Stained Glass: Art at the Surface

Creation, Recognition, Conservation

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Enamel Deterioration: The Thermal Properties of Modernist Enamels and Stained Glass from the City of Barcelona

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Introduction
Stained glass art in Catalonia - especially that made at the end of the nineteenth century and in the first twenty years of the twentieth century - is a large collection remarkable for its quality. However, most of this fragile heritage is suffering some degree of deterioration, part of it being the degradation of enamels (fig.1). While some structural problems within the lead matrix, or breakage of the glass, are noticeable, damaged enamel is not as obvious, and its slow advance might, in some cases, lead to total paint loss. What complicates the matter even further is that there are no effective active intervention methods that offer a long-term solution.

Enamels are a finely-ground glass powder with a very low melting temperature. In order to lower that melting-point even further, flux is sometimes added. The first part of this paper analyzes raw materials used by the stained-glass company Rigalt i Granell while the second part analyzes different enamel samples from Rigalt i Granell, Maumejean, Amigó and Bazin & Latteaux.

Fig. 1: Barcelona stained glass at Gran Via 684. Detail of a flaking blue enamel.

One of the main issues in the conservation of the decorative layers (enamels and grisailles) is the quality of the adherence, and this depends on the thermodynamic properties of both substrate glass and decorative layers. The glass transition, glass deformation and glass softening temperatures determine the range of firing temperatures necessary to obtain correct adherence of the decorative layers. The enamels should be fired at a temperature close to their softening point to favour their adherence to the base glass. The deformation temperature of the base glass, on the other hand, must not be reached. Moreover, the atomic diffusion coefficients necessary for a good inter-diffusivity of the enamels and the background glass increase dramatically at the glass transition temperature, the temperature above which the glass behaves as a liquid. Therefore, the glass transition temperature of the base glass has to be reached in order to obtain a good adherence. Consequently, the optimal firing temperature is a compromise between the base glass deformation and glass transition temperatures, and the enamel softening temperature. Moreover, if the viscosity of the enamels is too high during the firing, large bubbles may be produced. The large surface/volume ratio is also a handicap to the enamels preservation. It is obvious that, depending on the composition of the base glass, and of the enamels, this restriction may leave a very narrow temperature range.

The thermal properties depend on the chemical composition of the enamels and base glass. One of the difficulties is the fact that both lead oxide and borax are commonly used to decrease the viscosity and reduce the softening point of the enamels. Both are common fluxes, which in large quantities act as glass forming structures. Therefore, the use of both may induce immiscibility and produce a heterogeneous glass. Finally, the presence of particles either to give opacity or color to the enamels may also affect their stability. Consequently, both the chemical composition and the microstructure of the enamels are very important.

The data presented are the first obtained on firing temperature, chemical composition and microstructure of a collection of blue enamels used in the period, part of the material from the Rigatti Granelli company.

Enamel Stability

Approaching the conservation of unstable enamels is especially complicated in architectural panels. Stained glass if often made on a large scale and is constantly exposed to the weather conditions. While it is clear that installing protective glazing is effective in creating a more stable environment that contributes to long term preservation of the windows, it is uncertain whether the use of a coating can be an effective long-term strategy. The conservation guidelines advise that, as a general rule, coatings should only be used when there is an "in imminent danger of loss". There has not yet been developed a coating that can guarantee reliable results that satisfy demands expected from conservation product. Most of the products available today result in yellowing, shrinking, loss of adhesion and/or blistering. Most polymers cannot even ensure stability that would be required for the average periods between inspection and maintenance conservation campaigns of the object.

This presents quite a wide margin for the conservator to discuss and take an individual decision based on their judgment of the risk to the specific object. It is clear that flaking paint must be consolidated but it might be decided that powdery enamel is not in "imminent risk" or does not need urgent consolidation. The controversy and difficulty of these decisions is well illustrated by at least one unfortunate case in Joespeh Church at Lesseps Square in Barcelona – all the enamel was gone after ten years of inaction. If a coating had been used, the window's original paint would have been preserved despite the fact that the coating might have yellowed. In this case the rate of the paint loss was much faster than would have been the deterioration of the coating. While it is true that not all deteriorated enamel with this external aspect ages at the same pace, it is also true that most fired colour on stained glass shows this lightening to some degree. In order for conservators to take the best decisions for enamel conservation, more in-depth knowledge of the problem is urgently needed.

