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Physico-Chemical Insights into Sanguine and Carnation based on Reproduced Historic Recipes

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Aperçu physico-chimique de la sanguine et de la carnation à partir de recettes historiques reproduites – Résumé

La carnation (aussi connu sous le nom de « Jean Cousin ») et la sanguine sont deux types de peintures vitreuses à base d'oxyde de silicium (Si), d'oxyde de plomb (Pb) et d'oxyde de fer (Fe). Utilisées depuis la fin du XV[e] siècle, elles produisent une gamme unique et lumineuse de tons chair et d'orange. Malheureusement, sur les vitraux historiques, ces peintures présentent parfois de sévères dégradations. Afin de bien comprendre les couches de décoration de surface gravement détériorées et complexes, et donc de pouvoir appliquer un traitement de conservation approprié, il est essentiel de comprendre clairement les comportements et les différences entre la sanguine, la carnation et la grisaille colorée.

D'un point de vue terminologique, la carnation est la peinture transparente de couleur chair, tandis que celle à l'aspect opaque de couleur orange brique est appelé sanguine. Lors de la première étape de l'étude, une différence de dommages entre ces deux peintures a été constatée. La sanguine s'effrite généralement à partir du centre et survit mieux sur les bords, en particuliers près des grisailles. Contrairement à la carnation qui se décolore sur une zone plus générale, parfois jusqu'à ce qu'il ne reste que l'irisation à la surface du verre qui prouve son existence antérieure. Ces propriétés, associées à leurs couleurs spécifiques, permettent de les distinguer aisément des autres types de peintures sur verre.

Dans la deuxième étape de l'étude, l'accent a été mis sur les différentes strates, obtenues lors du processus de sédimentation d'où se forment ces peintures. Ainsi, la sédimentation a été reproduite sur différents échantillons en utilisant les recettes développées par les moines Antoine et Maurice écrites dans le livre de Pierre Le Vieil. Ces échantillons ont été étudiés en appliquant plusieurs techniques microscopiques. Les observations révèlent que la couche supérieure présente plus de similitudes avec une couche de carnation, alors que la couche juste en dessous ressemble plus à une sanguine. En comparaison, les deux dernières couleurs obtenues lors des deux dernières étapes de sédimentation, présentent plus de similitudes avec la grisaille. De plus, il devient clair que les couches séparées pendant le processus de sédimentation ont une taille de grains différente et contribuent de façon inhérente aux caractéristiques respectives et distinctes de la carnation et de la sanguine. L'étude a permis d'établir que la carnation est toujours une peinture vitreuse, où le pigment est entouré d'un fondant, mais aussi qu'il y a une interaction avec le support comme si la peinture rongeait la surface du verre. Ainsi, la transparence de la carnation pourrait s'expliquer par la diffusion des grains de pigment dans le verre. Ce phénomène diffère de la sanguine où les plus gros grains restent en surface, arrêtant la dispersion de la lumière, et expliquant un aspect opaque.

Physico-Chemical Insights into Sanguine and Carnation Based on Reproduced Historic Recipes – Abstract

As a follow-up to the study of Sanguine and Carnation, executed and submitted by Anne Catherine Perreau, the physico-chemical approach will be discussed in this contribution. As mentioned in her abstract, in order to understand properly the sometimes severely deteriorated and complex layers of surface decoration and hence to fulfil a proper conservation treatment, it is essential to clearly understand the behaviour, the differences and the manufacturing processes of Sanguine, Carnation and coloured grisaille. The various series of mockups prepared by A.-C. Perreau were based on historic recipes. A detailed observation of grainsizes, distributions, representations and glass surface – paint interface was done by using high performance optical microscope (ZEISS) and a digital microscope (HIROX). All these mockups were analysed by applying SEM-EDX and a few were selected for RAMAN spectroscopy. The obtained results will be outlined in this presentation. In extension of this study a selected number of 16th century stained glass panels from STAM museum of Ghent, Belgium were scanned by MA-XRF (BRUKER) in order to evaluate the presence of Carnation and Sanguine. During this contribution it will be demonstrated how MA-XRF can contribute in reading sometimes heavily deteriorated Stained Glass.

