EDS analysis. The iron content was measured in the enamel from the enamel/steel interface to the enamel matrix through 40 µm and is shown in Figure 21.

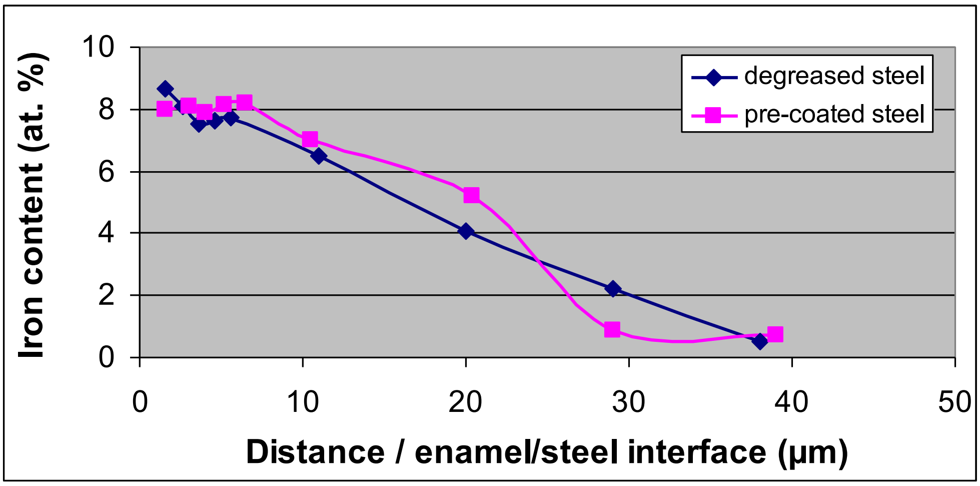


Figure 21 : Iron content in low cost ground-coat applied on R2E steel at 780°C at 0,70 m/min

A higher quantity of iron oxide was dissolved by the enamel on the pre-coated steel in comparison with only degreased steel. This can explain the difference in adherence.

4. Enameling results - Pre-primed Steel for Direct White Enameling (DWE)

4.1. Enameling Process

A new steel pre-primed with a specific coating was dry electrostatically sprayed (300 g/m^2) with a white cover coat (usually fired at 820°C at 0,56 m/min on ground-coated or nickeled steel). Bond and surface were tested against different firing conditions and thicknesses of the bonding layer (0,3-0,6 µm and 1,0-1,9 µm). Results are shown in Table 7.

		800°C - 0.99 m/min	820°C - 0.99 m/min	820°C - 0.56 m/min	840°C - 0.99m/min
0.3-0.6µm	**Adherence**	5	5	5	5
	Surface	Acceptable	Acceptable	Acceptable	Acceptable
1.0-1.9µm	**Adherence**	1	1	1	2
	Surface	Blue spots	Blue spots	Blue spots	Blue spots

Table 7 : Adherence of white enamel on pre-primed steel for DWE with thick thin and thick bonding layers

The adherence impact tests are shown below in Figure 22.

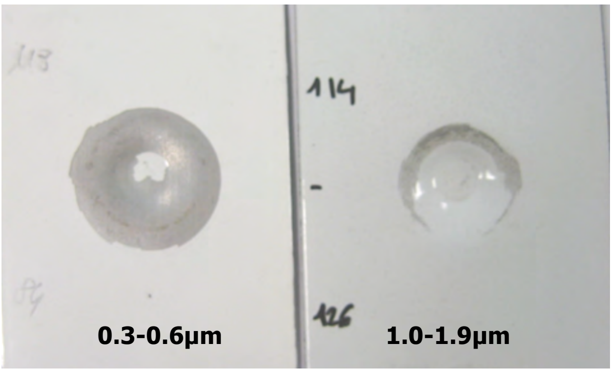


Figure 22 : Adherence impact test on white enamel applied on pre-primed steel for DWE at 820°C at 0,56m/min with thin bonding layer (left) and thick bonding layer (right)

4.2. Results of Enameling

To explain the difference in adherence and confirm the ability of the bonding layer to replace ground coat or nickeling, SEM/EDS analysis was conducted. Results are shown in Figures 23 and 24.