Deterioration Types

Analyzing deteriorated enamel is a particular problem because we are observing only the remains of the paint. This means that it is always difficult to know what the initial stages in the process looked like. The stages of deterioration that were found have been classified as follows:

- Pitting/Pinholes and rough surface
  The surface of some enamels, once they are fired are full of pinholes from vapours that have escaped the melted paint. As some enamels have high viscosity, these bubbles leave characteristic crater holes. The enamels allow the accumulation of dirt and moisture that could accelerate deterioration.

- Cracked surface
  The bulk of the enamel is cracked through, reminiscent of a type of glass deterioration known as crazing, with the difference that network of cracks does not reach into the glass and the surface is dry. The edges of the material are whitish and the paint loss begins on the perimeter. Examples of this can be observed on the Dames de Cerdanyola crown yellow enamel. It resembles a silver stain but it is actually a molten powder on the internal side of the window which shows a cracked pattern.

- White powdery aspect
  This might be an initial stage of all enamel deterioration and most commonly occurs when it has been applied to the exterior side of the panel. The enamel is fixed and solid to touch, but part of the colour disappears from some areas of the glass. This is the most widely found form of deterioration and is especially common in blues, greens and lilacs. Lewis F. Day describes it as “Pitted with specks of raw white light.”

Some recent windows show great damage on the enamel and in at least one case, a full blue enamelled shield lost its paint completely after just ten years.

Lost Flakes

In appearance, this is very similar to grisaille deteriorated and lost flakes. Some areas of the enamel are lost and leave sharp edges on the
edges of the remaining adhered enamel. As it is clearly in imminent risk of loss it is the case that demands more urgent intervention.

Appearance of normality but no fixation
This can only be seen in recent windows or windows displayed in interiors. The enamels have a normal translucent appearance but are not fixed to the glass and can be removed by scratching gently with a rag. Where the cleaning of these windows is not entrusted to trained conservators, the risk of losing all paint is very high.

Case Studies

Domes de Cerdanyola: Cerdanyola Art Museum
This triptych is one of the best-known art nouveau stained glass works in Catalonia. It was designed as a mosaic window in 1912, its background and figures being represented in rolled glass in a lead network. However, hands, faces, and some ornaments of the figures are delicately painted. In the course of the last conservation it could be seen that the greens applied on the external side of the crowns of the ladies were vanishing. During preliminary investigation, the deterioration looked like flaking paint, however a careful observation under the microscope revealed a multitude of lines that surrounded the preserved enamel, suggesting that the damage might have been caused or accelerated by the presence of water. In this case, rather than flaking off as an entire piece, the deterioration occurred through the dissolving of small portions in a mechanism that seems to be similar to erosion (fig. 2).

The yellow enamel has been lost following a cracked pattern, with all the paint loss on the outer borders of the material. The isothermal protective glazing was installed during the 2009 conservation campaign.

Amigó Studio: Palma de Mallorca Cathedral
The Amigó workshop was the largest workshop in Catalonia of the late nineteenth century, with roots that go as far back as the eighteenth century. This studio can probably be credited with the late nineteenth- century renaissance of stained glass. The majority of their work, which was religious, shows some signs of deterioration, especially in grisailles and caramnias but also on green and blue enamels. The recent restoration of the 1889 window of the Trinity chapel from Palma de Mallorca Cathedral showed very typical damages of grisaille paint that looked as if the paint had flaked off. Enamel had a whitish appearance on the outside, and had completely vanished in some areas, despite the fact that no flaked paint could be found. Furthermore, no flakes could be extracted from any of the edges of the damaged paint. The Trinity case is especially interesting regarding damaged paint. From a set of three windows, the one in the central position is oriented towards East. The other two windows, on each of the sides, showed different degrees of the paint deterioration. The one on the south side, receiving direct sunlight and direct air from the sea, has a better-preserved paint that the one on the north side.

J.M. Bonet Studio: Josepets Church, Barcelona
The windows depicting the Montserrat Sanctuary are a set of typical post Spanish Civil war windows built in 1949-1953. This example does not date the same period as the majority of the samples analysed for the study, but illustrates rather vividly how fragile the enamels can be. These unprotected windows underwent routine maintenance in 2004. Especially the blue enamel was white on the external side and had vanished in some areas to the point of showing the supporting glass. In 2017, only 12 years later, all enamel had disappeared.