Introduction

Carnation (also known as Jean Cousin) and sanguine are both types of vitreous paints made from silicon oxide (Si), lead oxide (Pb), and iron oxide (Fe).[1] They have been in use from the late 15th-century and produce a unique luminous range of flesh tones and oranges (fig. 1).[2] This colouration is produced by the small iron oxide particles (Fe_2O_3) selected during a sedimentation process which happens in their production.[3] In historic fragments, the depth of Carnation layers has been measured to around 5µm.[4]

Fig. 1. Ghent, Belgium, STAM Museum: panel showing the feast at Joseph's house: the amazement of his brothers at being seated according to their age, Southern Low Countries, second half of the 16th century (09019). © STAM Museum.

[1] Olivier SCHALM, "Characterization of the paint layers in stained-glass windows: main causes of the degradation of nineteenth century grisaille paint layers", PhD *thesis*, Universitaire Instelling Antwerpen, 2000. p. 269.

[2] Ângela SANTOS & Márcia VILARIGUES, "Sanguine Paint: Production, Characterization, and Adhesion to the Glass Substrate, Studies in Conservation", 64:4, 221-239, DOI: 10.1080/00393630.2018.1482708, 2019, p. 221.

[3] Joost M. A. CAEN, *The production of stained glass in the County of Flanders and the Duchy of Brabant from the XVth to the XVIIIth centuries: materials and techniques*, Harvey MILLER (Publ.), 2009, p. 254.

[4] Olivier SCHALM, "Une étude historique et chimique de peinture de verre « rouge Jean Cousin » ", in : *Dossier de la Commission royale des monuments, site et fouilles, 3- Grisaille, jaune d'argent, sanguine, émail et peinture à froid, technique et conservation*, Forum pour la conservation et la restauration des vitraux, Liège 19-22 juin 1996, 1996, p. 161.

In most historical texts, two different fired products are identified. Writers often observe an application of a thin flesh colour layer of carnation, also named *sanguine transparent* or *Jean Cousin*, which is applied on the external side of window glass[5] and is visible in reflected light as iridescent marks.[6] This layer is different to sanguine, also named *sanguine opaque*, which is usually applied on the internal side and recognisable by a unique bright orange brick colour.[7] However, some exceptions to this pattern have been observed on historical stained-glass windows. The choice between which one of those paints has been applied, varies depending on the production time, the size of the panel, and the location for which it has been made.[8] The use of these paints helped artists achieve optical effects which added realism to the painting's style. However, over time stained glass often faces adverse circumstances and can suffer from alterations, breaks, or humidity. These effects can increase the difficulty to distinguish carnation from sanguine, and both from other types of paint on historic glass.

Consequently, to properly understand severely deteriorated and complex layers of surface decoration and hence fulfil a proper conservation treatment, it is essential to clearly understand behaviours and differences between sanguine, carnation and coloured grisaille. The aim of this contribution is to present the outcome of the on-going physico-chemical investigation of sanguine and carnation via a set of reproduced historical recipes.

Carnation and Sanguine: Appearance

Firstly, It seems important to observe alterations of sanguine and carnation, to work towards understanding the behaviour of these paints on stained glass over time. During visits to various museums, some very specific damage phenomena have been observed. It has been in particular the case for the stained-glass collection held at the STAM museum in Gent, where observations were made by glass painter Anne-Catherine Perreau and conservator and art historian Aletta Rambaut.

Fig. 2. Ghent, Belgium, STAM Museum: panel showing a view from reverse and front side of a detail of the Annunciation, from Southern Netherlands, second half of the 16th century (09011). © STAM Museum.

[5] Joost M. A. CAEN 2009, p. 273.
[6] Irène PORTAL, *Sanguine et Jean-Cousin : deux matériaux utilisés pour rendre les carnations dans les vitraux : histoire des termes, nature des matériaux* ; mémoire d'étude de l'École du Louvre (1^{re} année de 2^{e} cycle), Paris, 2010-2011, vol. 2, p. 16.
[7] Joost M. A. CAEN 2009, p. 254, 273.
[8] Joost M. A. CAEN 2009, p. 273-274.