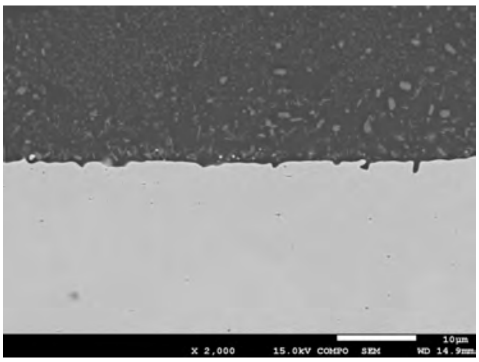


Figure 23. Steel/enamel interface with steel coated 0.3-0.6µm bonding layer with no adherence

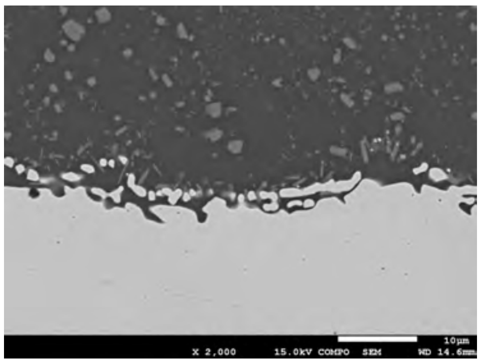


Figure 24. Steel/enamel interface with steel coated with 1.0-1.9µm bonding layer with good adherence

The interface with the thin bonding layer was very smooth, without metallic particles close to the steel surface.

On the other hand, the interface with the thick bonding layer was typical of the normal reactions between a white enamel and a nickeled steel, showing many metallic particles at the steel surface together with iron titanate needles [9,10] confirmed with chemical analysis. A SEM micrograph of this is shown in Figure 25.

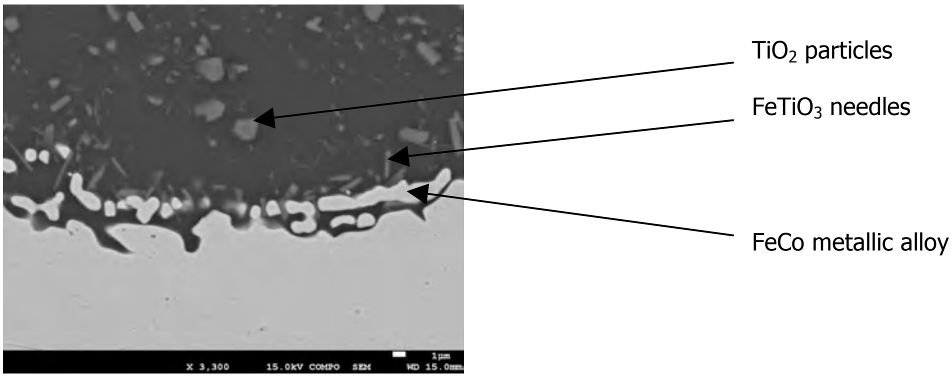


Figure 25 : Steel/enamel interface : steel coated

To compare, the typical interface of white enamel applied on nickeled steel is shown in Figure 26.

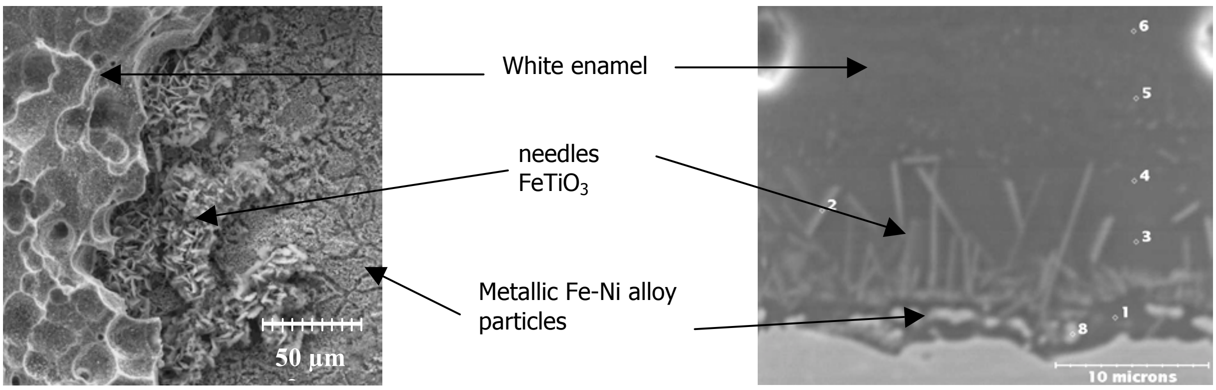


Figure 26 : Typical white enamel/nickeled steel interface [2]

This new bonding layer coating applied on steel allowed good adherence to be obtained using a Direct White Enameling process, without a nickeling step. The only improvement required is to eliminate the blue spots which are sometimes observed after firing. New trials on the white enamel formulation are in progress to solve this issue.

5. Conclusion

New steels were developed thanks to new technologies in order to simplify the enameling process and also to make it less expensive in term of energy consumption or environmental impact. To use these new substrates, enamels have been developed to obtain as high of a quality as obtained in the past with conventional products. End products like cookers, oven cavities and bathtubs should be produced soon to test the laboratory results under industrial conditions.

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