Vilanova E. Ricart
These very recent interior windows dating from 1951 exhibit poorly fired paint. The enamel has a few scratches on it, some of it was lost by flaking off and some, despite not showing any signs of deterioration, could easily be removed during the test that was done previous to cleaning. This may not be called deterioration since it is not a change in an initial state of the enamel; it is poorly adhered to the glass surface now as it was when the window was made. Most of the enamel has an opaque appearance.

Possible Approaches Against Enamel Deterioration
The decision to be made by the conservator involves stepping onto slippery ground. At the same time, with deteriorating object in hand, taking potentially controversial decisions cannot be avoided. As the least invasive method, protective glazing should be installed. Unfortunately, this method might not always be an available choice. In a few cases, intervention such as retouching of the enamels might be considered. Some windows in religious building with damaged enamels may be difficult to read by the viewer, especially when the paint loss occurs in faces or hands of the figures. It might seem to be natural to repaint the parts where there is no doubt about how and where the original was, but even here conservation-restoration ethics have to be considered.

Brandt’s theory of restoration warns that the sentence “as it once was, where it was” is the
opposite of the grounds of restoration and is an offense to history and aesthetics, as it considers time reversible and the work of art to be reproducible at free will.

According to Viñas, the term authenticity means an original state (the one that the object had when it was produced). This creates the paradox that the object was made with unstable enamel, so the preservation of the authentic nature of the object becomes an unattainable aim. At some point, even the discussion of returning the object to its “original state” could be controversial since some of the enamels have not deteriorated in the course of time but because the point was underlined when the object was originally made. At the same time, most stained glass carries a religious symbolism which may be lost with the decay of the paint.

The range of options for the conservator is limited when products such as have been used BS31, epoxy resin, heteropolysiloxane, Paradol B72, Ormocer, Z2A. None are yet proven to be of longer duration than stained glass itself and it is still to be proven that they are harmless to glass over a long period of time.

**Protective Glazing and Monitoring**

This is a preventive conservation measure that has proven to give the best results in order to stop or slow down the deteriorations of enamels. While it is a preventive action, it is also a costly intervention, with an aesthetic impact to the facade or external appearance of the building.

Monitoring different environmental parameters such as temperature and relative humidity could help in understanding the degree of possible damage to the glass depending on its conservation atmosphere.

**Plating: Reintegrating Paint on a Backing Glass**

Reintegration of enamel can be made by adding a layer of thin glass that imitates the lost traces of enamel or paint. Some space is left between the layers so that the glass can be cleaned. This technique has the advantage of being reversible and of not mixing original and added material. A disadvantage is the extra weight added to the panel.

**Retouching**

Although controversial some retouching can be found in the bibliography to varying extents and in various materials. From very specific applications to recover the legibility of the windows, as in Lichfield Cathedral, to the reintegration of full lost areas with acrylic paint.

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**Literature Research**

Christopher Whall, the stained-glass maker and writer of the renowned book *Stained Glass Work* mentioned the main precaution regarding stained glass paint and enamel as giving the process enough time. “I believe that under firing is far more the cause of stained-glass perishing than the use of untrustworthy pigment or flux...” He also warns against the use of pigments containing borax in the glossary of the book, where he describes the term flux “I would warn the student to buy no pigment without a guarantee from the manufacturer that it does not contain this tempting but very dangerous and unstable ingredient.”

William Morris describes in a letter to George Howard how the use of soft enamel had led to disastrous results on the conservation of the paint, to the point of having to replace some of the pieces after a very short period of time, also described in the work of Girlich.

The German stained-glass maker Friedrich Jaenickel describes in his 1897 book *Handbuch der Glasmaleri* zugleich anleitung für Kunstanfänger zur Bearbeitung von Glasmalereien some types of failures that can occur in a chapter of his manual named “Accidents while firing.” He mostly describes two errors that are dependent on the heat of the kiln “When the heat is insufficient, the colours are usually only imperfectly flowing, and then they are not transparent enough” and the opposite “With too much heat, they become thin, run into another and provide mixed images... When colours are subjected to excessive fire more powerful than they are able to endure, they firstly fail to adhere to the base glass, change in tone, and finally disappear. This is rare in blue, green, and black, but often in red, yellow and brown [enamels].” The author goes on to say that if the dull appearance of the colours remains, it can be corrected by adding flux. After describing the influence of the kiln, the author adds another two reasons that lead to obtaining poor results, the first one is the use of borax as a flux and second application of paint too thickly: “the failure of the colour of the paint, is due in particular to too strong boric acid, but on the other hand it is also caused by too strong, that is, too thick application of the paint.” In the final part of the chapter the influence of moisture is also mentioned as another factor separate of the firing that may cause damage, especially in golden enamels.