To start with, a difference in damage between sanguine and carnation has been noticed. Sanguine is really fragile, particularly if it is applied in a thick layer. Scuff marks have often been observed, as if the layers have been scraped by somebody. Also, some form of corrosion, similar to that which occurs with grisaille, was seen and can cause paint to crumble into micro pieces. The particular nature of sanguine corrosion causes it to start deteriorating from the centre outwards and means that it survives better near grisaille paint. It leaves a very light pink transparent layer on the surface, or just a mark. In contrast, carnation seems not to crumble, but it leaves an iridescent mark which indicates its presence on the external side. However, sometimes it is not possible to see by eye the presence of the paint in flesh tone when it is observed from the front side, as it is already partially missing. It is possible that the layers are so fragile and so thin that they can be damaged by the atmospheric condition and lose their colouration (fig. 2).

Another form of damage to carnation and sanguine can be experienced when they are applied on top of a grisaille. In this case they often survive better than the grisaille itself. When the grisaille corrodes and flakes off, it can take with it the carnation or the sanguine and looks like a negative image of the drawing. Probably because of the difference in characteristics of the two paints, carnation and sanguine seem to have a better grip to the glass surface than some grisaille paints.

Reproduction of Historic Recipes

Secondly, in order to understand the main differences among sanguine, carnation and coloured grisaille, a focus was placed on the sedimentation phenomenon which occurs while separating the pigments into different layers. It is often mentioned in old recipes that after collecting the top layer from the sediment process, the layers underneath can be used for creating the effects of drapery, wood, and so on.[9] Therefore in the following step of the investigation and in order to understand the colours produced in each sedimentation step, various tests were made by applying the different layers produced during the sedimentation process. At the end they were compared to one another. The sedimentation was reproduced using the recipes developed by the monks Antoine and Maurice as recorded in the book of Pierre Le Vieil. These recipes were recreated with the help of conservator Ângela Santos at the VICARTE Research Unit of NOVA University in Lisbon and Anne-Catherine Perreau.[10]

For this test series, the paint was applied with a smear-shading brush made of squirrel hair and smoothed with a badger brush. The paint was diluted with deionized water only. The glass support was a microscope lab slide, brand Deltalab, Eurotubo®. The prepared painted glass slides were fired at 620°C, holding for 30 minutes.

Microscopic Evaluation of the Test Series

Purely with the naked eye, evaluation of these test pieces makes clear that a difference can be noticed between the two top layers compared to the others beneath. The two upper layers are brighter and more luminous than the others. Additionally, it was observed that the very top layer of the solution is more transparent but paler than the next, which is semi-transparent and more colourful. The two bottom layers are completely opaque, with warm colours, but are not luminous.

If these four reproduced layers are compared to the paints occurring on old stained glass, some similarities in the luminous coats can be observed. First of all , the use of the different colours that were reproduced according to historic texts can be distinguished by the experienced naked eye. Additionally, according to the terminology, it can be deduced that the top layer shows more similarities with a carnation layer, whereas the layer just underneath looks more a sanguine. In comparison, the last two colours obtained from the last two sedimentation steps, show more similarities to grisaille paint.

In order to gain a deeper understanding and put forward more objective differential features between these types of paint, some of the test samples were further investigated by applying different microscopic techniques. This part of the study was conducted at the KIK-IRPA laboratories in Brussels, Belgium and executed by Helena Wouters. The microscopic techniques used include optical microscopy (ZEISS, Imager-M1), Digital microscopy (HIROX), and scanning

[9] Pierre Le Vieil, *L'art de la peinture sur verre et de la vitrerie*, Impr.de L.-F. Delarour, Paris,1774, p. 128.
[10] Pierre Le Vieil 1774, p. 127-128.

electron microscopy coupled to X-ray detection, SEM-EDX (ZEISS, EVO 15LS; Oxford Instruments, AzTec).

From the microscopic observations, the size selection of the pigment grains which occurs during the sedimentation process[11] could be established. In fig. 3 a schematic overview of the different separation layers obtained as a result of the sedimentation process of the paint is shown as photographic record of the surface of the respective mock-up, as well as observed by the applied microscopic techniques. The different measurements makes clear that the bottom layer of the sedimentation (fig. 3, 4th layer) represents the residue of the recipe with the biggest grains and has an heterogeneous appearance. Just above this residual layer, after the stratum's separation between the previous layer and the two following, the remains of bright pigments are found. As has been presented in fig. 3, 3rd layer, this resulted layer is more homogeneous with a visible demarcation between the grains and the glass surface. The observed consistency is comparable and identical to coloured grisaille. This feature explains the opacity of the paint.

The following layer above, shows even more interesting features and is indicated as the second layer in fig. 3. Interestingly, although the individual grains can still be seen under the optical microscope, the layer is very thin (≈0.5µm) as derived from the cross-section in the SEM-EDX. In this particular layer, surprisingly, the amount of iron is measurably higher than that of lead. Additionally, it was observed that the layer is so thin that the demarcation between the glass and the paint is more difficult to distinguish compared to the cases before, and above all, under the optical microscope the pigment appears less dense. Also some black areas are detected which showed the beginning of transparency, a feature which did not appear in the previous layers beneath (third and fourth layer in fig. 3). Finally, looking at the very top layer (first layer in fig. 3), it can be noticed that the grains are even smaller, so small that they can be barely distinguished. They appear like tiny red dust on the surface of the glass, and the density of the pigment is very light, which explains the increased transparency of the paint. Looking to the cross-section of this layer under the SEM-EDX microscope, it can be noticed that the layer is even thinner than the layer just above. The area delimiting the paint and the surface of the glass appears cloudier, as if something is happening between the two materials.

In order to comprehend better the interaction of the glass and the carnation paint of the first layer (fig. 3), also other carnation pigments, like the one produced by Debitus studio in Tours, and an unknown paint made by Leonie Seliger, director of Canterbury Cathedral Studio in Kent, were measured under the SEM-EDX.

In the research executed by Irène Portal,[12] a theory about the function of the small particle size was introduced and explained, suggesting that because of the micro size of the iron oxide particles, some of them can enter the surface of the glass when melting occurs during the firing process. The iridescence observed on the surface of the glass could be a partial reflection of these micro particles. From our observations, shown in fig. 4, we can confirm er theory and have demonstrated that carnation is still a vitreous paint, with pigment surrounded by flux, but there is an interaction with the glass as if the paint was eating into the surface.

Added to this, the analysis of the samples shows that the transparency of the carnation could be explained by the diffusion of the pigment grains into the glass. This differs from sanguine where the bigger grains still remain on the surface, stopping the dispersion of the light, and explaining an opaque appearance. This interaction with the glass could also explain why those pigments survived better than other vitreous glass paints when they were applied directly to the substrate.

[11] Olivier Schalm 2000, p. 243-268.
[12] Irène Portal 2011, p. 55.