In his book *Windows*, a book about stained and painted glass Lewis F. Day has a similar explanation for the use of soft enamel and introduces the possibility of thermal expansion as a reason for decay. He states: “...the later the work, and the more pictorial its character, the more surely the painting proves at this date to have lost its hold upon the glass.”

This did not occur in the same way in Catalonia, where only some short articles that spoke about it have been found. All of them are mentioned in the publication by Catelles and Gil. The stained-glass maker Anton...
Rigalt was the most capable of describing technical issues, if not the only one. Gil describes how a harmless glass maker and founder of a leading company at the beginning of the twentieth century, had difficulties in matching the quality of the paint of his predecessors.  

Regarding our country, it can be said that not until the first third of the century [nineteenth] did the renaissance of this art. It was during the restoration of the windows at the churches of Nuestra Señora del Pino and San Justo y Pastor.

I still remember the disappointment of my dear friend and mate Mr. Tomás Padrón, responsible for the glass painting during those restorations. He had to work without knowing the procedure, with glasses that did not have any similarity with the old ones, not having grisaille only red carnation which gave them an unpleasant look and black for the garments that made the colour hues look dirty.

The responsible for other operations were not at higher level than him, regarding technique. It can be assured that it is due to his energy and persistency, together with the generous advice of Mr. Eulogio Ramón Amigó, that this art took the role that it deserved in the churches of Barcelona.

The same article has a short passage describing the use of grisaille with up to four layers of grisaille during a single firing and his advice about using enamel only is small part. The enamels were supposed to be used on the exterior side like the French practice or on the interior on the modelling grisaille (like the Dutch).  

Rigalt’s sentences prove how limited the knowledge of stained glass technique was in the middle of the nineteenth century, despite the great improvement of the following fifty years, which allowed studios to work at the highest level of skill, the fundamental knowledge of this art was a lot poorer.

This lack of information is quite surprising since it is known for a long time that enamel from Amigó workshop, the most prolific one of the late XIX century, has not aged well and from oral knowledge in the studios master glass painters can be heard saying that enamel does not last as long as grisaille.

A hypothesis often mentioned is the influence of the atmosphere of the kiln. The appearance of electric kilns in the beginning of the twentieth century meant that progressive studios abandoned the coke or turf kiln, as on these devices the firing chamber was full of smoke, meaning that the resulting atmosphere was reductive.

The use of a gas kiln is mentioned also as an influence in the stained-glass paint durability. Despite the fact that the atmosphere of the kiln was still reductive, the speed of the firing was much faster and Whall, at least, mentions the difficulties of achieving the same results.

![Fig. 3: Amigó studio kiln room. Around 1913.](image)

Some of the gas kilns also had a separated chamber for firing, meaning that the resulting atmosphere was just as oxidizing as in an electric kiln. However, the risk of explosion while using the kiln prevented them from becoming a popular device in the studios.

The influence of the electric kiln as a factor in the production of the worst quality fired paint has not been proven. On one hand recently found pictures from 1913 showed that the kilns were still heated with wood, both at the studios of Amigó (Fig. 2) and Rigalt, while other smaller and humbler studios, such as the Altamira family workshop, used a turf kiln because it was much more economical and easier to run. This family also provided the service of firing the works for smaller stained-glass makers.

Despite the fact that the electric furnace provided ease of use, and no risk of explosion compared to coal and gas equipment, the electric kiln posed other risks regarding firing paint. On one hand, they heat up faster but once they were shut down the cooling rates were also faster. The electricity supply in Catalonia not fully guaranteed during the take-up of this energy source, and ounces often occurred leaving some of the firings at an uncertain stage of the process.

### Sampling and Analysis

Polished cross sections of the enamels were obtained by embedding small fragments in epoxy resin, cross sectioning the samples and embedding the cross sections again in epoxy resin for further polishing with a diamond paste.

The microstructure of the enamels was determined by SEM using a crossbeam workstation (Zeiss Neon 40, Jena, Germany).