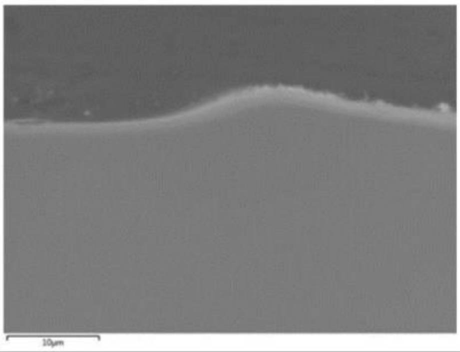
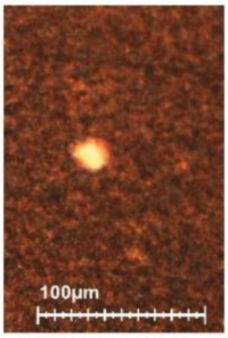
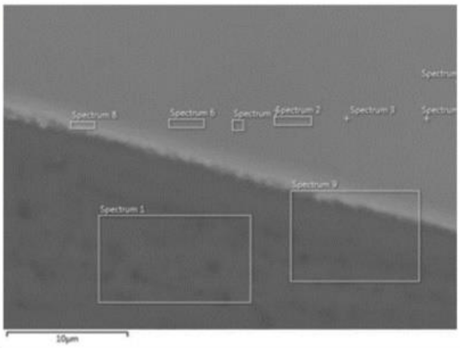
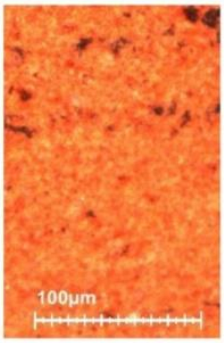
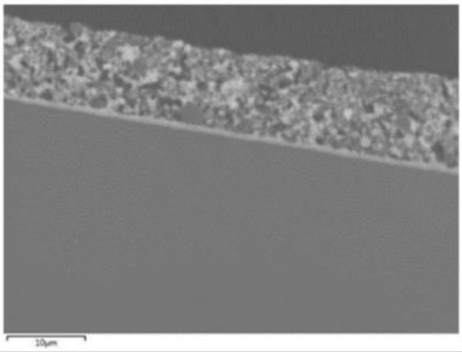
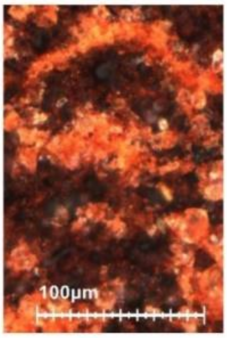
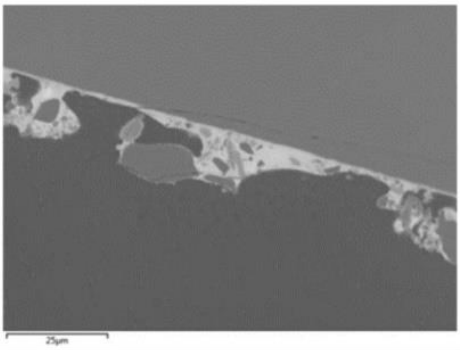
Sedimentation process of a carnation	Mock-up at actual scale	Optical Microscope, Polarised mode, x200	SEM- EDX microscope
Top 1st Layer			
2dn Layer			
3rd Layer			
Bottom 4th Layer			

Fig. 3. Schematic overview of the different sedimentation layers with corresponding observed appearance, respectively, the actual scale photograph, optical microscopic view and the back-scattered electron image recorded in the SEM-EDX. The samples of the four layers were reproduced by Â. Santos and A-C. Perreau according to the Monks Antoine and Maurice's recipe and prepared on Deltalab, Eurotubo®'s microscope lab slide, fired at 620°C-holding 30 minutes. ©KIK-IRPA, A-C. Perreau, Helena Wouters.

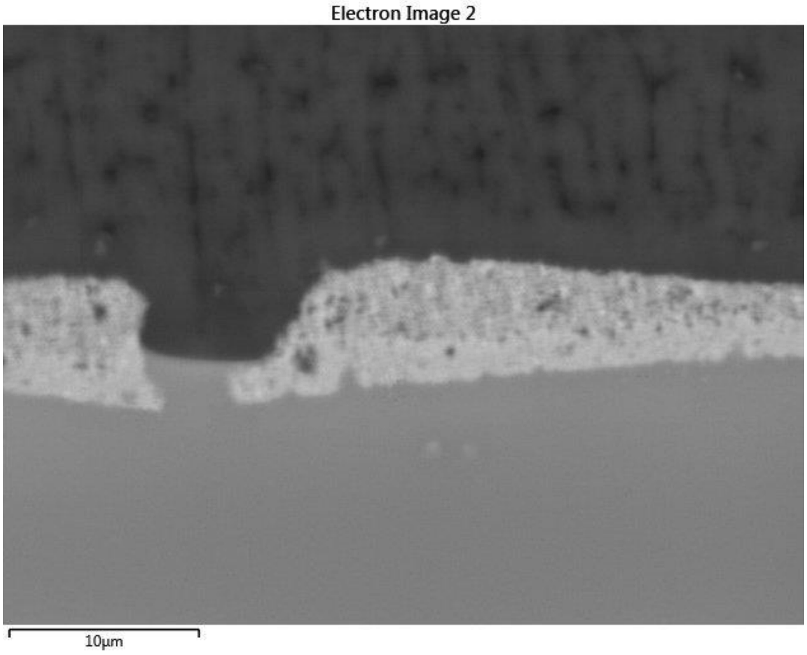


Fig. 4. Back-scattered electron image of a cross-section of glass substrate with the bottom layer of the sedimentation paint. Sample made by A-C. Perreau: Debitus carnation rouge on non-tinted side of a 3mm float glass, fired at 680°C - holding 20 minutes. The granular white layer corresponds to the paint layer, while the light grey zone represents the glass carrier. ©KIK-IRPA, Helena Wouters.

Conclusions

The investigation was executed in order to clearly understand differences between sanguine, carnation and coloured grisaille and their remarkable deterioration behaviour. Carnation (also known as Jean Cousin) and sanguine are both types of vitreous paints in use from the late 15th century and produce a unique luminous range of flesh tones and oranges.

Throughout the study, a difference in damage phenomena between sanguine and carnation has been noticed. In particular, sanguine starts to deteriorate from the centre outwards and leaves a very light pink transparent layer on the surface. In contrast, carnation seems not to crumble but it leaves an iridescent mark which indicates its presence on the external side.

The sedimentation procedure, which is the basic production of the glass paint, was recreated using the recipes developed by the monks Antoine and Maurice. The prepared test series was investigated by applying different microscopic techniques. The results have shown that sanguine and carnation are two different paints produced during a separate stage of the long sedimentation process. Specific features could be established and makes them distinguishable. In general, sanguine is more opaque while carnation is more transparent. The transparency of the carnation is due to the size of the particles in the layer and the subsequent penetration effect of the smallest micro-pigment grains into the surface of the glass. Sanguine has bigger pigment grains in the layer which sits on the surface of the glass, giving it its increased opacity. The study is still going on and is specifically currently undergoing enlargement by the application of elemental X-ray analysis of the different test series. By the time of the presentation at the Forum, we hope to show you how the presence of carnation and sanguine on heavily deteriorated stained glass can be evaluated by applying macro scanning X-ray fluorescence (MA-XRF), so that those glass paintings can literally be read.

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Bibliography

- Joost M.A Caen, *The production of stained glass in the County of Flanders and the Duchy of Brabant from the XVth to the XVIIIth centuries: materials and techniques*, Harvey Miller (Publ.), 2009.
- Pierre Le Vieil, *L'art de la peinture sur verre et de la vitrerie*, Impr. de L.-F. Delatour, Paris, 1774.
- Irène Portal, *Sanguine et Jean-Cousin : deux matériaux utilisés pour rendre les carnations dans les vitraux : histoire des termes, nature des matériaux*, mémoire d'étude de l'École du Louvre (1re année de 2e cycle), Paris, 2010-2011, 2 vol.
- Ângela Santos & Márcia Vilarigues, "Sanguine Paint: Production, Characterization, and Adhesion to the Glass Substrate", *Studies in Conservation*, 64:4, 221-239, DOI: 10.1080/00393630.2018.1482708, 2019.
- Olivier Schalm, "Characterization of the paint layers in stained-glass windows: main causes of the degradation of nineteenth century grisaille paint layers", PhD *thesis*, Universitaire Instelling Antwerpen, 2000.
- Olivier Schalm, "Une étude historique et chimique de peinture de verre « rouge Jean Cousin » in *Dossier de la Commission royale des monuments, site et fouilles, 3- Grisaille, jaune d'argent, sanguine, émail et peinture à froid, technique et conservation*, Forum pour la conservation et la restauration des vitraux, Liège, 19-22 juin 1996, 1996.