<table>
<thead>
<tr>
<th>Blue Enamel</th>
<th>T_g(°C)</th>
<th>T_s(°C)</th>
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<tbody>
<tr>
<td>E33</td>
<td>411</td>
<td>548</td>
</tr>
<tr>
<td>E114</td>
<td>441</td>
<td>584</td>
</tr>
<tr>
<td>E115</td>
<td>437</td>
<td>579</td>
</tr>
<tr>
<td>E122</td>
<td>425</td>
<td>566</td>
</tr>
</tbody>
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**Table 1.** The glass transition temperature (T_g) and the softening temperature (T_s) of the studied enamels.

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equipped with SEM GEMINI (Shortky FE) column working conditions between 4 pA–20 nA current and 0.1–30 kV acceleration voltage, with 1.1 nm resolution at 20 kV. Polished cross sections of the glasses, coated with sputtered carbon layer (<20 nm thick) at 20 kV acceleration voltage and 8 mm working distance. Backscattered electron (BSE) images of the microstructures were obtained at 5 and 10 kV acceleration voltage.

The direct solid laser ablation sampling system (Q switched Nd:YAG 213 nm laser ablation system, new wave research) coupled with a quadrupole ICPMS (Thermo Electron Corporation XSERIES 2, operating in standard mode, Xet cone) was employed to perform 20-50 s spot-mode analyses (crater of 80 lm) on the same polished cross sections of the enamels as those previously used for SEM analysis. Synthetic certificate reference glasses (NIST 612 and 610) were measured at the same working conditions of analysis. The accuracy was evaluated with respect to Corning Museum of Glass (CMG) A. The results achieved on Corning A were very similar to other runs using similar analytical equipment.

XRD measurements were made on the surface of the enamels using a conventional diffractometer, Bruker D8 with monochromatic Cu-Kα (1.5606 Å) radiation with 4-90° two theta range, the penetration depth of the X-rays being less than about 100 μm. Identification of the compounds has been performed based on the Powder Diffraction File (PDF) database from the International Centre for Diffraction Data (ICDD).

The glass transition temperature of the glass was determined by Differential Scanning Calorimetry (DSC) at 20 K/min, in a Netzsch F404 Pegasus. The enamel powders were loaded in aluminum holders and were then submitted to a thermal cycle including two heating stages up to a maximum temperature of 700°C. The first heating was used to produce the enamel and the second to measure the glass transition temperature.

A collection of blue enamels from the Rigalt i Granell company are analysed. Enamels were obtained from the enamel powders and the chemical composition obtained by Laser ablation ICP mass spectroscopy. The results of the analysis are shown in the table I. The workshop used four different blue enamels (E33, E114, E115 and E122) corresponding to different manufacturing companies. Wengers, Lacroix and l'Hospied respectively. They have different chemical compositions as shown in the table. In all the cases, they have a B-Si-Zn-Pb glass mixed with a cobalt base pigment. However, the enamels show a different glass composition and pigment characteristics. All the enamels contain lead (between 40 and 70% PbO) Wengers and Lacroix contain also between 15-20% B2O3, and between 9 and 15% ZnO. l'Hosped on the contrary contains only 3-8% B2O3 and 0.22% ZnO. The enamels appear non-crystalline but heterogeneous before firing. They are sodium, potassium, aluminium, calcium and magnesium poor with the exception of those from Wengers.

The colour is due to the presence of a cobalt blue pigment, Lacroix and l'Hospied enamels show the blue pigment fully dissolved in the glass. The cobalt appears associated with iron, nickel and arsenic. Skutterudite, (Co, Fe, Ni)As, and other related pigments are used. Wengers blue pigment, on the contrary is a synthetic ceramic pigment, a cobalt aluminate, CoAlO4, used in porcelains.

Finally, the presence of small and variable amounts of cassiterite, SnO2 particles, typically added to increase the opacity of the enamels, area also found (fig. 4).

The glass transition temperature of the enamels and base glass was determined by DSC at 20K/min heating rate, in a Netzsch F404 Pegasus. The DSC curve is shown in the figure for the enamel E115, for which the glass transition temperature determined is 437°C. The softening temperature is typically of about 1.2·Tg, therefore, in this case the firing temperature should be higher than 580°C. The other enamels have glass transition temperatures varying between 441°C and 441°C, which correspond to softening temperatures varying between 548°C and 584°C table II. These temperatures are close to the nineteenth century base soda-lime glass deformation point (~612°C).

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